

Sommaire

Remerciements.....	6
Résumé.....	10
Abstract.....	11
Sommaire	12
Table des Figures	16
INTRODUCTION GENERALE.....	24
CHAPITRE I : Etat de l'art des connaissances sur la géologie du désert d'Atacama et l'altération supergène des porphyres cuprifères.....	34
I.1 La géologie des Andes et du désert d'Atacama	36
I.1.1 Géologie des Andes.....	36
I.1.2 Tectonomagmatisme et métallogénie des Andes Centrales et du désert d'Atacama du Mésozoïque au Cénozoïque.....	38
I.1.3 Géomorphologie et évolution climatique du désert d'Atacama chilien au Mésozoïque-Cénozoïque	43
I.2 L'altération supergène des porphyres cuprifères et la formation des minéralisations cuprifères supergènes dans le désert d'Atacama chilien	50
I.2.1 L'altération hydrothermale hypogène.....	50
I.2.2 L'altération supergène et la formation des minéralisations cuprifères supergènes <i>in situ</i> et exotiques.....	52
I.2.3 L'âge du cuivre supergène du désert d'Atacama.....	58
CHAPITRE II : Méthodes et outils.....	64
II.1 La géochronologie U-Pb.....	68
II.1.1 le chronomètre U-Pb : principes et limites	68
1.1.1 Principe	68
1.1.2 Le diagramme Concordia Wetherill	70
1.1.3 Le diagramme Concordia "Tera-Wasserburg"	70
1.1.3 Les causes de la perturbation du chronomètre U-Pb.....	72
II.1.2 Datation U-Pb via un spectromètre de masse à torche plasma couplé à un système d'ablation laser : U-Pb LA-ICP-MS.....	72
1.2.1 Principe de fonctionnement d'un LA-ICP-MS	73
1.2.2 Le choix d'un double laser pour la datation des minéralisations cuprifères supergènes.....	74
1.2.3 Appareillage et traitement de données.....	76

II.2 La caractérisation texturale	76
II.3 La microsonde électronique.....	76
II.4 La microsonde ionique	77
CHAPITRE III : Caractérisation minéralogique et chimique des minerais cuprifères supergènes : cas d'étude des districts miniers de l'Atacama et de Gaoua	94
III.1 Mineralogical and chemical characterization of supergene copper-bearing minerals: examples from Chile and Burkina Faso.....	96
CHAPITRE IV : Apport des isotopes du cuivre dans la compréhension de l'altération supergènes des porphyres cuprifères.....	116
IV.1 Understanding reduction-oxidation processes in supergene exotic copper deposits from Atacama Desert, northern Chile: what Cu isotope can tell us ?	119
IV.2 Discussions complémentaires	141
IV.2.1 Rôle des paramètres géologiques et climatiques sur le fractionnement isotopique du cuivre.....	141
IV.2.2 Contrôle analytique	142
CHAPITRE V : Première datation U-Pb de la minéralisation cuprifère supergène : cas d'étude dans le district minier de Chuquicamata	144
V.1 First U-Pb LA-ICP-MS <i>in situ</i> dating of supergene copper mineralization: case study in the Chuquicamata mining district, Atacama Desert, Chile	146
CHAPITRE VI : Préservation et perturbation du signal chronométrique U-Pb dans les minéraux cuprifères supergènes.....	162
VI.1 Understanding the preservation and disruption of U-Pb chronometer in supergene copper minerals from Atacama Desert, northern Chile: U-Pb dating coupled to U-Pb LA-ICP-MS mapping and isotopic in study of chrysocolla and pseudomalachite.....	165
VI.2 Insights of the timing of supergene copper mineralization in the Gaoua porphyry Cu-Au district, southwestern of Burkina Faso.....	201
VI.3 U-Pb dating of calcite from Tesoro Central exotic copper mineralization: a window into post-crystallization fluid circulation.....	208
CHAPITRE VII : Synthèse et discussion.....	214
VII.1 Genèse des minéralisations cuprifères supergènes.....	218
VII.2 Comportement du chronomètre U-Pb dans la pseudomalachite et la chrysocolle.....	220
VII.3 Age de l'altération supergène dans les districts miniers de l'Atacama et du sud-ouest du Burkina Faso.....	230
VII.4 Les paramètres géologiques et climatiques contrôlant le chronomètre U-Pb dans les minéralisations cuprifères supergènes.....	234
VII.5 Guides d'exploration.....	242

CONCLUSIONS GENERALES ET PERSPECTIVES.....	250
Annexes.....	256

Table des Figures

Introduction Générale

Figure 1 : Carte de répartition des porphyres cuprifères à l'échelle mondiale (modifié d'après Sillitoe, 2010).....	27
Figure 2 : Genèse des porphyres cuprifères en zone de subduction (modifié d'après Jébrak and Marcoux, 2008).....	27
Figure 3 : Représentation schématique de l'altération supergène d'un porphyre cuprifère et de son lien avec la formation des minéralisations exotiques de cuivre (basé sur Münchmeyer, 1996).....	29

Chapitre I

Figure I.1 : A. Illustration de la tectonique des plaques autour de la plaque tectonique sud-américaine. B. Carte du continent sud-américain montrant la segmentation de la cordillère des Andes (modifié d'après Sillitoe and Perelló, 2005).....	37
Figure I.2 : A. Carte du continent sud-américain montrant les différentes époques métallogéniques de la cordillère des Andes (modifié d'après Sillitoe and Perelló, 2005). B. Carte du désert d'Atacama chilien montrant les principales ceintures métallogéniques (modifié d'après Arancibia et al., 2006).....	38
Figure I.3 : Carte de la répartition des plutons magmatiques Eocène et des porphyres cuprifères le long de la Precordillera (modifié d'après Mpodozis and Cornejo, 2012).....	41
Figure I.4 : Représentation schématique de la formation des pédiments (modifié d'après Dohrenwend and Parsons, 2009).....	44
Figure I.5 : Photographie montrant une surface d'érosion dans la Dépression Centrale du désert d'Atacama.....	44
Figure I.6 : Carte du sud du continent sud-américain montrant le taux de précipitation annuel du désert d'Atacama par comparaison au reste du continent sud-américain (modifié d'après Strecker et al., 2007).....	45
Figure I.7 : Carte du continent sud-américain montrant les phénomènes responsables de l'hyperaridité du désert d'Atacama.....	46
Figure I.8 : Résumé des études géochronologiques, sédimentologiques, pédologiques, isotopiques et cosmogéniques montrant la prévalence de l'aridité dans le désert d'Atacama depuis le Paléocène et l'initiation d'un climat hyperaride au Miocène.....	49
Figure I.9 : Représentation schématique de l'altération hydrothermale hypogène d'un porphyre cuprifère (modifié d'après Kouzmanov and Pokrovski, 2012).....	52
Figure I.10 : Représentation schématique de l'altération supergène d'un porphyre cuprifère.....	55
Figure I.11 : Carte de répartition des minéralisations exotiques de cuivre et de leur porphyre cuprifère parent dans la Précordillère du désert d'Atacama (modifié d'après Mpodozis and Cornejo, 2012).....	56
Figure I.12 : Résumé des âges de l'activité hydrothermale hypogène, de la durée de l'altération supergène et de l'âge de formation des pédiplains de la Dépression Centrale et de la Cordillère de Domeyko du désert d'Atacama.....	61

Chapitre II

Figure II.1 : Diagramme concordia Wetherill (A) et concordia Tera-Wasserburg (B) montrant les cas de figure où les systèmes isotopiques fournissent au âge concordant et lorsque ceux-ci fournissent des données discordantes (modifié d'après Schoene, 2014)..... 71

Figure II.2 : Principe de fonctionnement d'un LA-ICP-MS montrant le système d'ablation laser (Ablation cell), l'ionisation dans la torche plasma (Inductively coupled plasma) et la séparation et la détection des ions dans le spectromètre de masse (Mass spectrometer)..... 74

Figure II.3 : Diagramme concordia Tera-Wasserburg montrant A) la calibration de la pseudomalachite (à matrice phosphatée) par un standard de zircon (à matrice silicatée) et B) la calibration de la pseudomalachite par un standard d'apatite (à matrice phosphatée). La discordance inverse en A) montre un effet de matrice significatif. Vue schématique de l'impact de l'interaction laser-matériau entre un laser nanoseconde C) et un laser femtoseconde D). Notez que le cratère d'ablation obtenu avec un laser femtoseconde ne présente aucune poire d'interaction ni de dépôts autour du cratère..... 75

Figure II.4 : Schéma de fonctionnement d'une microsonde électronique..... 77

Figure II.5 : Schéma de fonctionnement d'une microsonde ionique. L'échantillon est bombardé par un faisceau d'ions puis transportés vers le spectromètre qui séparera les ions suivant leur rapport masse/charge via u secteur électrostatique puis magnétique et finalement détectés et comptés via un système mono-collecteur ou multi-collecteur..... 78

Chapitre III

Figure 1: Schematic representation of the relationships between hypogene porphyry copper mineralization and supergene copper mineralization (SCM) forming in situ and exotic copper deposits (modified after Sillitoe, 2005)..... 98

Figure 2: Location and geological map of the studied areas. a) location of major SCM in the world map, including Atacama Desert of northern Chile and Gaoua Cu-Au district (after Sillitoe, 2010). b) Structural map of the Precordillera of northern Chile (after Mpodozis and Cornejo, 2012) showing the location of the in situ and exotic SCM deposit studied. Black squares mark the location of the Chuquicamata, Salvador and Potrerillos mining districts in which the Mina Sur, Damiana and El Cobre exotic SCM deposits are located, respectively c) Location (black square) of the Gaoua Cu-Au district within the simplified geological map of Burkina Faso (BGB: Boromo Greenstone Belt; HGB: Houndé Greenstone Belt after Béziat et al., 2008). d) Detailed geological map of the Gaoua Cu-Au district showing the location of the Mont Biri, Diénémara, Gongondy and Bousséra in situ supergene Cu-Au occurrences (Baratoux et al., 2015; Le Mignot et al., 2017)..... 99

Figure 3: Synthetic paragenetic sequence for the studied exotic and in situ SCM deposits. Stage 1 corresponds to the main supergene oxidation while Stage 2 corresponds to the late filling empty spaces..... 101

Figure 4: Sample and thin sections photographs showing the relationships between Mina Sur copper minerals. a) Black chrysocolla (B-Ccl) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. b) Plane-polarized light photograph showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. c) Cross-polarized light and d) SEM photomicrographs showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite needles (Ata) on chrysocolla and pseudomalachite..... 102

Figure 5: Sample and thin sections photographs showing the relationships between Damiana copper minerals. Chrysocolla (Ccl) filling empty spaces and porosity of the gravels at a) Damiana gravels and fractures at b) Damiana bedrock. c) Cross-polarized light photograph showing chrysocolla (Ccl) filling fractures at Damiana bedrock. d) Plane-polarized light and e) SEM photomicrographs showing copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl) and e) pseudomalachite (Psm) coating chrysocolla. f) Plane-polarized light and g) cross-polarized light photographs of chrysocolla (Ccl) filling porosity of the gravels at Damiana gravels. h) Cross-polarized light and i) SEM photomicrographs showing chrysocolla (Ccl) filling porosity of the gravels and pseudomalachite (Psm) crystallizing in empty spaces and an overgrowth of apatite (Apa) on chrysocolla..... 102

Figure 6: Sample and thin sections photographs showing the relationships between El Cobre copper minerals. a, b) Chrysocolla (Ccl) filling fractures of the altered andesite bedrock. c) Plane-polarized light photograph showing copper wad (Cwad), chrysocolla (Ccl) and pseudomalachite filling fractures of the andesite bedrock. d) Plane-polarized light, e) cross-polarized light and f) SEM photomicrographs showing chrysocolla (Ccl), with a banding mammillary texture, coating on copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl) and pseudomalachite (Psm) and amorphous quartz filling empty spaces.....103

Figure 7: Sample and thin sections photographs showing the relationships between Zaldivar copper minerals. a) Hand-samples of Zaldivar supergene copper minerals. b) Plane-polarized light photograph showing Brochantite (Bct) thin green prismatic shape, brown-color chrysocolla (Ccl) and pseudomalachite (Psm) replacing brochantite. c) Plane-polarized light photograph showing relicts of altered sulfides replaced by brochantite and brown chrysocolla and pseudomalachite gradually replacing brochantite. d) Plane-polarized light photograph showing brown-color chrysocolla and pale green pseudomalachite co-crystallization. e, f) SEM photomicrographs showing a complex textural relationship between brochantite, copper wad (Cwad) thin band, chrysocolla and pseudomalachite.....104

Figure 8: Sample and thin sections photographs showing the relationships between Gaby copper minerals. a) Hand-samples of Gaby showing chrysocolla (Ccl) filling fractures in the Gaby micro-diorite host-rock. b) Plane-polarized light photograph showing copper wad (Cwad) and chrysocolla filling fractures of the host-rock. (c) Plane-polarized light photograph showing an altered sulfide replaced by brochantite (Bct) and brochantite crystallizing in a host-rock veins. d, f) SEM photomicrographs showing an altered sulfide replaced by brochantite and chrysocolla and atacamite (Ata) overgrowing on brochantite. e) SEM photomicrograph showing copper wad thin band and fractured and homogeneous texture of chrysocolla, crystallizing within host-rock veins.....105

Figure 9: Sample and thin sections photographs showing the relationships between Gaoua copper minerals. a) Hand-samples of Gaoua showing chrysocolla (Ccl) filling fractures in the Gaoua quartz-andesite host-rock. b) Plane-polarized light and c) cross-polarized light photographs showing chrysocolla (Ccl) filling fractures of the host-rock. d) Plane-polarized light and e) SEM photographs showing thin green crystals of cuprite (Cup) and pseudomalachite (Psm) coating on quartz crystals and chrysocolla filling empty spaces f) SEM photomicrograph showing chrysocolla texture, crystallizing within host-rock veins.....106

Figure 10: Representative diagrams of oxidized supergene copper mineralization chemical analyses showing in Triplot diagrams. a) chrysocolla chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM deposits. b) black chrysocolla chemical analyses from Mina Sur exotic SCM deposit. c) Pseudomalachite chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM deposits. d) Chrysocolla chemical analyses from Zaldivar, Gaby and Gaoua in situ SCM deposits.....107

Figure 11: EPMA chemical characterization of supergene copper minerals from Mina Sur exotic SCM deposit. a) Si map b) Cu map and c) P map at the transition between black chrysocolla (B-Ccl), chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the homogeneity/heterogeneity distribution of silicon, copper and phosphorus. Dotted square represents the area analysed.....108

Figure 12: EPMA chemical characterization of supergene copper minerals from a, c, e) Damiana and b, d, f) El Cobre exotic SCM deposits. a, b) Si map c, d) Cu map and e, f) P map at the transition between chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analysed.....109

Figure 13: EPMA chemical characterization of supergene copper minerals from Zaldivar and Gaby in situ SCM deposit. a, b) Si c, d) Cu and e) P maps at the transition between chrysocolla (Ccl), copper wad (Cwad) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analysed.....110

Figure 14: Chondrite normalized REE patterns for oxidized supergene copper minerals. a, b) REE patterns of chrysocolla and black chrysocolla from exotic and in situ SCM deposits. c, d) REE patterns of pseudomalachite from exotic and in situ SCM deposits. Chondrite normalizing values are taken from McDonough and Sun (1995).....111

Chapitre IV

Figure 1: Schematic representation of an in situ supergene column from a porphyry copper deposit showing its typical copper isotopic signatures and its relationship with a downstream exotic copper deposit.....124

Figure 2: Location of the mining district studied within the Eocene-Oligocene Precordillera belt of the Atacama Desert of Chili.....126

Figure 3: Sample and thin sections photographs showing the textural relationships of the exotic copper minerals from the Mina Sur, Damiana and El Cobre deposits. a) Plane-polarized light photograph showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. b) Cross-polarized light showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite needles (Ata) on chrysocolla and pseudomalachite. c) Plane-polarized light showing chrysocolla filling fractures of the andesite bedrock. d) Plane-polarized light showing chrysocolla (Ccl), with a banding mammillary texture, filling porosity of the gravels and pseudomalachite (Psm) filling empty spaces. e) Plane-polarized light photograph showing copper wad (Cwad), chrysocolla (Ccl) and pseudomalachite (Psm) filling fractures of the andesite bedrock. f) Plane-polarized light photograph showing chrysocolla (Ccl), with a banding mammillary texture, coating on copper wad (Cwad) and pseudomalachite (Psm) filling empty spaces.....128

Table 1 Copper isotope compositions results of black chrysocolla, pseudomalachite and chrysocolla from Mina Sur, Damiana and El Cobre exotic copper deposits.....132

Figure 4: Schematic model displaying the development of three copper isotope reservoirs during the in situ supergene alteration of a porphyry copper deposit and the contemporaneous migration of the heavy copper solutions to create an isotopically enriched exotic copper deposit. During supergene alteration, the leached cap is progressively depleted in heavy ^{65}Cu . The ^{65}Cu -rich aqueous solutions migrate downward and generate the chalcocite-rich enrichment zone and the oxidized area, both ^{65}Cu -rich realm. The hypogene ore keeps the $\delta^{65}\text{Cu}$ values near $\sim 0\text{‰}$. The values are reported from this study and from the literature (Braxton and Mathur, 2011; Mathur et al., 2009; Palacios et al., 2011).....135

Chapitre V

Figure 1: Location and geological map of the studied area. a Physiographic setting of the Atacama Desert of northern Chile (CC, Costal Cordillera; CV, Central Valley; PC, Precordillera; HA, High Andes; DFZ, Domeyko Fault Zone; from Arancibia et al., 2006). b Detailed geological map of the Chuquicamata mining district after Zentilli et al. (2018). c Google Earth aerial photography of the Chuquicamata porphyry copper deposit and Mina Sur exotic copper mines and d its schematic geological cross-section. Yellow pushpin represents the location of the collected samples.....149

Table 1 Chemical compositions of Mn-rich chrysocolla clasts, chrysocolla and pseudomalachite bands carried out with EPMA. Structural formula has been calculated for 6 oxygens (chrysocolla) and 7 oxygens (pseudomalachite). N = number of analyses.....151

Figure 2: Sample and thin sections photographs showing the relationships between Mina Sur main copper minerals. a Black chrysocolla (1) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands at Mina Sur mine. b, c Plane-polarized light photomicrograph showing Mn-rich chrysocolla clast (1) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. d, e Cross-polarized light and f photomicrographs showing Mn-rich chrysocolla clast (1) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite (Ata) on chrysocolla and pseudomalachite.....152

Figure 3: Tera-Wasserburg and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagrams displaying the analyses made on pseudomalachite bands. The white circle corresponds to the concordia ages calculated using Isoplot. Errors ellipses and age calculations are reported with 2σ errors. a, b, c, d Tera-Wasserburg concordia diagram and corresponding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite with common Pb corrected made on ns-LA-Q-ICP-MS (a, b) and on fs-LA-HR-ICP-MS (c, d). e, f Tera-Wasserburg concordia diagram and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram showing data obtained on both ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS.....155

Figure 4: Tera-Wasserburg concordia diagram and density plot of $^{206}\text{Pb}/^{238}\text{U}$ dates displaying the analyses on Mn-rich chrysocolla clasts. a, b Tera-Wasserburg concordia diagram and density plot for Mn-rich chrysocolla of $^{206}\text{Pb}/^{238}\text{U}$ ages by ns-LA-Q-ICP-MS. c, d Tera-Wasserburg concordia diagram and density plots for Mn-rich chrysocolla of $^{206}\text{Pb}/^{238}\text{U}$ ages by fs-LA-HR-ICP-MS. e, f Tera-Wasserburg concordia diagram and density plot for Mn-rich chrysocolla of $^{206}\text{Pb}/^{238}\text{U}$ ages by both ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS. In all the diagrams, data point error ellipses are 2σ156

Chapitre VI

Figure 1: Structural map of the Eocene-Oligocene copper belt (i.e. Domeyko cordillera) of northern Chile and the Domeyko Fault System showing the main tectonic features, the Paleozoic basement and the Eocene plutons and their porphyry stocks. Location of the copper mining districts studied are indicated by black squares. Simplified from Mpodozis and Cornejo (2012)..... 172

Figure 2: Sample and thin sections photographs showing the textural relationships between Mina Sur, Damiana and El Cobre copper minerals. A) Black chrysocolla (black-Ccl) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. B) Plane-polarized light photograph showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. C) SEM photomicrographs showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite (Ata) prismatic crystals on chrysocolla and pseudomalachite. D) Chrysocolla (Ccl) filling empty spaces and porosity of the gravels. E) Plane-polarized light and F) SEM photomicrographs showing chrysocolla (Ccl) filling porosity of the gravels and pseudomalachite (Psm) crystallizing in empty spaces and an overgrowth of apatite (Apa) on chrysocolla. G) Chrysocolla (Ccl) filling fractures of the altered andesite bedrock. H) Plane-polarized light photograph showing chrysocolla (Ccl), pseudomalachite (Psm) with an inherited core texture and amorphous quartz (Qtz) filling empty spaces filling fractures of the andesite bedrock. I) SEM photomicrographs showing copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl), pseudomalachite (Psm) and amorphous quartz filling empty spaces.....177

Figure 3: Representative diagrams of chrysocolla, black chrysocolla and pseudomalachite EPMA chemical composition showing in Triplot diagrams. A) chrysocolla chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM. B) Black chrysocolla chemical analyses from Mina Sur exotic SCM. C) Pseudomalachite chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM.....179

Figure 4: Tera-Wasserburg concordia diagrams and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagrams displaying the analyses made on black chrysocolla and pseudomalachite from Mina Sur exotic SCM. A) Tera-Wasserburg concordia diagram of black chrysocolla made by ns-LA-Q-ICP-MS. B) Tera-Wasserburg concordia diagram of black chrysocolla made by fs-LA-HR-ICP-MS. C) Tera-Wasserburg concordia diagram and D) corresponding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite made on ns-LA-Q-ICP-MS. E) Tera-Wasserburg concordia diagram and F) corresponding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite made on fs-LA-HR-ICP-MS.....182

Figure 5: ^{238}U and ^{206}Pb isotopes and maps made on the transition between A, B) Black chrysocolla, chrysocolla and pseudomalachite and within C, D) Black chrysocolla from Mina Sur exotic SCM. E) $^{206}\text{Pb}/^{238}\text{U}$ monoclone age map made within black chrysocolla from Mina Sur exotic SCM. The black square represents the area used to produce monoclone map.....183

Figure 6: Tera-Wasserburg concordia diagram of A) chrysocolla and B) pseudomalachite made by ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS and C) ^{238}U , ^{206}Pb and ^{204}Pb isotopes and maps made on the transition between chrysocolla and pseudomalachite from Damiana exotic SCM. Tera-Wasserburg concordia diagram of D) chrysocolla and E) pseudomalachite made by ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS and F) ^{238}U , ^{206}Pb and ^{204}Pb elemental ratio made on the transition between chrysocolla and pseudomalachite from El Cobre exotic SCM.....184

Figure 7: $\delta^{18}\text{O}$ isotope profiles in black chrysocolla, chrysocolla and pseudomalachite from Mina Sur, Damiana and El Cobre exotic SCM. Pictures A), E) and H) show the location of the $\delta^{18}\text{O}$ profile made on each single mineral. The graphs B), C) and D) represent the A-A', B-B', C-C' $\delta^{18}\text{O}$ profile made on black chrysocolla, chrysocolla and pseudomalachite from the picture A) from Mina Sur exotic SCM. The graphs F) and G) represent the A-A' and B-B' $\delta^{18}\text{O}$ profile along chrysocolla and pseudomalachite from the picture E) from Damiana exotic SCM. The graphs I) and J) represent the A-A' and B-B' $\delta^{18}\text{O}$ profile along chrysocolla and pseudomalachite from the picture H) from El Cobre exotic SCM.....186

Figure VI.2.1: Location and geological map of the Gaoua porphyry Cu-Au district. A) Black square represents the location of the Gaoua district within the geological map of Burkina Faso (after Béziat et al., 2008). B) Detailed geological map of the Gaoua Cu-Au district showing the location of the Mont Biri, Diénémara, Gongondy and Bousséra in situ supergene copper occurrences (Baratoux et al., 2015; Le Mignot et al., 2017)..... 202

Figure VI.2.2: Tera-Wasserburg concordia diagrams of chrysocolla made by A) ns-LA-Q-ICP-MS and B) fs-LA-HR-ICP-MS. C) ^{238}U , ^{206}Pb and ^{204}Pb elemental ratio made on chrysocolla. D) $\delta^{18}\text{O}$ isotope A-A' profile made on chrysocolla. The distance between each spot is 40 μm204

Table VI.2.1: U-Th-Pb data carried out on chrysocolla from ns-LA-Q-ICP-MS (Table 1) and fs-LA-HR-ICP-MS (Table 2) and Oxygen isotope analyses of chrysocolla (Table 3) from the Gaoua supergene copper ore205

Figure VI.3.1: Tera-Wasserburg diagrams displaying the analyses made on calcite veins. A) T-W concordia diagram representing the unforced discordia B) T-W concordia diagram showing the lower intercept if the initial common Pb value forced to $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.837.....209

Table VI.3.1: LA-ICP-MS U-Th-Pb data for the studied calcite veins.....209

ESM VI.3.1: Representative ^{207}Pb -corrected final age and average ages for the WC1 calcite standard used to monitor the analyses.....210

Chapitre VII

Figure VII.1 : Synthèse de l'évolution géologique du district minier de Chuquicamata depuis l'exhumation du porphyre (A) jusqu'à l'altération supergène (B)..... 239

Figure VII.2 : Synthèse de l'évolution géologique du district minier de Salvador/Potrerillos depuis l'altération supergène (C) jusqu'à l'hyperaridification du désert d'Atacama (D)..... 240

Figure VII.3 : Synthèse de l'évolution géologique du district minier de Gaoua depuis l'exhumation du porphyre lors de l'ouverture de l'océan Atlantique (step 1) et durant le fonctionnement de l'altération supergène dans le district minier tout au long du Tertiaire.....241

INTRODUCTION GENERALE

Derrière l'aluminium, le cuivre (Cu) est le métal de transition le plus exploité depuis la révolution industrielle du 18^e siècle. Doté d'une excellente résistance à la corrosion, ductile, malléable, le cuivre à la particularité d'être le meilleur conducteur électrique et thermique de tous les métaux après l'argent (Ag). Sa métallurgie remonte à des millénaires avant J.-C. Sa gamme d'applications dans les secteurs de l'électricité, la construction, l'industrie automobile, les alliages pour l'aérospatiale, l'électronique et les télécommunications en fait un métal d'un très grand intérêt économique et stratégique. Par ailleurs, pour accompagner la transition écologique et le développement des pays émergents, nombre d'experts et de bureaux géologiques nationaux estiment que le cuivre sera « le » métal nécessaire pour répondre à la croissance de la demande mondiale en énergie. De plus, l'excellente recyclabilité du cuivre en fait un métal très prisé.

Bien qu'il soit distribué de manière non homogène sur notre planète, on retrouve le cuivre sur tous les continents ainsi que dans les fonds marins. Il existe aussi bien à l'état natif (i.e. sans association avec un autre élément chimique) que sous la forme de composés sulfurés, oxydés, silicatés, carbonatés, phosphorés, etc. Le premier gisement de cuivre fût découvert sur l'île de Chypre, en Méditerranée orientale, dont le nom anglais « Cyprus » est tiré du latin « cuprum » signifiant « cuivre ».

De nos jours, les gisements de cuivre exploités à la surface du globe sont les porphyres cuprifères, les amas sulfurés riches en cuivre et les sédiments gréseux riches en cuivre. En plus de ces gisements dits « classiques », le dragage des métaux, dont le cuivre, au fond des océans constitue une importante source de cuivre bien qu'elle demeure peu documentée et non-officielle. De tous ces gisements suscités, les porphyres cuprifères représentent environ 60% de la production mondiale de cuivre (Sinclair, 2007; Jébrak and Marcoux, 2008). Ils se rencontrent principalement dans les arcs magmatiques actifs (e.g. la ceinture de feu du Pacifique) comme éteints (Mongolie, Iran, Europe Centrale). Ils sont associés au magmatisme calco-alcalin des zones de subduction actives (Fig. 1; Sillitoe, 2010). On les retrouve aussi dans des terrains précambriens (craton Ouest Africain, Australie, Canada ; Seedorff et al., 2005; Sinclair, 2007). De nos jours, la quasi majorité des gisements porphyriques à cuivre exploités se situe autour de la ceinture de feu du Pacifique, d'âge tardi-Mésozoïque à tardi-Cénozoïque (Fig. 2; Seedorff et al., 2005; Sillitoe, 2010). Ils sont reconnus autant aux niveaux des cordillères continentales (i.e.

Andes, SW de l'Amérique du Nord ; Sillitoe, 2010) que dans les arcs insulaires du Pacifique Ouest (Indonésie, Papouasie Nouvelle-Guinée, Philippines ; Perelló, 1994; Braxton et al., 2012).

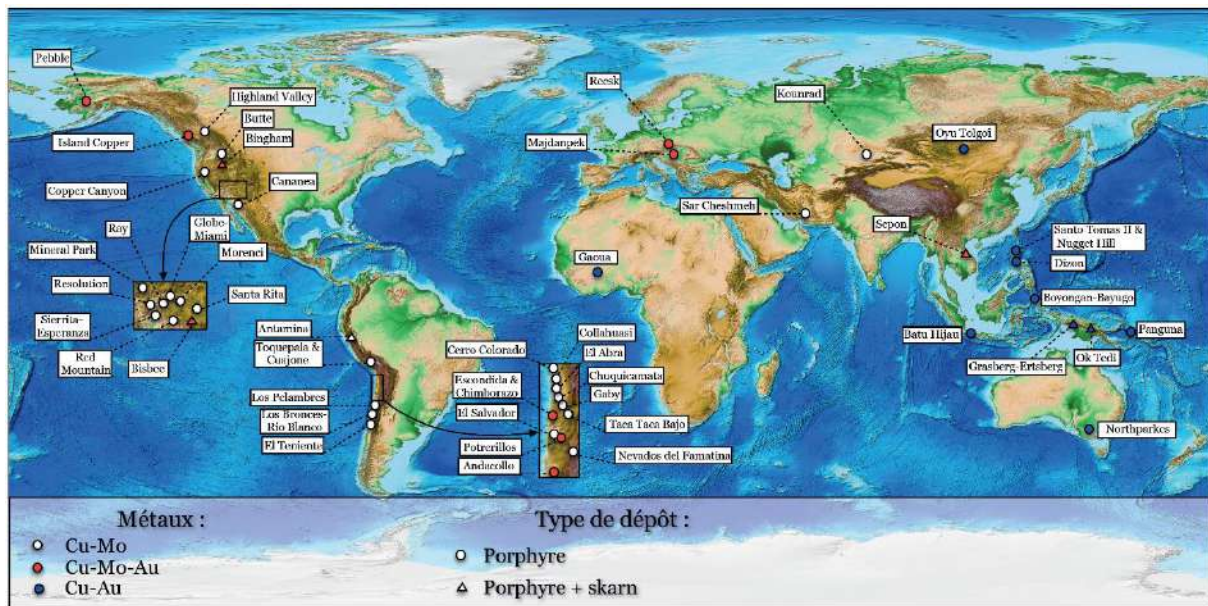


Figure 1 : Carte de répartition des porphyres cuprifères à l'échelle mondiale (modifié d'après Sillitoe, 2010)

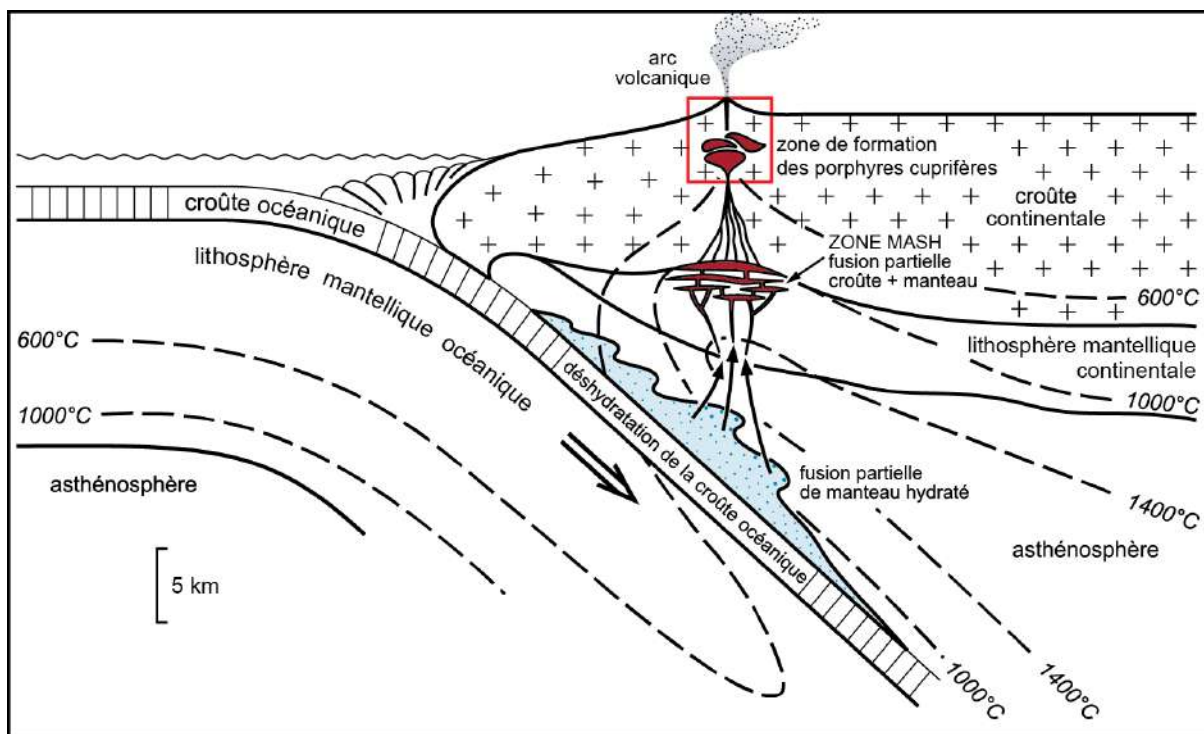


Figure 2 : Genèse des porphyres cuprifères en zone de subduction (modifié d'après Jébrak and Marcoux, 2008)

Les systèmes magmatiques couvrent les quatre premiers kilomètres de la croûte et sont connectés à une chambre magmatique située entre 5 et 15 km de profondeur (Sillitoe, 2010). Par la suite, le mélange entre les fluides magmatiques hydrothermaux et les fluides météoriques est responsable de la précipitation du cuivre primaire, hypogène (Kouzmanov and Pokrovski, 2012). Au cours de son évolution, ce porphyre cuprifère sera exhumé. Et par une balance subtile entre l'érosion, l'exhumation et le climat, le porphyre cuprifère subira une altération supergène qui favorisera la précipitation *in situ* du cuivre secondaire, supergène, par-dessus le cuivre primaire.

Au Chili, la région minière de l'Atacama produit environ le tiers de la production mondiale de cuivre (USGS, service géologique américain, 2015). Cette richesse en cuivre est née de la présence d'énormes minéralisations hypogènes quasiment uniques au monde et de l'altération supergène qu'ont subi ces minéralisations hypogènes. L'altération supergène a été définie la première fois par Ransome (1912) comme étant : « sulfide oxidation and leaching of ore deposits in the weathering environment, and any attendant secondary sulfide enrichment ». Deux types de minéralisations supergènes de cuivre naissent de cette altération supergène : i) les minéralisations cuprifères supergènes *in situ*, formées au-dessus du porphyre cuprifère primaire, par altération des sulfures de cuivre primaires et ii) les minéralisations cuprifères supergènes "exotiques", liées à un transport latéral des solutions cuprifères ou de clastes (observation de terrain) depuis le porphyre cuprifère en amont vers les bassins en aval (Fig. 3; Munchmeyer, 1996; Sillitoe, 2005). A l'échelle du désert d'Atacama, de nombreuses études ont montré le lien entre le tectono-magmatisme lié à l'orogénèse Incaïque (42-33 Ma ; Maksaev and Zentilli, 1999) et la formation des porphyres cuprifères primaires (Sillitoe, 1974; Sillitoe and Perelló, 2005; Mpodozis and Cornejo, 2012). La mise en place de l'altération supergène, quant à elle, reste discutée. Certains auteurs proposent qu'elle se met en place durant la phase de formation du relief et d'exhumation des porphyres (Sillitoe, 2005; Sillitoe and Perelló, 2005), voire durant la période d'élévation maximale de la chaîne lorsque les pentes sont fortes et l'incision importante (Braxton et al., 2009). D'autres, par contre, estiment l'altération supergène contemporaine de la phase de pénéplanation du relief (Clark et al., 1990; Bouzari and Clark, 2002; Bissig and Riquelme, 2009; Riquelme et al., 2017; Sanchez et al., 2018). Si le cuivre supergène *in situ* n'a pas été daté directement, la présence de minéraux d'altération (e.g. alunite, cryptomélane, jarosite), contemporains ou postérieurs à la formation

du cuivre supergène *in situ* a permis d'obtenir une contrainte d'âge quant à la mise en place de la minéralisation cuprifère supergène *in situ*, et partant, du fonctionnement de l'altération supergène. Par le biais de datations K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ sur ces minéraux d'altération, plusieurs auteurs (Münchmeyer, 1996; Hartley and Rice, 2005; Riquelme et al., 2017) suggèrent que l'altération supergène dans le désert d'Atacama a fonctionné entre 44 Ma et 9 Ma, voire jusqu'au Pléistocène et à l'actuel (Reich et al., 2009). Tout comme le cuivre supergène *in situ*, les minéralisations cuprifères supergènes exotiques n'ont jamais fait l'objet d'une datation directe vue la non ubiquité des minéraux d'altération sus-cités. De fait, les seules contraintes d'âge quant à la formation du cuivre supergène, *in situ* ou exotique, reposent sur la présence ou non des minéraux d'altération et la chronologie relative. Ceci empêche *in fine* de retracer l'histoire globale, depuis la mise en place du porphyre cuprifère primaire jusqu'à la formation du cuivre supergène et, de plus, de juger de la contemporanéité ou non de la formation des dépôts cuprifères supergènes *in situ* et exotique (Mote et al., 2001b; Bouzari and Clark, 2002; Sillitoe, 2005). Pourtant, les données chronologiques, combinées aux études thermochronologique, tectonique, géomorphologique, métallogénique et climatique seraient une clé, d'une part, pour retracer l'histoire de l'évolution métallogénique, géomorphologique et paléoclimatique du district minier de l'Atacama et d'autre part, serviraient à la prospection des dépôts cuprifères supergènes.

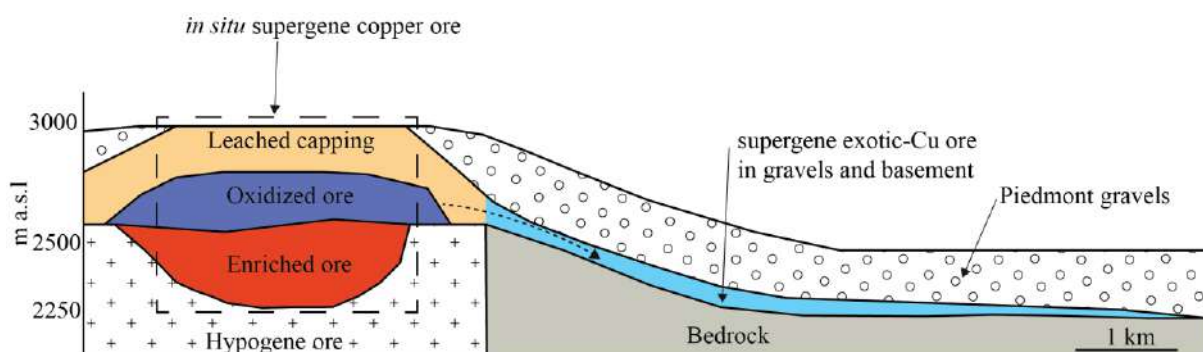


Figure 3 : Représentation schématique de l'altération supergène d'un porphyre cuprifère et de son lien avec la formation des minéralisations exotiques de cuivre (basé sur Münchmeyer, 1996)

Le but de cette thèse est d'explorer le potentiel chronométrique des minéraux cuprifères supergènes, en l'occurrence la chrysocolle et la pseudomalachite, à retenir le signal chronométrique uranium-plomb (U-Pb), ceci afin d'obtenir, pour ce qui constitue une étude pionnière, une contrainte chronologique directe sur l'âge de formation des minéralisations cuprifères supergènes, *in situ* et exotique, dans le désert d'Atacama. Au-delà de la datation, un accent est mis sur la compréhension des paramètres contrôlant la préservation et la perturbation du chronomètre U-Pb dans la chrysocolle et la pseudomalachite, c'est à dire les fluides minéralisateurs, la structure cristalline, le milieu de dépôt, etc. Enfin, la caractérisation isotopique permettra d'identifier la nature et la source aussi bien des fluides minéralisateurs que perturbateurs des chronomètres U-Pb et comprendre l'effet des processus d'oxydation-réduction sur la formation des minéralisations supergènes de cuivre.

Les différentes thématiques et méthodes utilisées alliant échantillonnage de terrain, caractérisations minéralogique et chimique, géochronologie U-Pb et caractérisations cristallographique et isotopique s'articulent autour des chapitres suivants :

- 1) Le chapitre I revient brièvement sur l'état de l'art des connaissances sur la géologie du désert d'Atacama, le processus de formation des minéralisations cuprifères supergènes et les facteurs qui contrôlent la formation de ces minéralisations.
- 2) Le chapitre II présente les méthodes et outils utilisés tout au long de ce travail de thèse.
- 3) Le chapitre III présente la caractérisation minéralogique et chimique des minéralisations cuprifères supergènes du désert d'Atacama et compare les résultats avec des échantillons de cuivre supergène du district minier de Gaoua au Burkina Faso (Béziat et al., 2008a; Siebenaller et al., 2015; Baratoux et al., 2015; Le Mignot et al., 2017). Ce chapitre a fait l'objet d'un article accepté à la revue *Ore Geology Reviews*.
- 4) Le chapitre IV s'intéresse à la caractérisation isotopique du cuivre dans les minéralisations cuprifères supergènes exotiques dans l'optique de comprendre l'impact des processus d'oxydation-réduction sur la formation des minéralisations exotiques de cuivre et apporter un élément de réponse sur la nature des fluides minéralisateurs. Ce chapitre fera l'objet d'une soumission prochaine à une revue scientifique.

- 5) Le chapitre V présente les premiers résultats de la datation U-Pb via LA-ICP-MS sur la chrysocolle et la pseudomalachite, deux minéraux cuprifères supergènes oxydés. Ces résultats, pionniers, montrent qu'il est possible de dater la minéralisation cuprifère supergène et obtenir un âge de cristallisation. Ce chapitre a fait l'objet d'un article publié à la revue *Mineralium Deposita*.
- 6) Le chapitre VI montre ce qui contrôle la préservation et la perturbation du système U-Pb dans la chrysocolle et la pseudomalachite en alliant la caractérisation géochronologique à l'analyse des isotopes stables de l'oxygène et à la caractérisation isotopique. Ce chapitre est en préparation pour une soumission prochaine à la revue *Chemical Geology*.
- 7) Le chapitre VII, sous la forme d'une synthèse générale, remet en perspective toutes les données obtenues et discute du i) comportement du chronomètre U-Pb dans les minéralisations cuprifères supergènes et ii) des conditions géologiques locales et régionales favorisant la formation des minéralisations cuprifères supergènes dans le désert d'Atacama et partant, dans d'autres régions du monde.

CHAPITRE I :

Etat de l'art des connaissances sur la géologie du désert d'Atacama et l'altération supergène des porphyres cuprifères

I.1 La géologie des Andes et du désert d'Atacama

I.1.1 Géologie des Andes

La cordillère des Andes est la plus longue chaîne de montagnes à la surface de la Terre, s'étirant sur environ 7000 Km sur toute la longueur de la plaque continentale sud-américaine, depuis le Venezuela au nord, jusqu'à la Patagonie chilienne au sud. Elle résulte de la subduction de la microplaque océanique Nazca sous la plaque continentale sud-américaine (Fig. I.1.A), entraînant de fait une importante activité sismique tout le long de cette frange E-SE de la Ceinture de Feu du Pacifique. L'histoire de cette subduction commence dès la dislocation de Rodinia à la fin du Néoprotérozoïque (800-700 Ma ; Dalziel, 1997). Cette dislocation a entraîné la formation de l'Océan Iapetus, i.e. le proto-Pacifique. Dès le Phanérozoïque (~ 570 Ma), ce proto-océan pacifique a commencé une subduction sous la marge occidentale du Gondwana jusqu'au Trias moyen (Pankhurst et al., 1998; Chew et al., 2007), entraînant la formation d'un arc magmatique d'âge Paléozoïque depuis le Venezuela jusqu'au Chili. Au Mésozoïque, la dislocation de la Pangée suite à l'ouverture de l'Océan Atlantique a entraîné une subduction continue de la plaque océanique Nazca sous le continent sud-américain depuis le Jurassique jusqu'à l'actuel.

La cordillère des Andes est subdivisée en 3 zones physiographiques, tectonomagmatiques et métallogéniques (Fig. I.1B; Sillitoe, 1974; Sempere et al., 2002) : i) les Andes du Nord entre 10°N et 5°S, comprenant le Venezuela, la Colombie, et l'Equateur ii) les Andes Centrales, les plus importantes, entre 5°S et 35°S regroupant le Pérou, le Chili, la Bolivie et l'Argentine et iii) les Andes du Sud, de 35°S à 55°S, incluant le Chili et l'Argentine et les Andes patagoniennes. Les Andes Centrales constituent le segment le plus important autant d'un point de vue physiographique que métallogénique. Cette dernière peut être divisée en trois sections : 1) la partie nord des Andes Centrales, au Pérou, entre 10°S et 13°S 2) l'Orocline Bolivien ou partie centrale, entre 13°S et 28°S, entre le Pérou, la Bolivie et le nord du Chili et 3) le sud des Andes centrales, entre le Chili et l'Argentine (Sempere et al., 2002). De ces 3 segments, les Andes Centrales contiennent la majorité des gisements de Cu, situés majoritairement dans sa section centrale. Un descriptif détaillé du magmatisme et de la métallogénie de ce segment sera fait dans la section suivante.

Cinq époques métallogéniques, correspondant à 5 ceintures cuprifères ont donné aux Andes, et plus particulièrement aux Andes Centrales, leurs richesses en Cu et métaux associés (Sillitoe, 1992). Elles s'étalent depuis la fin du Paléozoïque jusqu'à la fin du Pliocène avec un intérêt économique devenant croissant depuis les ceintures séniles vers les ceintures les plus récentes.

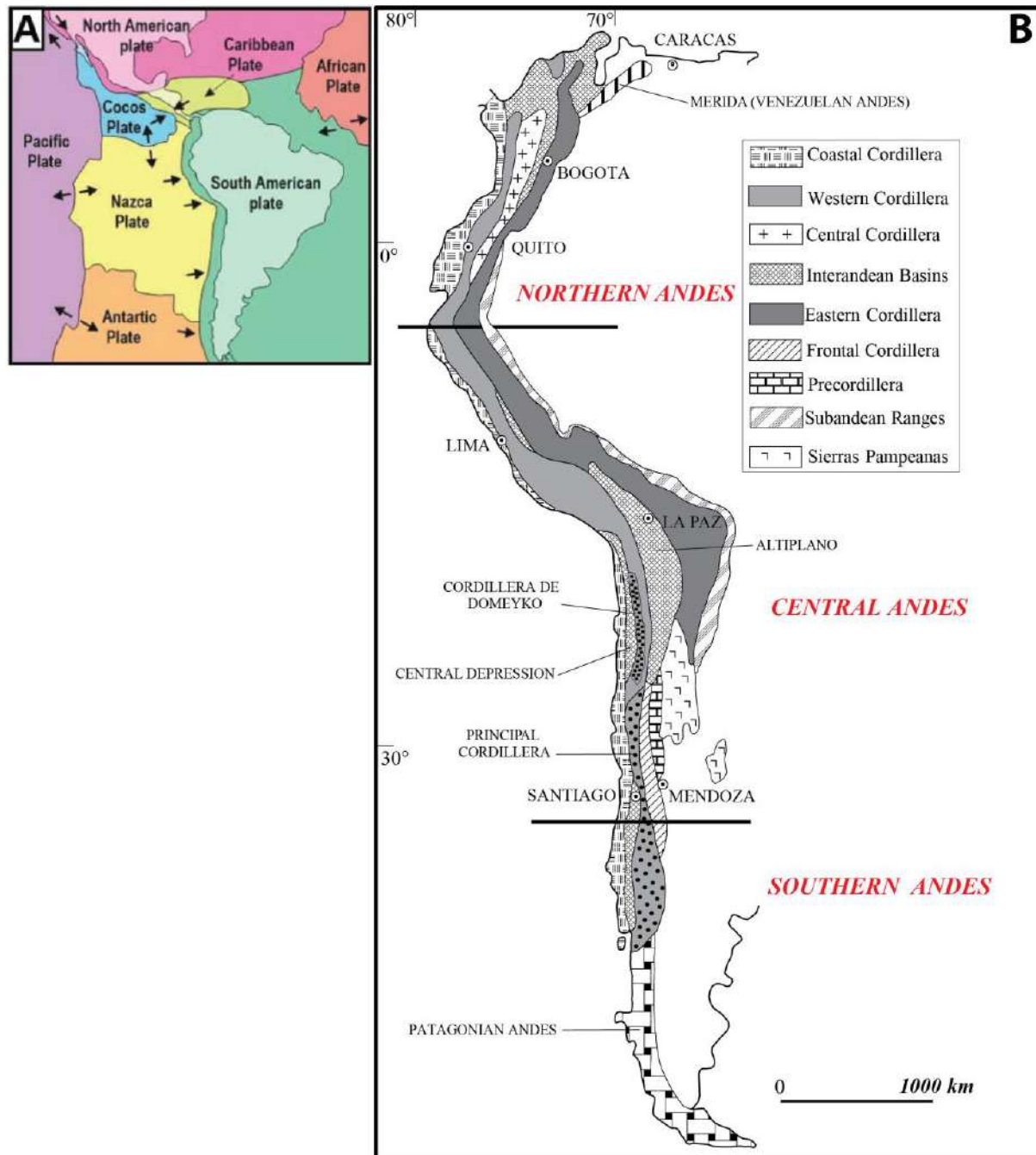


Figure I.1 : A. Illustration de la tectonique des plaques autour de la plaque tectonique sud-américaine. B. Carte du continent sud-américain montrant la segmentation de la cordillère des Andes (modifié d'après Sillitoe and Perelló, 2005)

I.1.2 Tectonomagmatisme et métallogénie des Andes Centrales et du désert d'Atacama du Mésozoïque au Cénozoïque

Les Andes Centrales et le désert d'Atacama, et partant toute la chaîne andine, ont réellement façonné leur morphologie actuelle depuis le Jurassique moyen jusqu'au Pliocène. Quatre événements tectonomagmatiques, correspondant à la formation de 4 ceintures cuprifères et métaux associés ont permis la structuration actuelle des Andes Centrales, et par conséquent, celle du désert d'Atacama, avec d'ouest en est, suivant la migration de la subduction (Fig. I.2.A, B; Jordan et al., 1983) : i) la cordillère côtière, d'âge Jurassique à tardi-Crétacé ii) la dépression centrale ou vallée longitudinale, structurée durant le Paléocène et l'Eocène précoce iii) la Precordillera ou cordillère de Domeyko, formée entre l'Eocène moyen et l'Oligocène moyen et iv) les Andes, constituées d'un plateau perché (Altiplano) et d'une cordillère, d'âge Miocène à Pliocène précoce.

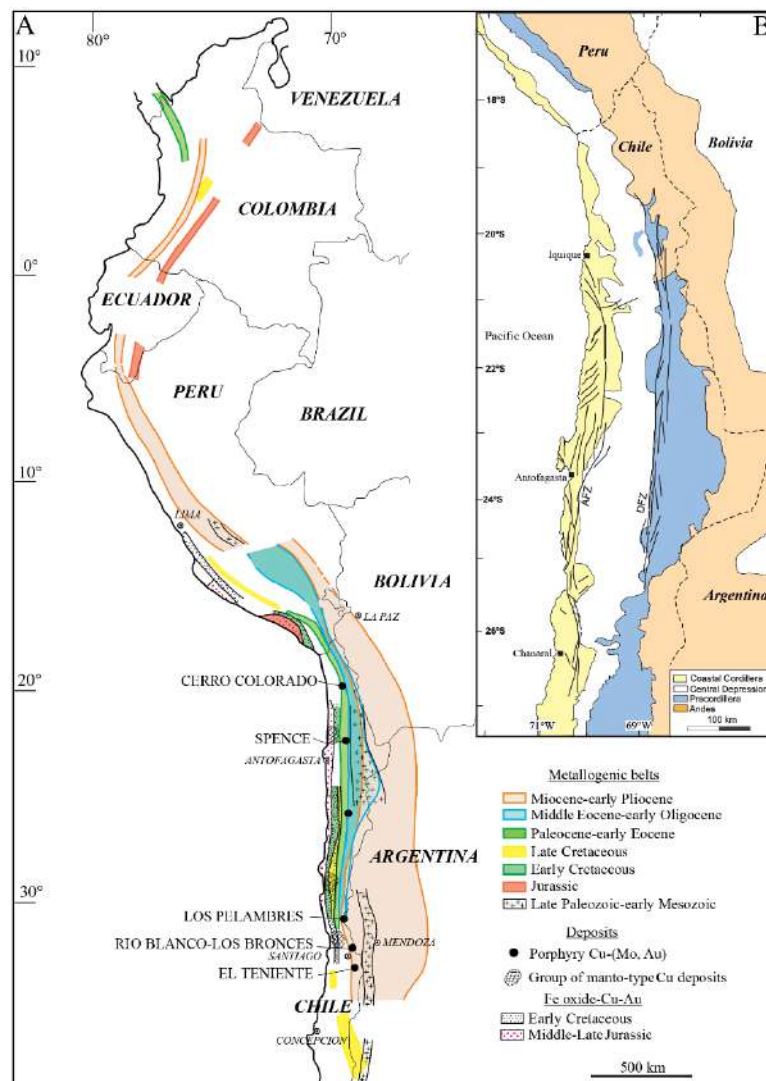


Figure 1.2 : A. Carte du continent sud-américain montrant les différentes époques métallogéniques de la cordillère des Andes (modifié d'après Sillitoe and Perelló, 2005). B. Carte du désert d'Atacama chilien montrant les principales ceintures métallogéniques (modifié d'après Arancibia et al., 2006)

Du Jurassique au début du Crétacé, la subduction de la plaque Nazca sous le continent sud-américain a permis la surrection de la cordillère côtière, du sud du Pérou au nord du Chili (Sillitoe et al., 1982). Le magmatisme de cet arc s'est produit dans des conditions extensionnelles à transtensionnelles favorisant la formation de bassins arrière-arc et intra-arc (Mpodozis and Ramos, 1989b; Boric et al., 1990). Ce magmatisme comprend des roches plutoniques et volcaniques encaissées dans un socle Paléozoïque et des coulées basaltiques à andésitiques encaissées dans les bassins intra- et arrière arcs. Ces conditions extensionnelles et transtensionnelles se sont terminées à la limite Crétacé-Tertiaire lors de l'inversion tectonique des bassins sous l'effet d'une déformation compressive (Mpodozis and Cornejo, 2012). Les minéralisations cuprifères comprennent une variété de dépôts avec, au nord du Chili, la formation de porphyres cuprifères sub-économiques, de gisements de type IOCG (Iron Oxide Copper Gold) et des gisements stratiformes de cuivre de type « manto-type », encaissés dans des formations sédimentaires à volcano-sédimentaires (Sillitoe, 2003; Kojima et al., 2009).

Le magmatisme Paléocène-Eocène se rencontre à l'est de la Dépression Centrale. Les données structurales et géochimiques indiquent une contrainte tectonique neutre à légèrement extensionnelle présente au-dessus d'une subduction abrupte et d'une croûte amincie (Sillitoe and Perelló, 2005). Le magmatisme s'est accompagné de la mise en place d'une ceinture cuprifère du sud du Pérou au nord du Chili avec des gisements d'importance économique tels Cerro Colorado, Spence et Lomas Bayas dans le désert d'Atacama chilien (Rowland and Clark, 2001; Bouzari and Clark, 2002). Ce magmatisme est de type calco-alcalin, avec des roches andésitiques à rhyolitiques encaissées dans des roches tardi-Crétacé à Paléocène. Ces porphyres ont subi plus tard (~ 44 Ma) un enrichissement supergène favorisant la formation d'horizons d'oxydes de cuivre et de sulfures secondaires de cuivre (Bouzari and Clark, 2002).

Le magmatisme Eocène-Oligocène corrèle parfaitement avec la phase tectonique Incaïque (45-33 Ma ; Makshev and Zentilli, 1988; Mpodozis and Perelló, 2003; Sillitoe and Perelló, 2005). Durant cette période, la courbure de la marge continentale a généré l'Orocline bolivienne et la formation du

système de failles de Domeyko (Maksaev and Zentilli, 1988; Boric et al., 1990; Maksaev, 1990). Le système de failles de Domeyko (Domeyko Fault Zone, DFZ), né de l'orogénèse Incaïque, est une zone de déformation s'étirant sur plus de 1000 km de long (Maksaev, 1990), parallèle à l'orogène et composée de plis, de failles inverses, normales et décrochantes, s'étendant le long de la précordillère entre 20°S et 28°S (Fig. I.3). Pour certains auteurs (Boric et al., 1990; Maksaev, 1990), le jeu des failles et plis a commencé au Crétacé tardif, lors de l'inversion des failles normales héritées de l'extension arrière-arc Mésozoïque. Pour d'autres (Scheuber and Reutter, 1992; Mpodozis et al., 2005), les bassins arrière-arc andins ont d'abord été inversés pour former une proto-cordillère puis une impulsion lors de l'orogénèse Incaïque a finalisé leur structuration actuelle. Les données traces de fission sur apatite (AFT) montrent que la Précordillère a été exhumée entre 42 et 30 Ma (Maksaev and Zentilli, 1999) en lien avec le soulèvement tectonique Inca et une érosion dont les produits se sont accumulés dans les bassins syntectoniques, e.g. la Dépression Centrale à l'ouest et les Salars à l'est. Les dépôts cuprifères de l'Eocène moyen à Oligocène sont majoritairement constitués de porphyres cuprifères à $\pm$ Au-Ag-Mo. Ces porphyres cuprifères se sont mis en place de manière contemporaine au magmatisme lié à l'orogénèse Incaïque, lors de la formation de l'Orocline bolivien (Fig. I.3; Sillitoe and Perelló, 2005). Si la moitié des porphyres cuprifères s'est mise en place le long de la DFZ, le contrôle structural des porphyres est diversifié et attribué à l'évolution des conditions tectoniques le long des différents segments annexes du système de failles de Domeyko durant les 10 Ma qu'a duré la tectonique Incaïque (Camus, 2003; Mpodozis and Cornejo, 2012). La ceinture de cuivre Eocène-Oligocène s'étend depuis le sud du Pérou (13°S) jusqu'au nord du Chili (30°S) sur environ $\sim$ 2500 Km de long. Elle contient la plus large concentration de Cu au monde, exclusivement sous la forme de porphyres cuprifères, avec la grande majorité des gisements situés dans le désert d'Atacama chilien. En plus des minéralisations sulfurées primaires, l'altération supergène a donné à ces porphyres leur énorme importance économique (Sillitoe and McKee, 1996; Sillitoe, 2005). La signature géochimique de ces porphyres est calco-alcaline, évoluant d'un stade mafique à un stade felsique, avec un ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ élevé, indiquant une fusion oxydée et un magma de type-I (Ishihara, 1980; Ishihara, 1981; Ishihara et al., 1984), riche en eau.

Depuis 30 Ma jusqu'à l'actuel, la migration de l'arc magmatique vers l'est, en lien avec la subduction, a achevé la formation de la Précordillère et le magmatisme Eocène-Oligocène. S'en est suivi la surrection de la ceinture Miocène à Pliocène précoce, principalement présente au nord et au sud des Andes Centrales.

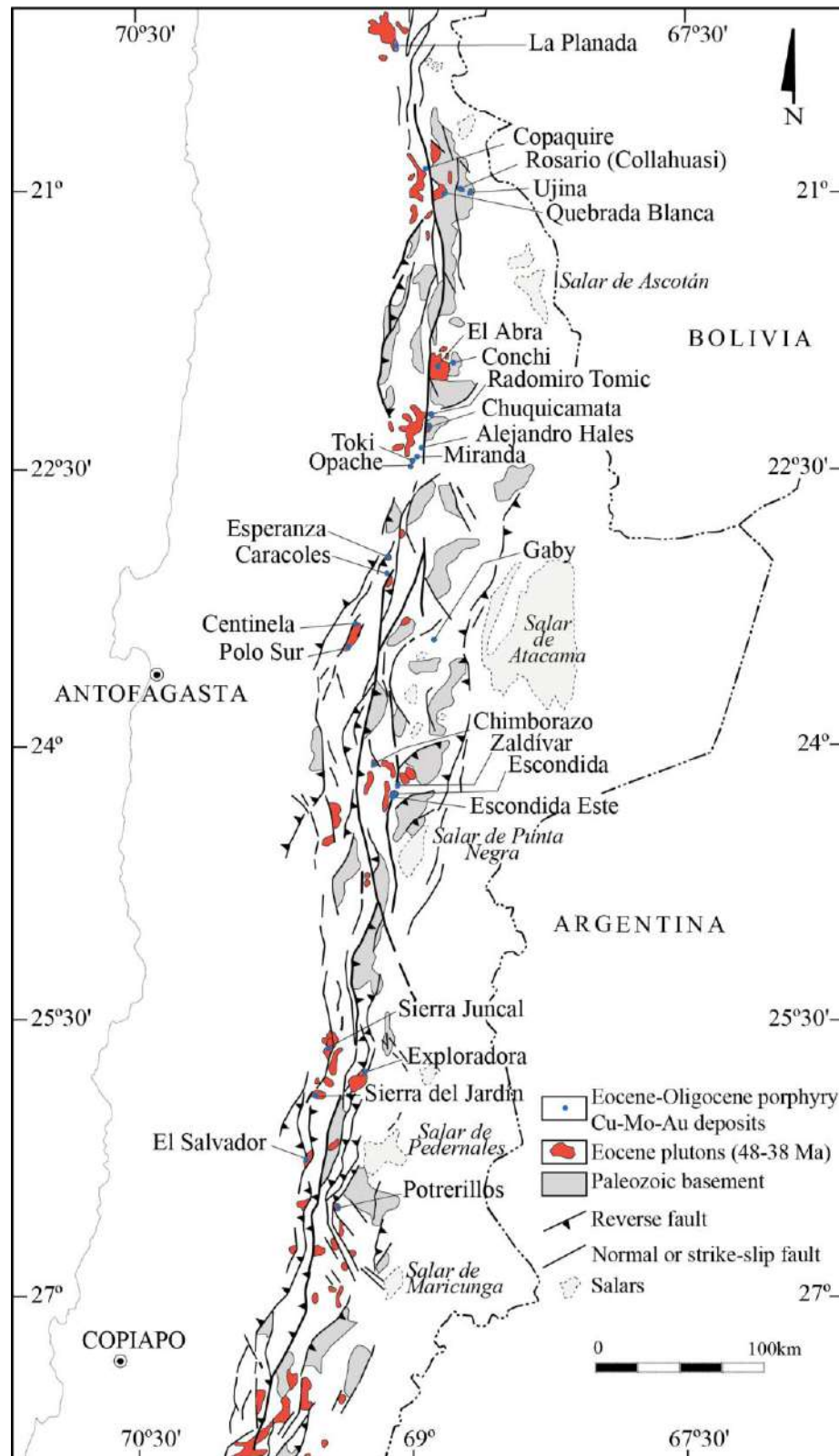


Figure I.3 : Carte de la répartition des plutons magmatiques Eocène et des porphyres cuprifères le long de la Precordillera (modifié d'après Mpodozis and Cornejo, 2012)

Le tectonomagmatisme Miocène à Pliocène-précoce des Andes Centrales s'étend depuis le nord du Pérou jusqu'au centre du Chili et de l'Argentine (région de Santiago et de Mendoza). Au Chili, cette chaîne s'étend sur environ 400 Km, dans une zone de transition entre une zone à subduction plate (pampa chilienne) et une zone de subduction plus abrupte sous le Chili (Camus, 2003; Sillitoe and Perelló, 2005). Au nord du Chili, dans le désert d'Atacama, le magmatisme Miocène à Pliocène précoce est représenté uniquement par un volcanisme ignimbritique et des coulées de lave. Aucun porphyre cuprifère lié à cet événement magmatique n'a été encore identifié. Cependant, au centre du Chili, entre 32°S et 35°S, le magmatisme est accompagné par la formation de porphyres cuprifères suivant 3 principaux stades : i) la mise en place de coulées mafiques et de roches volcanoclastiques hébergées dans des bassins en extension durant le Miocène précoce (Kay et al., 1999) ii) la mise en place de coulées andésitiques et dacitiques d'âge Miocène intrudées par des corps plutoniques et iii) la formation des porphyres cuprifères entre 7 et 4 Ma (Sillitoe and Perelló, 2005). Un épaissement et un raccourcissement crustal dû à un SLAB plat ont causé le soulèvement et la rapide exhumation des roches (3 km/m.y. ; Kurtz et al., 1997). Les produits de l'érosion se sont ensuite déposés dans les bassins en aval. Trois grands gisements porphyriques sont reconnus dans la région, Los Pelambres, Río Blanco-Los Bronces et El Teniente (Camus, 2003; Makshev et al., 2004; Cooke et al., 2005). Le magmatisme est de type-I, calco-alcalin, très évolué (riche en SiO_2 et K_2O), avec un ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ indiquant un fort degré d'oxydation (Garrido et al., 2002). Contrairement aux chaînes Paléocène-Eocène et Eocène-Oligocène, les profils complets d'altération supergène sont quasi-absents dans la ceinture Miocène-Pliocène (Sillitoe, 2005) même si certains dépôts montrent des horizons riches en chalcocite supergène (e.g. Los Pelambres, El Teniente, Río Blanco ; Sillitoe and Perelló, 2005). Ceci est à mettre aux crédits des faibles teneurs en pyrite et à leur âge de mise en place très récent malgré des apports d'eau plus importants. Cependant, d'après Sillitoe (2005), l'altération supergène semble s'être mise en place durant les 3 derniers millions d'années et serait toujours active.

I.1.3 Géomorphologie et évolution climatique du désert d'Atacama chilien au Mésozoïque-Cénozoïque

Le désert d'Atacama, au nord du Chili, représente un paradis pour les géomorphologues étudiant les interactions entre la tectonique, l'érosion et le climat. Le soulèvement Andin, initié au Mésozoïque, couplé à l'érosion qui s'en est suivi a permis la formation de larges surfaces d'érosion, plates, appelées pédiplaines, qui s'étendent depuis le sud du Pérou jusqu'à la limite australe du désert d'Atacama (Fig. I.4; Segerstrom, 1963; Mortimer, 1973; Mortimer and Sarič, 1975). L'exemple palpable est la dépression centrale ou vallée longitudinale qui s'étire sur tout le long du désert d'Atacama et qui correspond à une mosaïque de plusieurs surfaces d'érosion (Fig. I.5; Segerstrom, 1963; Evenstar et al., 2017). L'épaisseur de cette pédiplaine atteint des centaines de mètres dans les bassins pré-andins (e.g. bassin de Calama et de Centinela ; May et al., 1999) mais ne dépasse pas généralement la dizaine de mètres d'épaisseur. Par ailleurs, plusieurs études ont montré un lien entre la formation de ces pédiplaines et l'altération supergène depuis les travaux pionniers de Mortimer et al. (1977) jusqu'à ceux plus récents de Clark et al. (1990) et Riquelme et al. (2017). Ces pédiments se forment majoritairement en conditions climatiques arides d'où leur distribution dans le désert d'Atacama, aride depuis la transition Méso-Cénozoïque (Hartley et al., 2005; Clarke, 2006) mais aussi dans d'autres régions du monde, e.g. le craton ouest Africain (Beauvais and Chardon, 2013; Chardon et al., 2018). Ces surfaces d'érosion se forment par la troncature d'un relief suite à des conditions érosives lentes à modérées. On parle souvent d'érosion latérale (Guillocheau et al., 2015).

Dans le désert d'Atacama, la formation de ces surfaces d'érosion a été diachrone entre le nord et le sud du désert (Mortimer, 1973; Mortimer and Sarič, 1975; Riquelme et al., 2003; Bissig and Riquelme, 2010). Au nord du désert d'Atacama, les travaux pionniers de Mortimer and Sarič (1975) et ceux plus récents de Riquelme et al. (2003) ont montré que le soulèvement tectonique a commencé au Crétacé. Dès cette époque, l'aridité, combinée à la surrection de la cordillère côtière, a favorisé la formation de pédiplaines dans la dépression centrale et la proto-précordillère. Par la suite, l'hyperaridification du nord du désert d'Atacama, initiée au Miocène moyen, a permis de conserver ces surfaces d'érosion. Dans le sud du désert, la surrection du relief s'est faite au début du Tertiaire

(Mortimer, 1973) et atteint une altitude considérable au tardi Eocène-début Oligocène (Bissig and Riquelme, 2010) au cours d'impulsions tectoniques beaucoup plus régionales que globales. S'en est suivi la formation de plusieurs surfaces d'érosions depuis l'Oligocène jusqu'au Pliocène, e.g. dans le district minier de Potrerillos-El Hueso (Bissig and Riquelme, 2009; Bissig and Riquelme, 2010), dû à la prévalence tardive de conditions climatiques beaucoup plus humides dans la précordillère nord.

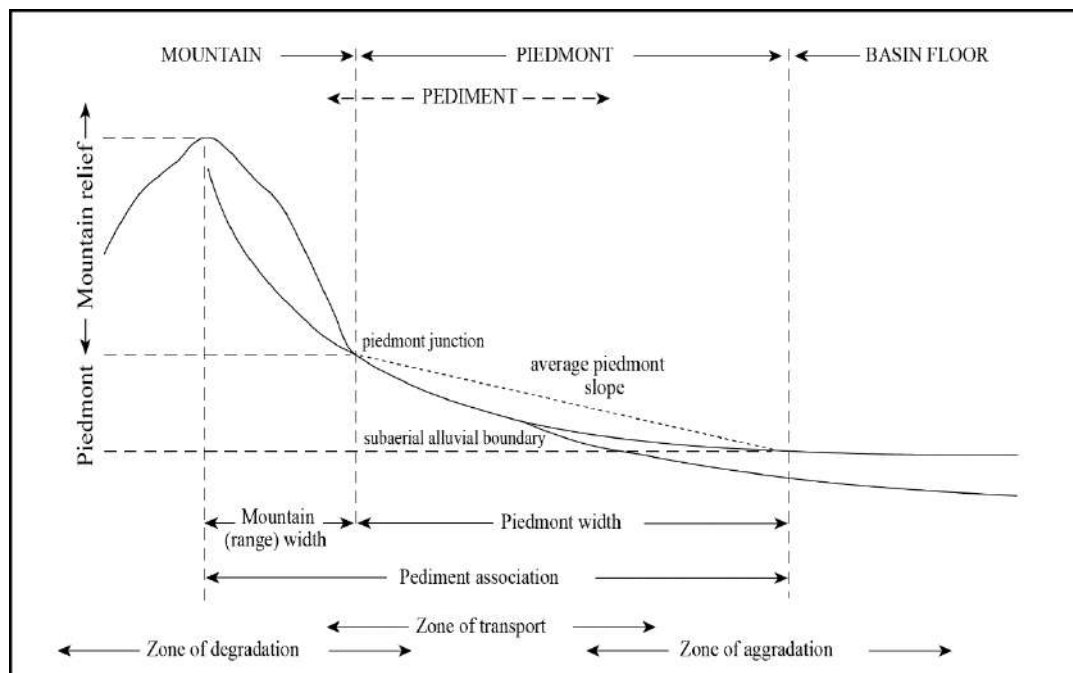


Figure 1.4 : Représentation schématique de la formation des pédiments (modifié d'après Dohrenwend and Parsons, 2009)



Figure I.5 : Photographie montrant une surface d'érosion dans la Dépression Centrale du désert d'Atacama

Cependant, si le climat est aujourd'hui hyperaride avec des précipitations inférieures à 20 mm de pluie par an (Fig. I.6; Houston and Hartley, 2003; Strecker et al., 2007), la formation de ces pédiplaines, qui requiert un climat plus humide, montre que le désert d'Atacama n'a pas toujours été hyperaride tout au long de son histoire.

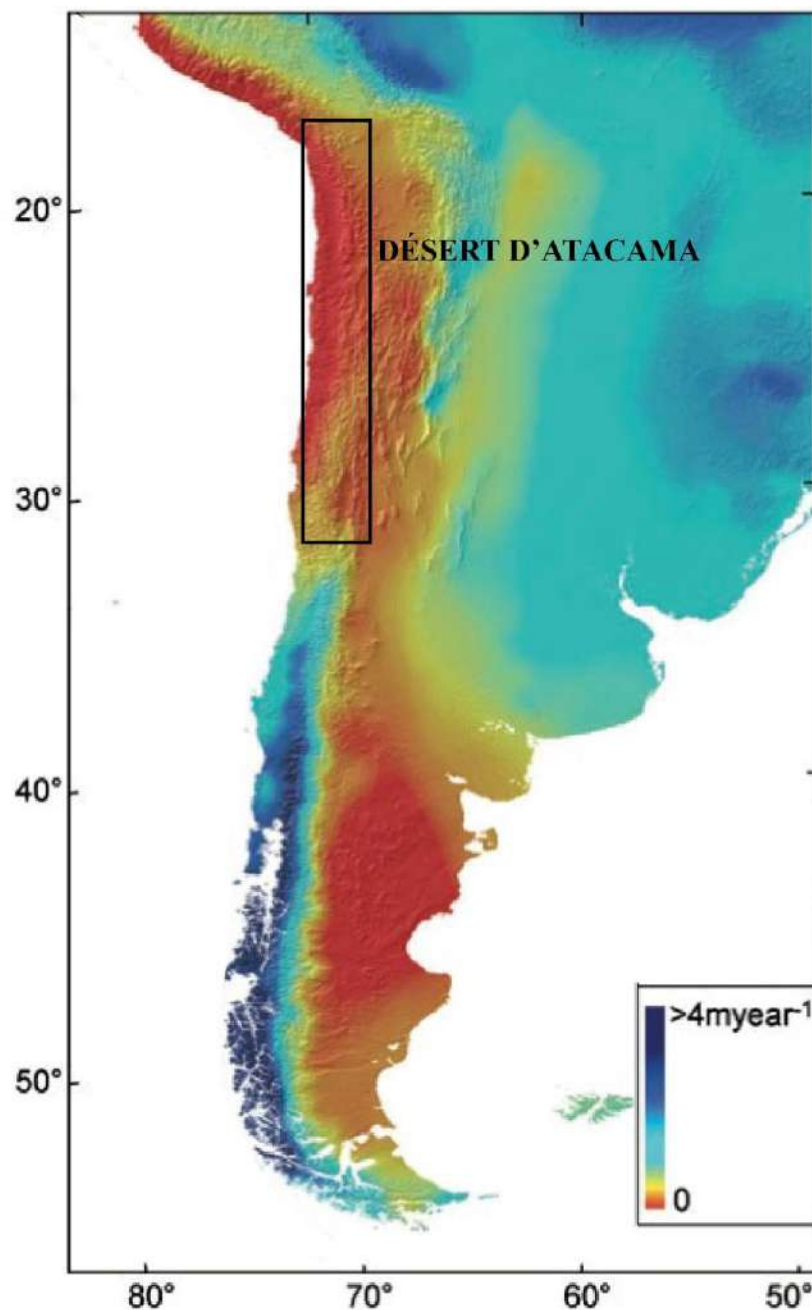


Figure I.6 : Carte du sud du continent sud-américain montrant le taux de précipitation annuel du désert d'Atacama par comparaison au reste du continent sud-américain (modifié d'après Strecker et al., 2007)

Comme mentionnée dans le paragraphe précédent, le désert d'Atacama est aride, d'après les enregistrements sédimentologiques, depuis la limite Jurassique-Crétacé (Hartley et al., 2005) voire depuis la fin du Trias (Clarke, 2006). Cependant, la date exacte de l'installation du climat aride reste sujet à controverse.



Figure I.7 : Carte du continent sud-américain montrant les phénomènes responsables de l'hyperaridité du désert d'Atacama

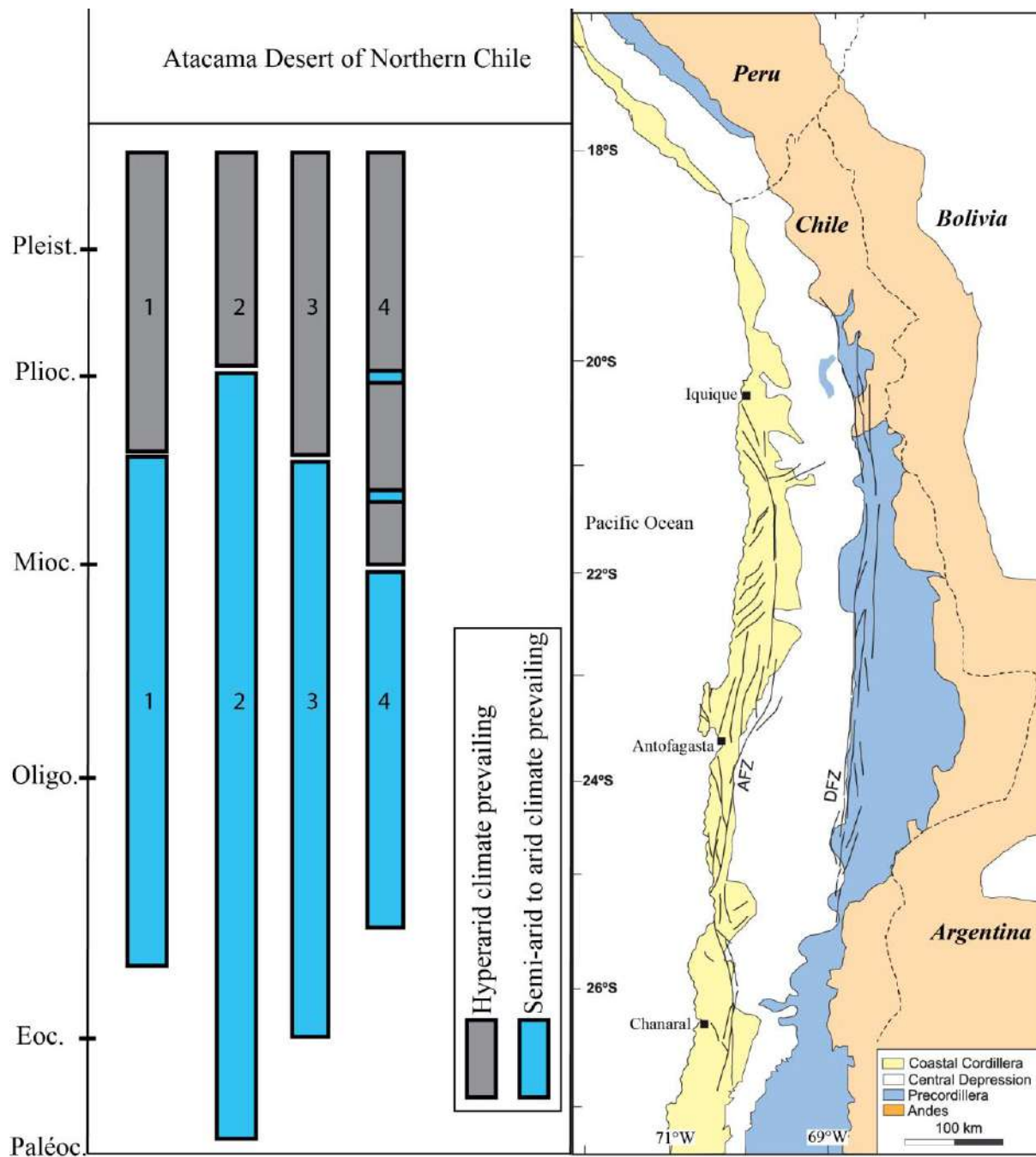
Maintes études s'opposent et se complètent quant aux facteurs ayant favorisé l'aridité du désert d'Atacama (Montgomery et al., 2001; Hartley and Chong, 2002; Garreaud et al., 2010). Trois facteurs font consensus (Fig. I.7) : 1) la présence du courant de Humboldt, un courant marin froid provenant de l'Antarctique qui maintient une zone de haute pression sur la côte est du Pacifique et empêche l'arrivée des pluies, actif depuis le Cénozoïque (Garreaud et al., 2010), 2) « the rain-shadow effect » dû à

l'élévation des Andes, qui crée une barrière orographique, empêchant aux masses d'air humide provenant de l'Atlantique et de l'Amazonie d'atteindre le pacifique (Zhou and Lau, 1998; Houston and Hartley, 2003), 3) la position du Chili dans la zone subtropicale sèche du Pacifique Est où la présence d'un anticyclone empêche l'arrivée des pluies (Garreaud et al., 2010). Si un consensus demeure quant à la complémentarité de ces trois facteurs pour expliquer l'aridité du désert d'Atacama, les facteurs expliquant l'initiation de l'hyperaridité dans le désert d'Atacama, climat qui demeure de nos jours, sont beaucoup plus débattues. Pour Houston and Hartley (2003) et Garreaud et al. (2010), l'intensification du courant de Humboldt est la cause primordiale du changement vers un climat hyperaride. Pour d'autres, l'installation d'un climat hyperaride s'expliquerait par un soulèvement tectonique au Miocène, augmentant significativement le « rain-shadow effect » et, de fait, initiant le passage à des conditions hyperarides (Dunai et al., 2005; Rech et al., 2010). Enfin, pour Hartley and Chong (2002), l'hyperaridification du désert d'Atacama n'est pas un phénomène régional mais global à l'échelle mondiale (e.g. les déserts du Kalahari et du Sahara) dû à la baisse des températures des océans du sud en lien avec la formation de la calotte glaciaire antarctique.

Si des questions demeurent sur la cause majeure du passage vers un climat hyperaride, la date à laquelle cette dernière s'initie pourrait nous donner des éléments de réponse. Différentes études, i.e. sédimentologiques, pédologiques, isotopiques et la datation de minéraux d'altération supergène tout comme des pédiplains ont été réalisées pour connaître le moment exact du passage à des conditions hyperarides (Fig. I.8). De prime abord, le passage à un climat hyperaride est diachrone entre le nord et le sud du désert d'Atacama (Mortimer, 1973; Mortimer and Sarič, 1975; Bissig and Riquelme, 2010). La datation des minéraux d'altération (e.g. alunite, jarosite, cryptomélane) a été utilisée pour définir le laps de temps durant lequel l'altération supergène s'est déroulée. Les datations K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ réalisées sur ces minéraux d'altération s'étalent entre 44 Ma et 14 Ma dans le nord du désert d'Atacama (Sillitoe and McKee, 1996; Bouzari and Clark, 2002; Hartley and Rice, 2005; Riquelme et al., 2017) et jusqu'à 6 Ma au sud du désert d'Atacama (secteur de Potrerillos-El Hueso, Marsh et al., 1997; Bissig and Riquelme, 2009). La cessation de l'altération supergène a donc été mis au crédit d'un passage vers des conditions climatiques plus extrêmes, l'altération supergène requérant un climat semi-aride à aride (Sillitoe, 2005). Les études sédimentologiques et stratigraphiques se sont quant à elles focalisées sur la

nature des dépôts enregistrées dans les salars (i.e. corps évaporitique sédimenté dans la partie la plus basse de bassins d'origine tectonique, formé en environnement désertique ; Díaz, 1988) et les bassins intra-arcs. D'après Hartley and Chong (2002) qui ont étudié la succession stratigraphique du bassin de Calama, de bassins pré-andins et celle de la Precordillera, le dépôt de cônes alluviaux et de sédiments fluviaux-lacustres entre 21 Ma et 6 Ma indiqueraient la prévalence d'un climat semi-aride à aride durant cette période. Par la suite, la précipitation d'évaporites et la formation d'une croûte saline entre 6 Ma et 3 Ma indiqueraient des conditions hyperarides. Ces arguments sont corroborés par d'autres études sédimentologiques menées par Clarke (2006) et Jordan et al. (2014). Les études pédologiques (Rech et al., 2006; Oerter et al., 2016) et celle des isotopes stables (Bissig and Riquelme, 2009; Rech et al., 2010) corroborent, de même, l'hypothèse du passage des conditions arides à hyperarides de la mi- Miocène à la fin du Miocène. Enfin, certains auteurs (Dunai et al., 2005; Evenstar et al., 2017) ont daté la formation des surfaces d'érosion via l'usage des nucléides cosmogéniques, e.g. ^3He and ^{21}Ne . L'âge de formation de ces surfaces est défini comme étant le moment où le dépôt des sédiments a cessé dû à l'hyperaridification. De part cette méthode, Dunai et al. (2005) et Evenstar et al. (2017) ont proposé un âge tardi-Oligocène pour l'initiation de l'hyperaridité marqué par des occurrences de brefs épisodes humides après l'Oligocène.

Comme on peut le constater, autant les causes que la période d'initiation de l'hyperaridité demeure sujet à débat au fur et à mesure que les techniques d'études progressent. Pour résumer, on retiendra que les études sédimentologiques montrent que le désert d'Atacama est aride depuis la fin du Trias (Clarke, 2006) et que l'initiation de l'hyperaridité a eu lieu entre 25 Ma et 3 Ma. Cependant, ces conditions hyperarides sont entrecoupées d'évènements pluvieux, catastrophiques et localisés liés aux phénomènes El Niño et La Niña (McKay et al., 2003; Houston, 2006).



1. Ar/Ar and K-Ar dating of altered minerals (Cryptomélane, Alunite, Jarosite; Bouzari & Clark 2002; Hartley & Rice, 2005; Bissig & Riquelme 2010)
2. Sedimentological study (Hartley & Chong, 2002; Clarke 2006; Jordan et al. 2014)
3. Pedological and stable isotope studies (Rech et al. 2006; Bissig & Riquelme 2009; Rech et al. 2010; Oerter et al. 2016)
4. ^3He and ^{21}Ne cosmogenic nuclides studies (Dunai et al. 2005; Evenstar et al. 2017)

Figure I.8 : Résumé des études géochronologiques, sédimentologiques, pédologiques, isotopiques et cosmogéniques montrant la prévalence de l'aridité dans le désert d'Atacama depuis le Paléocène et l'initiation d'un climat hyperaride au Miocène

I.2 L'altération supergène des porphyres cuprifères et la formation des minéralisations cuprifères supergènes dans le désert d'Atacama chilien

L'altération supergène est le principal critère qui donne aux porphyres cuprifères du Chili leur si grand intérêt économique. Cette altération est liée aux fluides supergènes (i.e. de surface) qui vont altérer et lessiver le cuivre des minéraux cuprifères primaires (e.g. chalcopyrite, bornite) puis précipiter des minéraux supergènes de cuivre. Les porphyres cuprifères qui ont en général de gros tonnages pour de faibles teneurs (jusqu'à 11 Gt pour 0.76 wt. % de Cu de à la mine de Chuquibambilla au Chili ; Ossandon et al., 2001) acquièrent ainsi, par le biais de l'altération (secondaire) supergène, des teneurs importantes (jusqu'à 2 wt. % Cu ; Reich and Vasconcelos, 2015), contribuant de manière significative à leur grand intérêt économique.

I.2.1 L'altération hydrothermale hypogène

Les porphyres cuprifères se mettent en place dans les quatre premiers kilomètres de la croûte supérieure et sont généralement liés à une chambre magmatique situés entre 5 et 15 kilomètres de profondeur. Cette chambre magmatique représente la chambre d'alimentation des magmas et fluides hydrothermaux responsables de la formation des porphyres cuprifères (Seedorff et al., 2005; Sillitoe, 2010). La durée du système magmatique est d'environ 10 m.y. tandis que celle de l'activité hydrothermale dure moins de 2 m.y. (Sillitoe, 2010). La grande majorité des porphyres cuprifères se rencontrent principalement dans les arcs magmatiques et les arrières-arcs. Ces terrains sont généralement soumis à des contraintes tectoniques à l'échelle régionale (l'épaississement crustal dû à la subduction, un soulèvement tectonique de surface et une exhumation rapide), et d'ailleurs les porphyres cuprifères sont bien souvent associés à des systèmes de failles et des linéaments qui vont servir de drain à la minéralisation. Les roches porphyriques proviennent de magma de type I, riches en eau, oxydés (Ishihara, 1981; Ishihara et al., 1984), de composition calco-alcaline avec des roches intermédiaires à felsique (Seedorff et al., 2005; Sillitoe, 2010). Associé au magmatisme, un système

hydrothermal se met en place via le mélange entre des fluides magmatiques et météoriques entre 350°C et 550°C. Ce fluide hydrothermal, chaud, hyper-salin, comporte une phase vapeur riche en métaux (Cu, Au, Ag, Sb, S, etc. ; Kouzmanov and Pokrovski, 2012). Proche de la surface, la baisse de la température engendre le changement de la fugacité du fluide. Ceci, couplé à l'interaction fluide-roche, favorise la précipitation de la minéralisation cuprifère (Sillitoe and Perelló, 2005; Sillitoe, 2010; Kouzmanov and Pokrovski, 2012). La minéralisation forme des dykes et des corps verticaux extensifs de plusieurs dm^3 à km^3 et est généralement zonée du cœur vers la périphérie. Du cœur vers la bordure, on retrouve les altérations potassique, chlorite-séricite, séricite et argileuse (Fig. I.9; Seedorff et al., 2005; Sinclair, 2007; Sillitoe, 2010; Kouzmanov and Pokrovski, 2012). Les altérations chloritique et propylitique sont observées distalement à des niveaux peu profonds. La biotite est le minéral d'altération prépondérant dans la zone d'altération potassique. La partie supérieure des porphyres cuprifères est caractérisée par un « lithocap » (encore appelé chapeau de fer ou couverture) ou zone d'altération argileuse avancée. Ce « chapeau de fer » ou couverture est très souvent zoné verticalement avec en profondeur une altération quartzo-pyrophyllitique, et en surface, une zone d'altération faite de quartz et d'alunite. Il constitue une cible d'exploration majeure des porphyres cuprifères. Comme décrit dans la section précédente, les porphyres cuprifères sont des gisements de gros tonnages, i.e. de dizaines de millions de tonnes à des centaines de millions de tonnes voire des milliards de tonnes. Par contre, les teneurs sont faibles, ne dépassant pas les 1 wt. % de Cu. Hormis les gisements disposant d'importants tonnages, les porphyres ne présentent pas un intérêt économique. Cependant, l'altération supergène que subissent ces porphyres cuprifères, confère à certains, leur viabilité économique (Sillitoe, 2005).

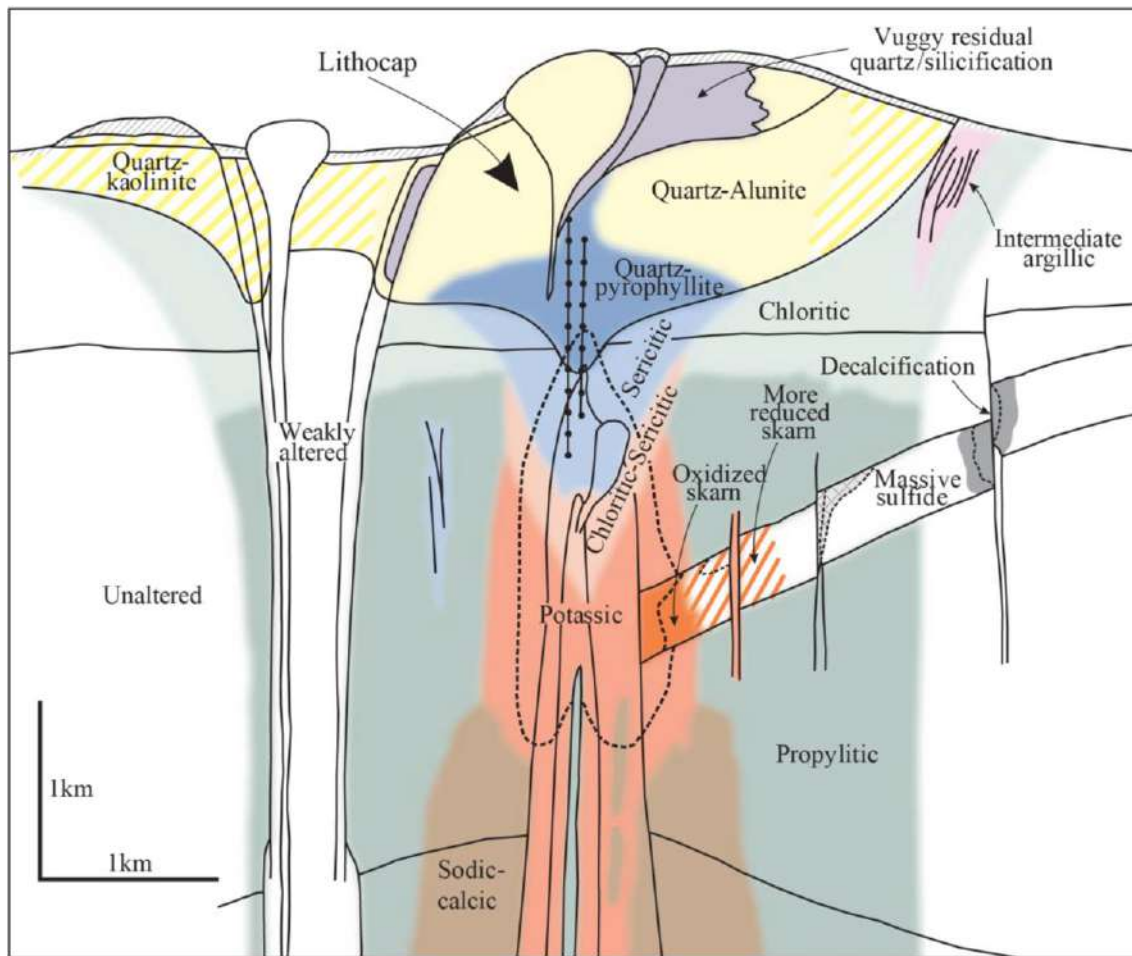


Figure 1.9 : Représentation schématique de l'altération hydrothermale hypogène d'un porphyre cuprifère (modifié d'après Kouzmanov and Pokrovski, 2012)

1.2.2 L'altération supergène et la formation des minéralisations cuprifères supergènes *in situ* et exotiques

L'altération supergène des porphyres cuprifères est un processus chimique, voire biochimique, qui, sous des conditions oxydantes et l'action combinée des eaux météoriques et de la biosphère, entraîne l'altération des sulfures primaires, i.e. principalement la pyrite et la chalcoppyrite, et la formation des sulfures de cuivre secondaires et des minéraux de cuivre oxydés. Elle peut se dérouler sous des conditions climatiques variées allant d'un climat semi-aride à aride à un climat tropical humide (Sillitoe, 2005). A une échelle régionale, la formation d'un horizon supergène au-dessus d'un porphyre cuprifère requiert un équilibre subtil entre le soulèvement tectonique, l'apport des eaux météoriques et l'érosion (Fig. 1.10). Dans les ceintures orogéniques actives (e.g. la Ceinture de feu du Pacifique), le soulèvement tectonique provoque la baisse de la nappe phréatique, induisant l'oxydation des sulfures

primaires. Par la suite, les eaux météoriques vont altérer les sulfures primaires, lessiver et transporter le cuivre, puis le précipiter. Dans les faits, tout part de la destruction de la pyrite (FeS_2). Cette altération produit des ions H^+ qui génère un milieu acide ($\text{pH} < 5.5$), entraînant la dissolution des sulfures de cuivre primaire (i.e. chalcopryrite et bornite). Même si leur impact a été peu documenté, les bactéries acidophiles (e.g. *Acidithiobacillus ferrooxidans*) agissent dans l'oxydation des sulfures primaires en réduisant le soufre en sulfate et en catalysant l'oxydation du Fe^{2+} en Fe^{3+} (Sillitoe et al., 1996; Sillitoe, 2005; Mathur et al., 2005; Enders et al., 2006; Zammit et al., 2015). Le cuivre est ensuite transporté, vers le bas, sous la forme de solutions sulfatées. Puis, sous les conditions réductrices de la nappe phréatique, dans la zone de cimentation, le cuivre précipite sous la forme de sulfures secondaires, triplement enrichis en cuivre, comparativement aux sulfures primaires : on parle d'enrichissement supergène et d'horizon enrichi. Cet horizon enrichi repose directement sur le minerai sulfuré primaire non altéré appelé aussi protore (Fig. I.10). Au-dessus du niveau d'eau, en condition oxydante, la précipitation des solutions sulfatées, tout comme l'oxydation des sulfures primaires, va engendrer la formation des sulfates, oxydes, carbonates, arsénates, chlorures, silicates et phosphates de cuivre : on parle de zone d'oxydation ou d'horizon oxydé. Au-dessus de la zone oxydée, au contact direct de la sub-surface, subsiste une zone appauvrie en cuivre et riche en minéraux lourds et résistants à l'altération : on parle de chapeau de fer, riche en limonite, alunite, jarosite et cryptomélane. Enfin, si la tectonique et le climat favorisent la formation d'un profil supergène, une érosion adéquate est nécessaire pour la sauvegarde du profil supergène ainsi créé.

A l'échelle du gisement porphyrique, plusieurs paramètres sont nécessaires à la formation d'un horizon supergène (Chávez, 2000; Sillitoe, 2005). Tout d'abord, les porphyres cuprifères avec un ratio pyrite-chalcopryrite élevé développent des horizons supergènes importants, comparativement à ceux ayant un ratio plus faible. De plus, les porphyres cuprifères avec une altération potassique bien développée, montrent des profils épais d'horizon enrichi. Enfin, une minéralisation verticale, combinée à des réseaux de veinules à extension verticale sont favorables au développement de profils supergènes.

D'un point de vue minéralogique, l'horizon enrichi est constituée principalement de chalcocite (Cu_2S). Lorsqu'il reste assez de cuivre en solution, la covellite (CuS) ainsi que d'autres sulfures secondaires (e.g. la digénite, la djurleite et l'idaïte) précipitent (Chávez, 2000). Cet horizon enrichi peut

atteindre une épaisseur d'une dizaine à plusieurs centaines de mètres avec des tonnages importants. Par exemple, le porphyre cuprifère de Chuquibambilla au Chili a un horizon enrichi de 750 m d'épaisseur pour un tonnage de 2.2 Gt de Cuivre et une teneur de 1.41 wt. % de Cu (Ossandon et al., 2001). La chalcocite est présente dans les parties centrales et supérieures de l'horizon enrichi tandis que la covellite est plus abondante en profondeur, proche du protore (Sillitoe, 2005). Ceci induit la diminution progressive de la teneur en Cu des solutions enrichies. Au-dessus de l'horizon enrichi, le niveau oxydé contient une multitude de minéraux de cuivre hydratés, hydroxylés et oxydés. Cet horizon se forme dans des conditions neutres à alcalines (Newberg, 1967; Chávez, 2000; Sillitoe, 2005). Le minéral le plus abondant est la chrysocolle (un silicate de cuivre hydraté, $[(\text{Cu}, \text{Al})_2 \text{H}_2\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}]$). Suivent la malachite, les hydroxy-sulfates de cuivre et l'atacamite. Dans des conditions faiblement acides, au contact direct des horizons enrichis, les hydroxy-sulfates de cuivre (e.g. antlérite et brochantite) sont les minéraux dominants. Les relations texturales et paragenétiques sont complexes et variées, indiquant une variation quasi-continue des conditions chimiques des fluides et du processus d'altération supergène (Schwartz, 1934; Chávez, 2000; Sillitoe, 2005). La cristallisation des hydroxy-sulfates et sulfates de cuivre reflètent un pH faible, une fois l'oxydation de la pyrite achevée. La malachite et l'atacamite quant à elles remplacent la brochantite et l'antlérite. La chrysocolle, qui montre très souvent une texture collomorphe, indiquent des concentrations élevées de silice dans des solutions neutres à alcalines, résultant d'une décomposition des minéraux siliceux (e.g. les feldspaths ; Newberg, 1967; Crane et al., 2001). Des relations indiquent qu'elles cristallisent en dernière position, par remplacement de l'atacamite et de la malachite (Reich et al., 2009). Cependant, l'atacamite qui requiert des conditions salines pour se former et un climat hyperaride pour être préservé, serait probablement le dernier minéral porteur de cuivre à se former (Cameron et al., 2007). Les oxydes de cuivre (cuprite, tenorite) et le cuivre natif cristallisent à la limite inférieure de la zone oxydée, en remplacement des sulfures secondaires. Recouvrant les horizons oxydés et enrichis, le chapeau de fer est comme son nom l'indique, riche en minéraux ferreux et alumineux. Ce chapeau de fer se forme simultanément ou postérieurement à l'altération supergène. La limonite est l'assemblage minéralogique caractéristique du chapeau de fer. Suivent les minéraux riches en potassium (alunite, jarosite, cryptomélane, etc.) et le quartz, minéral ubiquiste par excellence (Chávez, 2000; Sillitoe, 2005). Ces chapeaux de fer sont caractérisés par la

rareté de minéraux de cuivre oxydés mais présentent parfois des argiles et des limonites riches en cuivre. Ils peuvent atteindre des centaines de mètres d'épaisseurs. Comme évoqué dans la section précédente, le chapeau de fer est le principal métallotecte pour la recherche de porphyres cuprifères dans certaines régions et districts miniers. L'abondance de goethite et/ou d'hématite renseigne sur l'intensité de l'altération et donc sur l'épaisseur et la maturité du profil supergène formé en-dessous. D'après Sillitoe (2005), un chapeau de fer riche en goethite est caractéristique d'un profil supergène immature et d'une altération supergène incomplète. En revanche, l'abondance d'hématite dans un chapeau de fer souligne la présence d'un profil supergène mature sous ce chapeau de fer, avec un horizon enrichi épais.

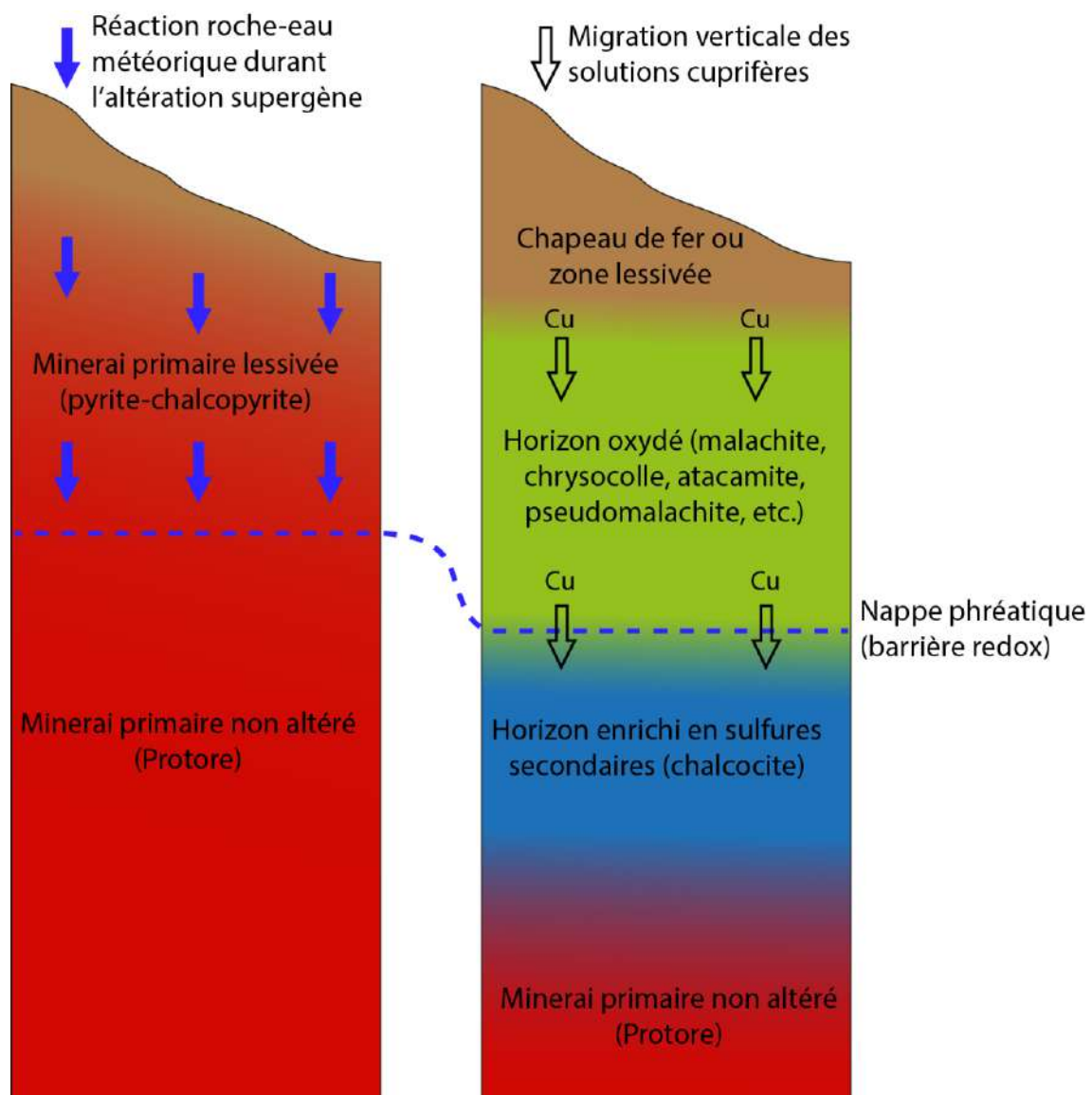


Figure I.10 : Représentation schématique de l'altération supergène d'un porphyre cuprifère

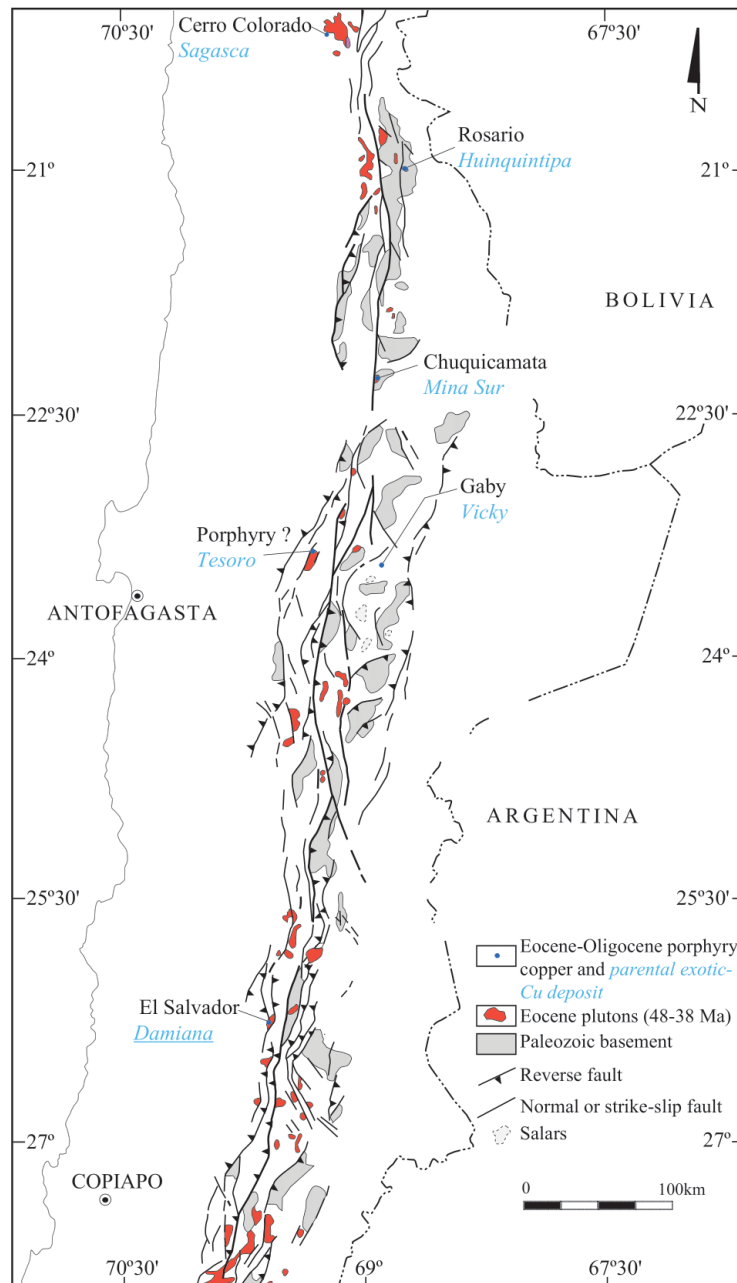


Figure I.11 : Carte de répartition des minéralisations exotiques de cuivre et de leur porphyre cuprifère parent dans la Précordillère du désert d'Atacama (modifié d'après Mpodozis and Cornejo, 2012)

En complément de l'altération supergène *in situ*, les solutions cuprifères peuvent migrer latéralement et engendrer la formation de minéralisations supergènes exotiques de cuivre (voir Fig. I.3). Les minéralisations exotiques de cuivre résultent principalement de la migration latérale des solutions acides, riche en Cu, issues de l'altération supergène *in situ* d'un porphyre cuprifère (Mortimer et al., 1977; Münchmeyer, 1996; Sillitoe, 2005). On retrouve principalement des minéraux oxydés de cuivre (i.e. silicates, chlorures, oxydes, phosphates et carbonates, etc., Tableau 1), qui imprègnent et cimentent

les graviers et sédiments du piedmont et remplissent les fractures du substrat rocheux sous-jacent. Cette minéralisation cuprifère exotique répond à une zonalité de l'altération qui dépend fortement de la nature des roches hôtes (i.e. siliceuses, carbonatés) et du ratio Cu/Fe/S des fluides minéralisateurs provenant du porphyre en amont. Proche du porphyre cuprifère, se distingue une zone proximale, située entre 0 et 2 km, avec des graviers et roches saines, contenant la pyrite et la chalcocite. Une zone intermédiaire, entre 2 et 4 km, qui présente des roches à altération argileuse et des graviers kaolinisés, riche en chrysocolle, atacamite et copper wad (un terme généralement utilisé par les miniers pour désigner un oxyhydrate de Cu, Fe, Mn et Co). Une zone distale, entre 4 et 8 km, où la minéralisation cuprifère est hébergée dans les graviers du piedmont. Cette dernière est riche en chrysocolle, copper wad et atacamite. A ces minéralisations oxydées de cuivre, s'ajoutent des oxydes de fer et de manganèse. Dans le désert d'Atacama, ces minéralisations exotiques sont hébergées principalement dans des paléo-chenaux, en aval des porphyres, où la morphologie est contrôlée par la tectonique (e.g. Mina Sur, Huiniquintipa, Quebrada Blanca, Sagasca, Fig. I.11) mais aussi dans des cônes alluviaux, formés en aval des hauts topographiques (e.g. Damiana et Tesoro Central, Fig. I.11). La minéralisation dans ce dernier cas est de faible épaisseur mais de grande étendue (Münchmeyer, 1996; Fernández-Mort et al., 2018). Dans les paléo-chenaux, les solutions acides vont d'abord percoler la roche-mère, altérer les graviers sus-jacents et précipiter la chalcocite dans la zone proximale. L'augmentation du pH à des valeurs neutres à basiques entraîne une altération argileuse et la formation de copper wad, de chrysocolle et d'atacamite dans la zone intermédiaire. Loin du porphyre, les graviers siliceux et la roche mère sont peu altérés, favorisant la précipitation massive de chrysocolle. La minéralogie cuprifère rencontrée est fonction du fluide minéralisateur supergène, provenant du porphyre en amont, et de la lithologie de l'encaissant sédimentaire (Newberg, 1967; Münchmeyer, 1996). Le fluide apporte le Cu, le Zn, le Mn, le Co, le Mo, l'U, etc. Les horizons carbonatés fournissent le calcium et les sédiments graveleux fournissent Mg, Ni, Al, Na, K, etc. Si la source de certaines minéralisations exotiques n'a jamais été trouvée (e.g. la minéralisation exotique de Tesoro dans le district minier de Centinela, Fig. I.11), la source de cuivre ne peut venir que de porphyres cuprifères enfouis sous des sédiments ou érodés ou encore de dépôts stratiformes de cuivre. Cependant, aucun dépôt stratiforme de cuivre n'est connu au Chili pour être associé à des minéralisations exotiques et de plus, aucun n'a été découvert dans la

Précordillère. La minéralisation exotique est contemporaine aux dépôts des graviers piémontais (Mortimer et al., 1977; Münchmeyer, 1996; Sillitoe, 2005; Hartley and Rice, 2005; Riquelme et al., 2017). Cependant, aucune donnée chronologique ne renseigne sur la contemporanéité ou non de la minéralisation cuprifère exotique, en aval, et le fonctionnement de l'altération supergène au-dessus du porphyre, en amont. Ces minéralisations exotiques sont généralement utilisées comme proxy pour remonter aux porphyres cuprifères supergènes en amont ou sont utilisées comme cibles, vu leur tonnage et leur teneur (Mortimer et al., 1977; Münchmeyer, 1996; Sillitoe, 2005). Les accumulations de pédiments, la géomorphologie et les configurations hydrologiques sont d'excellentes indications pouvant prédire des zones pouvant héberger des minéralisations exotiques de cuivre. Par ailleurs, la minéralogie des zones proximales des porphyres cuprifères supergènes et la modélisation des bilans de masse des porphyres cuprifères sont de parfaits outils pour prédire des sites favorables à la précipitation de minéralisations exotiques de cuivre (Mote et al., 2001a; Braxton et al., 2009; Braxton and Mathur, 2011).

1.2.3 L'âge du cuivre supergène du désert d'Atacama

De nombreuses études ont été entreprises pour dater la minéralisation supergène de cuivre et contraindre l'âge de fonctionnement de l'altération supergène. Dans le désert d'Atacama, l'altération supergène requiert un équilibre entre le soulèvement tectonique favorisant la baisse de la nappe phréatique, des précipitations adéquates, i.e. non abondantes pour éviter l'érosion du profil supergène (e.g. un climat semi-aride à aride), et un climat hyperaride pour préserver l'horizon supergène ainsi créé. Au nord du Chili, ces conditions étaient remplies dès la transition Mésozoïque-Cénozoïque. Cependant, les profils supergènes matures sont observés uniquement dans les ceintures cuprifères Paléocène-Eocène (e.g. Spence, Cerro Colorado) et majoritairement dans la ceinture Eocène-Oligocène (e.g. Chuquicamata, Radomiro Tomic, Salvador, Potrerillos, etc. ; Sillitoe and Perelló, 2005). Dans cette ceinture Eocène-Oligocène, l'orogénèse Incaïque (42-32 Ma ; Makshev and Zentilli, 1999), a permis la formation d'énormes volumes de porphyres cuprifères riche en pyrite, favorisant le processus d'altération supergène.

La première datation de l'altération supergène a été réalisée indirectement (i.e. non sur la minéralisation cuprifère supergène en elle-même), sur les minéraux d'altération issus du chapeau de fer (e.g. alunite, jarosite et cryptomélane ; Fig. I.12). Gustafson and Hunt (1975) furent les premiers à dater l'âge de l'altération supergène. Via la datation K-Ar, l'altération supergène du porphyre cuprifère de Salvador a été datée à ca. 36 Ma. S'en suivirent Alpers and Brimhall (1988), qui ont daté l'altération supergène du porphyre géant d'Escondida entre 18 Ma et 14 Ma. Par la suite, avec le développement de la technique de datation K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ (Vasconcelos, 1999), de nombreux autres auteurs (Clark et al., 1990; Sillitoe and McKee, 1996; Mote et al., 2001b; Rowland and Clark, 2001; Bouzari and Clark, 2002; Quang et al., 2003; Arancibia et al., 2006) ont pu dater l'altération supergène *in situ* des porphyres cuprifères du désert d'Atacama. La formation des minéralisations cuprifères exotiques a, quant à elles, été datée la première fois par Mote et al. (2001b) sur de l'alunite, inclus dans du copper wad, par la méthode K-Ar.

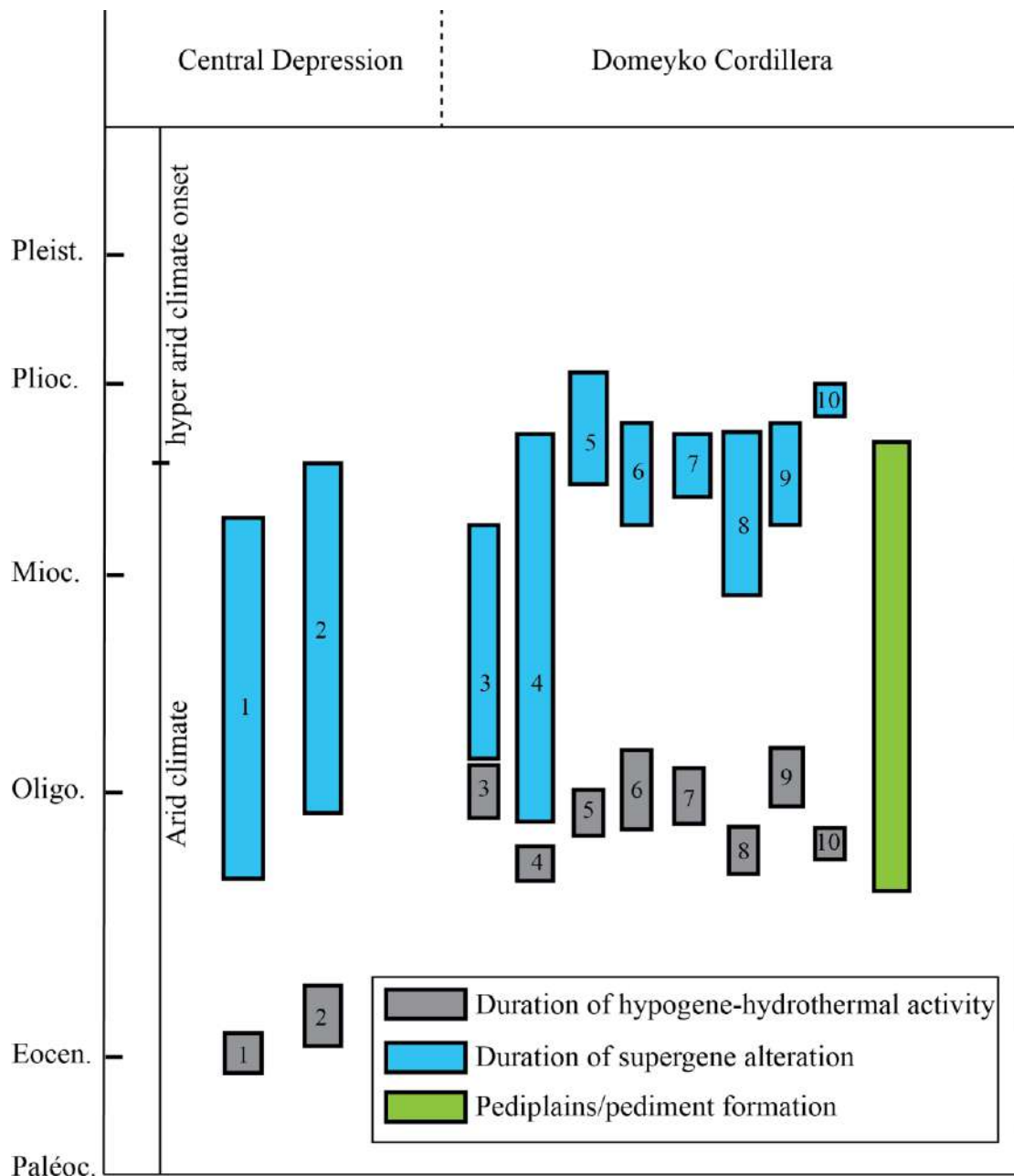
D'après ces auteurs, l'altération supergène dans le désert d'Atacama s'est déroulé entre 44 Ma (Rowland and Clark, 2001) et 9 Ma (Arancibia et al., 2006) voire jusqu'à 6 Ma (Marsh et al., 1997). Par ailleurs, la rareté des âges inférieurs à 14 Ma, a poussé Sillitoe and McKee (1996), dans une étude exhaustive, à affirmer que l'altération supergène s'est mise en place entre 23 Ma et 14 Ma. Induisant de fait la prévalence d'un climat hyperaride après 14 Ma, responsable de la rareté des âges post- 14 Ma. Cependant, les travaux de Reich et al. (2009), et ceux plus récents de Bissig and Riquelme (2010), ont montré, par la datation de l'atacamite, de la jarosite et de la natroalunite, que l'altération supergène des porphyres cuprifères a eu lieu jusqu'au Pliocène tardif (Reich et al., 2009) et même jusqu'à une époque plus récente dans la limite méridionale du désert d'Atacama (Bissig and Riquelme, 2010). Bien que l'âge de l'altération supergène soit en contradiction avec les contraintes temporelles, telles que soutenues par les études sédimentologiques et pédologiques, pour dater l'initiation de l'hyperaridité, elle permet toutefois de proposer, en accord avec les travaux de Sillitoe and McKee (1996), un âge de ca. 14 Ma comme étant celui de l'initiation de l'hyperaridité dans le désert d'Atacama. La période post-14 Ma serait marquée par des occurrences d'épisodes humides, responsables de l'altération supergène dans le sud du désert d'Atacama (Marsh et al., 1997; Bissig and Riquelme, 2010) et par des occurrences

d'évènements tectoniques locaux, responsables de la formation de l'atacamite au Pliocène tardif (Reich et al., 2009).

Parallèlement à la datation des minéraux d'altération, de nombreux auteurs ont montré un lien entre la formation des pédiplaines et l'altération supergène des porphyres cuprifères depuis l'étude pionnière de Segerstrom (1963) dans la Dépression Centrale du nord du Chili et du sud du Pérou. Abondant dans cette optique, de nombreux auteurs ont daté la formation de ces pédiments via l'utilisation de nucléides cosmogéniques et de méthodes isotopiques depuis les travaux anciens de Mortimer (1973) jusqu'à ceux plus récents de Riquelme et al. (2017). Ces auteurs soutiennent que la formation des pédiplaines a cessé à ca. 9 Ma, en lien avec l'hyperaridification du climat de l'Atacama. Ces pédiplaines, contemporaines ou postérieures à la formation de la minéralisation cuprifère supergène (Sillitoe and McKee, 1996; Riquelme et al., 2017), sont dès lors un marqueur de la cessation de l'altération supergène due à la dessiccation du climat.

Pour résumer, tant que les techniques de datation évolueront et que les minéraux d'altération seront présents dans le chapeau de fer des porphyres cuprifères, l'âge de l'altération supergène, et par ricochet, celle de l'initiation de l'hyperaridité sera sujet à débat. Par ailleurs, la non-ubiquité des minéraux d'altération et les limites des techniques de datation pionnières, K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ ont permis l'éclosion et le développement de nouvelles techniques radiométriques (âge de déséquilibre des séries de l'Uranium, nucléides cosmogéniques, géochronologie Uranium-Plomb) pour dater directement la minéralisation cuprifère et s'affranchir des artéfacts analytiques et d'échantillonnage. Le chapitre 5 de cette thèse discutera justement de l'utilisation du chronomètre U-Pb pour dater la minéralisation cuprifère supergène du district minier de Chuquicamata.

Figure I.12 : Résumé des âges de l'activité hydrothermale hypogène, de la durée de l'altération supergène et de l'âge de formation des pédiplaines de la Dépression Centrale et de la Cordillère de Domeyko du désert d'Atacama



Paleocene-Eocene porphyry copper

1. Spence
2. Cerro Colorado

Eocene-Oligocene porphyry copper

3. La Fortuna
4. Salvador
5. Potrerillos
6. Escondida mining district
7. Collahuasi district
8. Centinela mining district
9. Chuquicamata mining district
10. El Hueso

CHAPITRE II :

Méthodes et outils

Ce chapitre fait une description de toutes les méthodes et outils techniques utilisées pour mener à bien ce travail de thèse. Le cœur de cette thèse étant la datation U-Pb des minéralisations cuprifères supergènes, la première partie se voudra être un rappel des principes de la géochronologie U-Pb, méthode largement utilisée depuis des dizaines d'années pour dater les minéraux accessoires (e.g. zircon, monazite, baddeleyite, rutile, etc.). La seconde partie décrira succinctement les principes des différentes méthodes d'analyse utilisées au cours de cette thèse et leur intérêt dans l'étude des minéralisations cuprifères supergènes.

II.1 La géochronologie U-Pb

La recherche constante de l'âge des processus et phénomènes qui ont façonné l'histoire de la terre a donné naissance à la géochronologie. La datation d'évènements géologiques repose sur une mesure relative et une mesure absolue du temps. Avant la découverte de la radioactivité et l'essor des techniques analytiques, la géochronologie permettait d'obtenir un âge relatif via l'observation *in situ* de marqueurs géologiques sur la base de principes établis à partir des travaux de Nicolas Sténon au 17^{ème} siècle et qui sont à la base de la stratigraphie. Cette datation relative permettait d'avoir une idée globale de l'histoire géologique mais sans pouvoir ne donner ni d'âge absolu ni de durée ou de vitesse aux processus. L'essor de chronologie absolue a permis deux siècles plus tard d'obtenir l'âge des objets et évènements géologiques, permettant dès lors une compréhension de la chronologie des évènements géologiques ayant façonné l'histoire de la Terre. La découverte de la radioactivité par Becquerel (1896), puis le développement de la radiochronologie au début du 20^{ème} siècle par Rutherford, ont permis l'essor de la géochronologie absolue. Le premier système radiochronométrique utilisé par Rutherford était le système de désintégration de l'uranium en plomb, système qui est resté un des chronomètres phares pour la datation des processus géologiques jusqu'à nos jours.

II.1.1 le chronomètre U-Pb : principes et limites

A l'instar des différents géochronomètres existants (e.g. Rb-Sr, K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$, Lu-Hf, Sm-Nd, Re-Os), le chronomètre U-Pb est le plus utilisé et un des plus précis pour dater des évènements géologiques depuis la formation de la terre jusqu'au Pléistocène.

1.1.1 Principe

La géochronologie U-Pb se base sur i) l'incorporation de l'uranium dans la structure cristalline du minéral lors de sa formation ii) la désintégration radioactive de l'uranium en plomb radiogénique au cours du temps iii) la capacité du minéral à retenir le signal U-Pb dans son système eu égard aux évènements post-cristallisation pouvant altérer ce signal.

L'uranium possède trois isotopes radioactifs : ^{238}U , ^{235}U et ^{234}U avec pour abondances respectives 99.274%, 0.720% et 0.006%. Les plus abondants, ^{238}U et ^{235}U , se désintègrent selon une constante de

décroissance radioactive en ^{206}Pb et en ^{207}Pb : on parle d'isotope pères radioactifs (i.e. ^{238}U et ^{235}U) et d'isotopes fils radiogéniques (i.e. ^{206}Pb et ^{207}Pb). Ainsi, on évoque le terme « couple isotopique » U-Pb ou « chronomètre » U-Pb. Chaque chronomètre utilisé en géochronologie est caractérisé par sa période de demi-vie, notée T . Cette dernière équivaut à la période de temps nécessaire pour que la concentration en isotope radioactif soit réduite de moitié. Cette demi-vie est une fonction simple de la constante de désintégration λ ($\lambda = \ln 2/T$) avec $\lambda^{238}\text{U} = 1.55 \cdot 10^{-10}/\text{an}$ ($T = 4.47 \text{ Ga}$) et $\lambda^{235}\text{U} = 9.8485 \cdot 10^{-10}/\text{an}$ ($T = 0.704 \text{ Ga}$) (Schoene, 2014).

De fait, suivant le temps écoulé, l'uranium décroît alors que la teneur en plomb radiogénique augmente selon l'équation :

$$\frac{F^*}{P} = e^{\lambda t} - 1$$

Avec F^* = teneur en isotope fils radiogénique ($^{206}\text{Pb}^*$ et $^{207}\text{Pb}^*$), P = teneur en isotope père radioactifs (^{238}U et ^{235}U), λ = constante de désintégration, t = temps écoulé (i.e. l'âge de fermeture du système).

La quantité d'éléments fils radiogénique F^* peut-être estimée à partir de la mesure de la quantité actuelle d'isotopes fils F dans le minéral à condition de connaître la quantité F_0 d'isotopes fils présent initialement dans le minéral à dater (dit plomb commun), avec $F^* = F - F_0$.

L'équation sus-mentionnée permet ainsi de calculer deux âges dans le cas du chronomètre U-Pb.

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{238}\text{U}}{^{204}\text{Pb}}\right) (e^{\lambda^{238}t} - 1)$$

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{235}\text{U}}{^{204}\text{Pb}}\right) (e^{\lambda^{235}t} - 1)$$

Cependant, la concordance de ces deux chronomètres implique que i) l'équilibre séculaire soit atteint (tous les isotopes intermédiaires produits doivent être désintégrés), ii) le chronomètre ait évolué en système fermé après la formation du minéral, iii) le minéral à dater ait incorporé peu ou pas de plomb commun lors de sa formation afin que l'erreur sur son estimation ne crée pas une trop grande incertitude sur l'âge et iv) la quantité d'isotopes radiogéniques fils formés soit suffisante pour être analysée (Schoene, 2014), ce qui sous-entend que le chronomètre U-Pb est rarement utilisé pour dater des événements plus jeunes que le million d'années.

1.1.2 Le diagramme Concordia Wetherill

Le diagramme concordia Wetherill a été inventé comme son nom l'indique par Wetherill (1956). Il est surtout utilisé dans la datation et l'interprétation de minéraux incorporant peu ou pas de plomb commun et riches en uranium et plomb radiogéniques car les analyses doivent être corrigées du plomb commun pour y représenter le plomb radiogénique.

Dans ce diagramme, les âges apparents $^{206}\text{Pb}^*/^{238}\text{U}$ et $^{207}\text{Pb}^*/^{235}\text{U}$ sont dit *concordants* s'ils s'alignent le long de la courbe *concordia* (Fig. II.1.A). Lorsqu'un minéral cristallise dans un système fermé, les chronomètres $^{206}\text{Pb}/^{238}\text{U}$ et $^{207}\text{Pb}/^{235}\text{U}$ évoluent de telle sorte que les deux rapports isotopiques suivent la concordia en s'éloignant de l'origine à mesure que l'âge croît. Si le système s'ouvre partiellement, les rapports isotopiques s'aligneront sur une droite appelée *discordia*, marqueur d'une perte et/ou d'un gain en Pb et/ou en U par des événements post-cristallisation, e.g. altération d'un minéral/d'une roche, métamorphisme, diagenèse, etc. Par la suite, si le système se retrouve clos, l'intercept supérieur correspondra à l'âge de la cristallisation tandis que l'intercept inférieur représentera la date de l'ouverture du système.

1.1.3 Le diagramme Concordia "Tera-Wasserburg"

Pour les minéraux incorporant des quantités non-négligeables de plomb commun lors de leur cristallisation ou lors d'événements post-cristallisation (e.g. apatite, titanite, rutile, etc.), le diagramme concordia Tera-Wasserburg (Tera and Wasserburg, 1972) est plus adapté. Il représente les rapports isotopiques $^{207}\text{Pb}/^{206}\text{Pb}$ et $^{206}\text{Pb}/^{238}\text{U}$ corrigées ou non du plomb commun. Tout comme pour le diagramme concordia Wetherill, si un minéral évolue en système clos et ne possède pas de plomb commun (ou si celui-ci a été corrigé), l'âge apparent de formation de ce minéral sera sur la concordia (Fig. II.1.B). Par contre, si ce minéral a incorporé du plomb commun à sa cristallisation ou postérieurement à celle-ci, les rapports isotopiques s'étaleront de nouveau sur une discordia où l'intercept avec la concordia donnera l'âge apparent de cristallisation et l'intercept inférieur (i.e. l'ordonnée à l'origine de la discordia) fournira la valeur du plomb commun initial. Si, en plus de l'incorporation du plomb commun, ce minéral perd du plomb lors d'événements post-cristallisation, les points d'analyses seront déplacés vers la droite de la discordia.

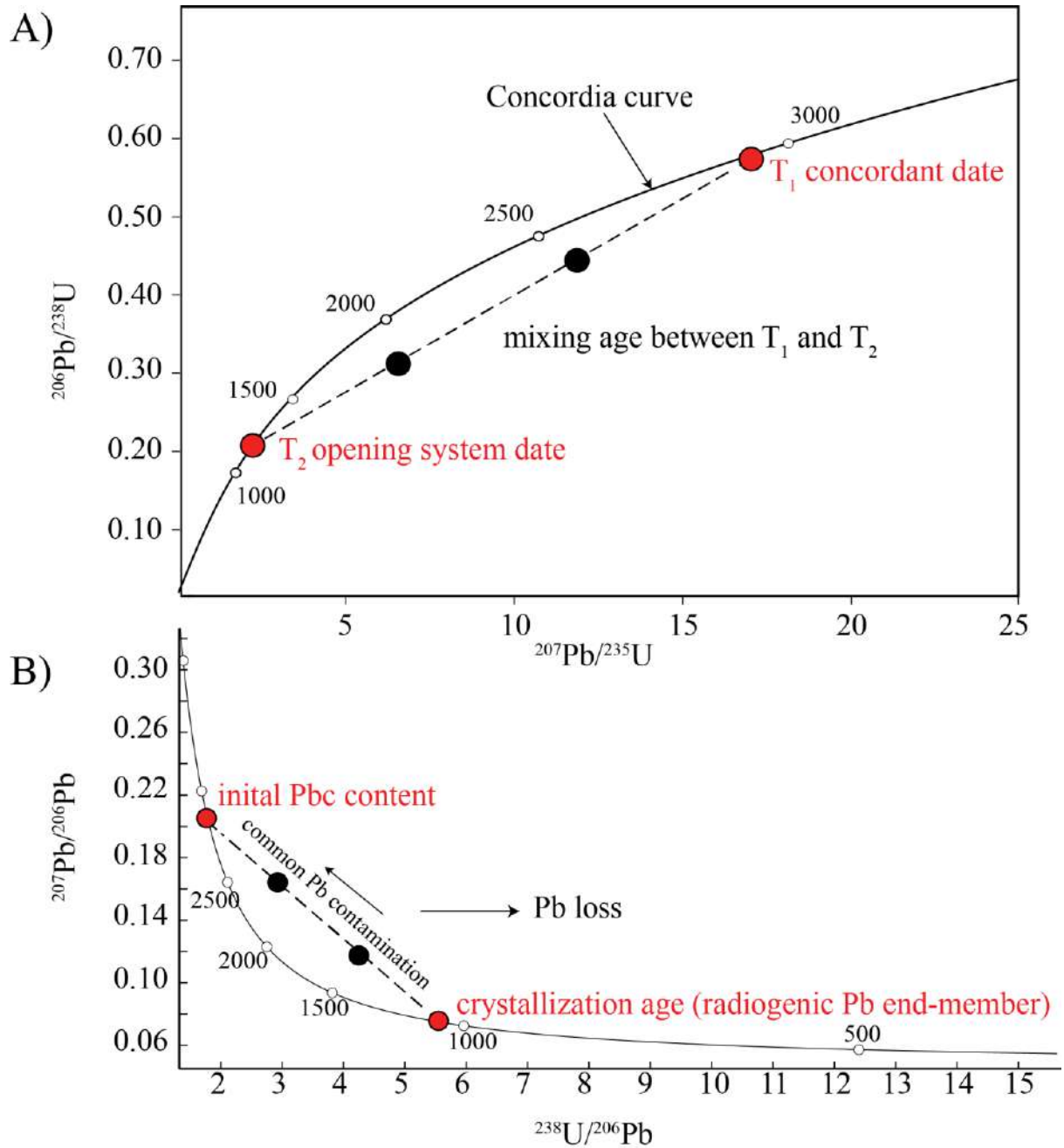


Figure II.1 : Diagramme concordia Wetherill (A) et concordia Tera-Wasserburg (B) montrant les cas de figure où les systèmes isotopiques fournissent au âge concordant et lorsque ceux-ci fournissent des données discordantes (modifié d'après Schoene, 2014)

1.1.3 Les causes de la perturbation du chronomètre U-Pb

Plusieurs causes peuvent expliquer la discordance des âges U-Pb. La première est le mélange de zones d'âges différents. De nombreux minéraux tels le zircon, la titanite et la monazite présentent des cœurs hérités et des bordures plus jeunes. Cette zonation, quand elle n'est pas identifiée via le MEB ou la cathodoluminescence, peut perturber l'interprétation des analyses. La seconde cause majeure est la perte de plomb radiogénique. Cette perte peut être due au métamorphisme, l'évolution en système ouvert ou par diffusion. Cherniak (2010) a montré que les minéraux accessoires (i.e. zircon, sphène, apatite, monazite, xénotime) utilisés en géochronologie étaient vulnérables à la diffusion du Pb, pouvant réinitialiser le système U-Pb. De plus, des minéraux souvent présentés comme étant de bons géochronomètres (e.g. la monazite) peuvent incorporer du plomb commun soit lors de leur cristallisation soit postérieurement via des processus de dissolution-précipitation (Poitrasson et al., 2000; Seydoux-Guillaume et al., 2002; Seydoux-Guillaume et al., 2012).

II.1.2 Datation U-Pb via un spectromètre de masse à torche plasma couplé à un système d'ablation laser : U-Pb LA-ICP-MS

La recherche de la rapidité et de la précision spatiale des analyses géochronologiques ont conduit à la mise au point de plates-formes analytiques permettant l'analyse de petites quantités de matériels faiblement dosées en uranium et en plomb (quelques centaines à des milliers de ppm). Dès la seconde moitié du 20^e siècle, des appareils de mesure tels que l'**ID-TIMS** (Thermal Ionisation Mass Spectrometry) ont été utilisés pour les analyses des isotopes de l'U et du Pb, suivis par la **SIMS** (Secondary Ion Mass Spectrometry) et la **SHRIMP** (Secondary High Resolution Ion Mass Spectrometry) dans les années 80-90, ces deux dernières techniques permettant de faire des analyses *in situ* sur des matériaux solides alors que la première nécessitait une séparation et une mise en solution des éléments. Au début des années 90, les développements technologiques ont permis de créer des spectromètres de masse à torche plasma à couplage inductif couplé à un système d'ablation laser : **LA-ICP-MS** (Jackson et al., 1992). Cet appareil sera par la suite énormément développé et utilisé dans la datation U-Pb. Cet outil, en plus de posséder une sensibilité élevée, est non destructrice pour le minéral

à analyser car elle permet d'analyser le minéral en contexte, directement sur la lame mince ou une section polie, au contraire de l'ID-TIMS.

Durant ces trois années de thèse, les analyses LA-ICP-MS ont été effectuées 1) au laboratoire Géosciences Environnement Toulouse (Toulouse, France) qui possède un Element-High Resolution HR-ICP-MS et un Multi-Collector-ICP-MS pouvant être couplé à un laser nanoseconde (ns-LA) et un laser femtoseconde (fs-LA) 2) au laboratoire Géosciences Rennes (Rennes, France) qui est doté d'un ICP-MS quadripolaire à secteur magnétique couplé à un laser nanoseconde, et 3) au Trinity College de Dublin (Dublin, Ireland) équipé d'un ICP-MS quadripolaire à secteur magnétique couplé à un laser nanoseconde (ns-LA).

1.2.1 Principe de fonctionnement d'un LA-ICP-MS

Un système d'ablation laser couplé à un spectromètre de masse à torche plasma à couplage inductif (LA-ICP-MS, Fig. II.2) est composé de deux unités : i) le système d'ablation LASER (i.e. Light Amplification by Stimulated Emission of Radiation) et ii) le spectromètre de masse à torche plasma à couplage inductif (ICP-MS). Les lasers de type Excimer sont les plus utilisés depuis le début des années 2000 (Bruguier, 2009). Ils combinent un gaz rare (argon, xénon ou krypton) et un gaz excité (fluor ou chlore). Ils permettent une ablation dans une courte longueur d'onde (193 nm pour le laser nanoseconde et 800 nm pour le laser femtoseconde) et une faible densité d'énergie (20-200 mJ, Bruguier, 2009). Dans les faits, l'échantillon, i.e. une lame mince ou une section polie, est placé dans une cellule d'ablation. L'échantillon est ensuite ablaté par le faisceau laser, transformé en un aérosol et transporté par un gaz vecteur (e.g. hélium, parfois mélangé à de l'argon) vers la torche plasma. Les éléments sont ionisés à haute température (entre 5000°K et 10000°K), accélérés, et le faisceau est focalisé par des lentilles vers le spectromètre de masse. Tous les spectromètres de masse (multi-collecteur ou mono-collecteur) sont équipés d'un filtre de masse quadripolaire et d'un détecteur. Le filtre de masse quadripolaire est équipé de quatre barreaux disposés en croix parcouru par des courants alternatifs et continus (D'Abzac, 2010). La variation de la tension du courant appliqué permet de sélectionner les ions, caractérisés par leur rapport masse/charge. L'ion sélectionné est ensuite envoyé au détecteur. Le

détecteur, composé d'un multiplicateur d'électrons, mesure le nombre d'impacts (ou de coups) de chaque ion par unité de temps (D'Abzac, 2010).

Les systèmes LA-ICP-MS ne sont pas exempts de biais analytiques. Ces derniers sont de trois ordres : i) le fractionnement inter-élémentaire qui se produit lors de l'ablation et qui dépend du matériaux utilisé (effet de matrice) ii) la discrimination de masse qui s'opère dans la torche plasma. Cependant, ces biais analytiques peuvent être corrigés pour permettre une meilleure détection des particules (Bruguier, 2009).

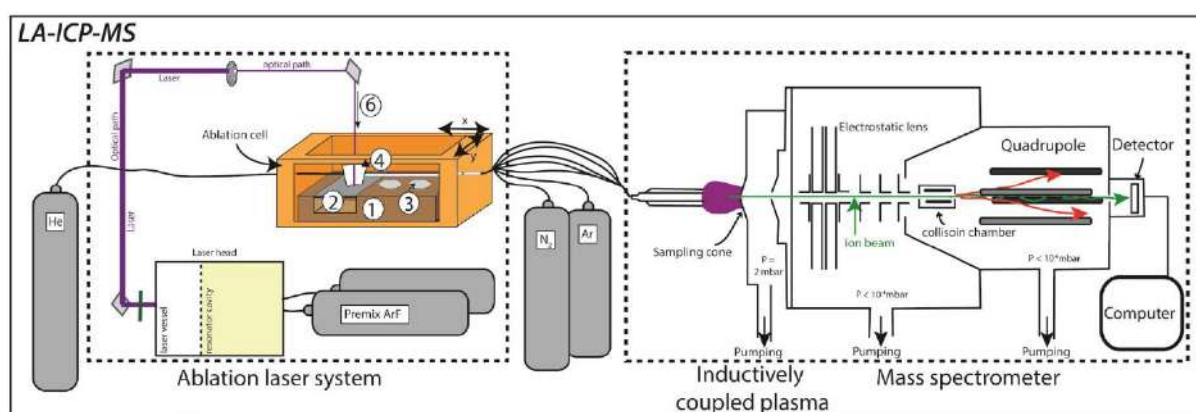


Figure II.2 : Principe de fonctionnement d'un LA-ICP-MS montrant le système d'ablation laser (Ablation cell), l'ionisation dans la torche plasma (Inductively coupled plasma) et la séparation et la détection des ions dans le spectromètre de masse (Mass spectrometer)

1.2.2 Le choix d'un double laser pour la datation des minéralisations cuprifères supergènes

La datation U-Pb avec un LA-ICP-MS requiert l'utilisation d'un standard de composition chimique connue pour corriger des effets de matrice et du fractionnement inter-élémentaire inhérent à chaque appareil. Ainsi, il est fortement conseillé d'utiliser des standards de composition et de matrice identiques aux minéraux à analyser (Fig. II.3.A, B; Bruguier, 2009). Cependant, l'absence de standards internationaux rend difficile l'analyse de minéraux accessoires présentant un fort potentiel chronométrique comme le rutile, la titanite, la baddeleyite et d'autres matériaux tels les minéraux cuprifères supergènes. Pour y remédier, le développement des lasers de très courte longueur d'onde (i.e. femtoseconde) permet de réduire fortement le fractionnement inter-élémentaire lors de l'ablation laser et donc les effets de matrice inhérents (Fig. II.3.C, D). Le choix a donc été fait d'utiliser un laser

nanoseconde, largement répandu dans les laboratoires de géochimie, et un laser femtoseconde avec le raisonnement suivant : si les résultats obtenus avec l'utilisation d'un laser nanoseconde (ns-LA) et d'un laser femtoseconde (fs-LA) sont les mêmes, les effets de matrice sont alors relativement modérés voire absents. L'utilisation d'un standard n'ayant pas la même composition chimique ne serait donc pas inadéquat.

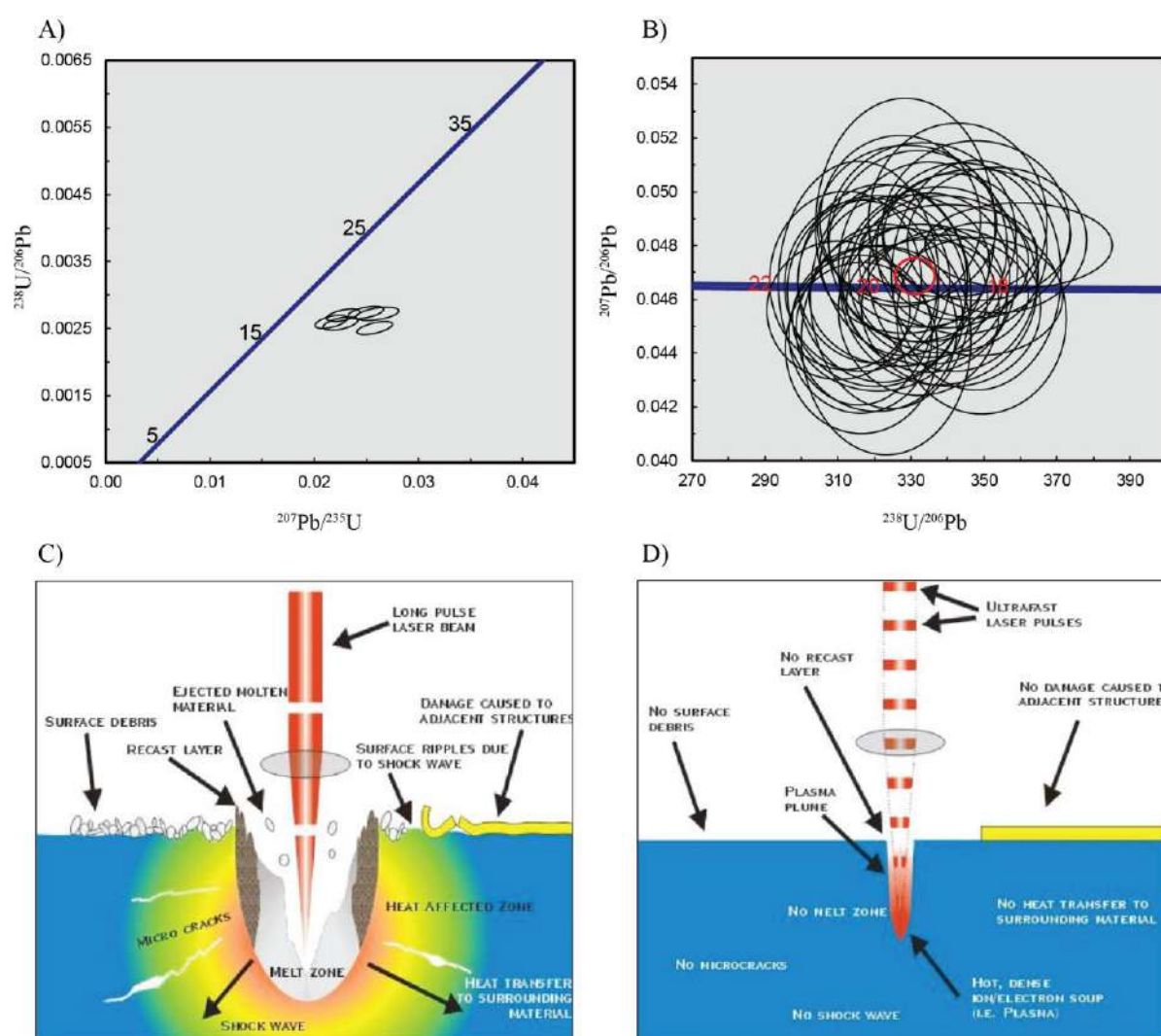


Figure II.3 : Diagramme concordia Tera-Wasserburg montrant A) la calibration de la pseudomalachite (à matrice phosphatée) par un standard de zircon (à matrice silicatée) et B) la calibration de la pseudomalachite par un standard d'apatite (à matrice phosphatée). La discordance inverse en A) montre un effet de matrice significatif. Vue schématique de l'impact de l'interaction laser-matériau entre un laser nanoseconde C) et un laser femtoseconde D). Notez que le cratère d'ablation obtenu avec un laser femtoseconde ne présente aucune poire d'interaction ni de dépôts autour du cratère

1.2.3 Appareillage et traitement de données

Le déroulement des analyses et le traitement des données géochronologiques et élémentaires sont explicités dans la section « methodology » des chapitres III, IV, V et VI de ce manuscrit. Les conditions analytiques sont reportées dans les annexes de ces mêmes chapitres.

II.2 La caractérisation texturale

Les analyses texturales, de même que les analyses qualitatives ont été réalisées au laboratoire GET à l'aide i) d'un microscope optique Nikon Eclipse E600POL équipé d'une caméra numérique, ii) d'un microscope électronique à balayage JEOL JSM 6360 LV iii) d'un système de cathodoluminescence LCL à cathode chaude Lumic HC6-LM, et à l'université d'Antofagasta par le biais d'un spectromètre de fluorescence de rayons X.

II.3 La microsonde électronique

La microsonde électronique ou sonde électronique (Electron Probe Micro Analyser, EPMA en anglais) est une technique d'analyse quantitative *in situ*, inventée par Raimond Castaing au début de la seconde moitié du 20^è siècle (Fig. II.4). Tout comme le LA-ICP-MS, c'est une technique d'analyse non destructrice. Elle permet d'analyser tous les éléments du tableau périodique depuis le béryllium jusqu'à l'uranium, à des limites de détection très basses (jusqu'à 100 ppm). Elle est constituée d'un canon à électrons, d'une colonne électronique dotée d'une source à filament de tungstène, de spectromètres à dispersion de longueur d'onde (WDS) et de détecteurs d'électrons secondaires, rétrodiffusés et de rayons X. L'analyse microsonde consiste à bombarder l'échantillon (quelques mm² d'une lame mince ou d'une section polie) par un faisceau d'électrons. De ce bombardement, les atomes sont expulsés de l'échantillon sous la forme d'électrons rétrodiffusés, d'électrons Auger, d'électrons secondaires et de rayons X. Cette émission de rayons X secondaires est par la suite analysée et comptée par cinq spectromètres, selon la longueur d'onde caractéristique de l'élément à analyser.

Bien qu'il ne mesure pas des rapports isotopiques, la sonde électronique a aussi permis la datation de minéraux accessoires riches en U et en Th à partir des concentrations élémentaires (e.g. la monazite ; Suzuki and Adachi, 1991; Suzuki et al., 1994; Montel et al., 1996; Williams et al., 1999). Au cours de

cette thèse, les analyses à la sonde électronique ont été réalisées au Centre de Microcaractérisation Raimond Castaing, doté d'une microsonde électronique CAMECA SX Five. Le protocole et les conditions analytiques sont répertoriés dans la section « methodology » des chapitres III, V et VI.

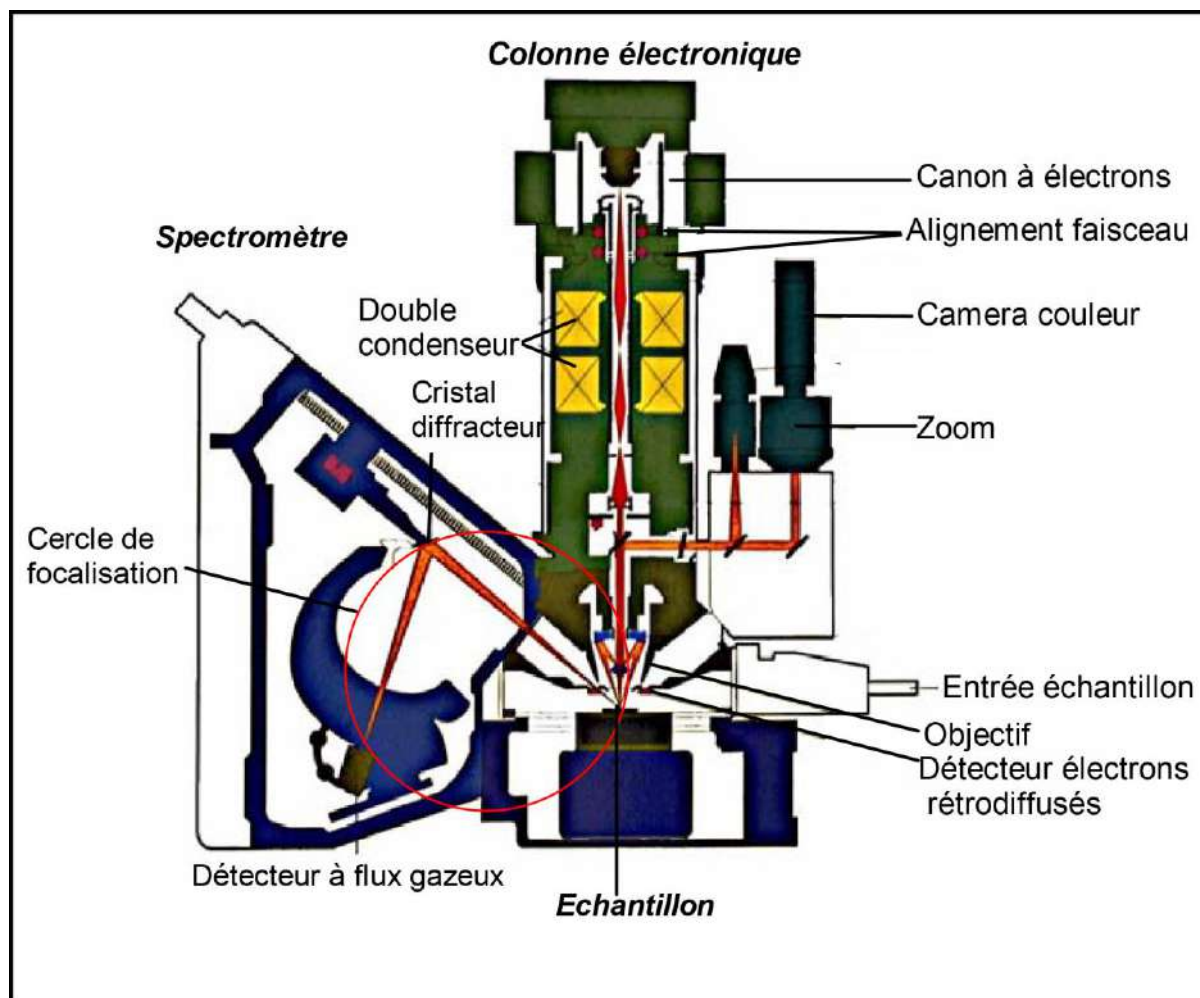


Figure II.4 : Schéma de fonctionnement d'une microsonde électronique

II.4 La microsonde ionique

Tout comme la sonde électronique, la microsonde ionique est un outil d'analyse permettant des analyses élémentaires et isotopiques, en contexte, et non destructrices (Fig. II.5). L'appareillage est constitué d'une source d'ions primaires (Oxygène O^- ou O^{2+} , et Césium Cs^+), d'un spectromètre de masse à secteur magnétique permettant de trier les isotopes/ions selon le rapport masse/charge et d'un détecteur permettant la détection et le comptage des ions/isotopes.

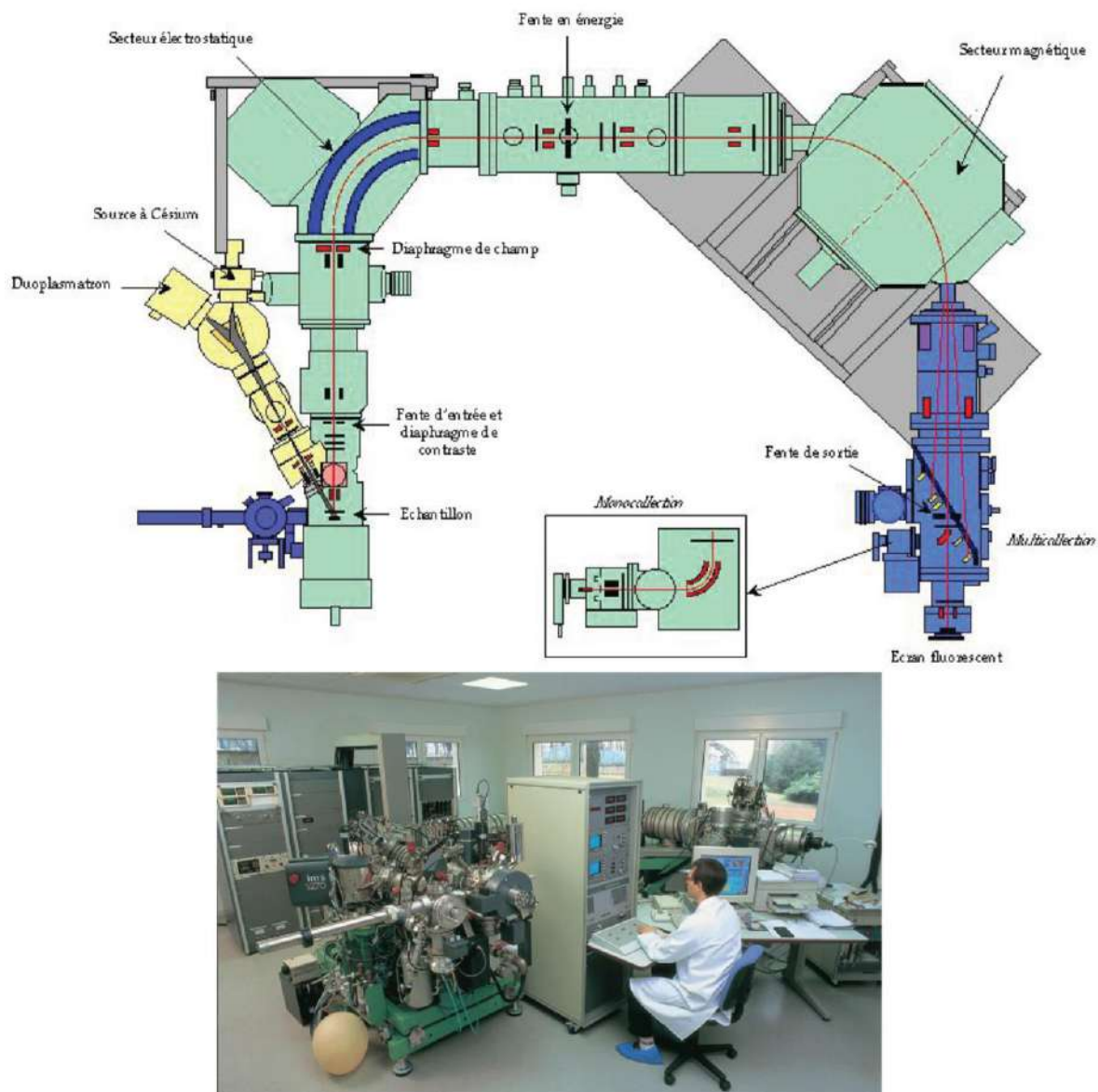


Figure II.5 : Schéma de fonctionnement d'une microsonde ionique. L'échantillon est bombardé par un faisceau d'ions puis transportés vers le spectromètre qui séparera les ions suivant leur rapport masse/charge via u secteur électrostatique puis magnétique et finalement détectés et comptés via un système mono-collecteur ou multi-collecteur

Dans les faits, un faisceau d'ions primaires bombarde un échantillon de quelques μm^2 . De cet échantillon, est éjecté un aérosol constitué d'atomes arrachés et ionisés. Ces ions secondaires sont ensuite focalisés et accélérés jusqu'au spectromètre de masse qui sépare les ions selon leur rapport masse/charge. Enfin, ces ions sont comptés par un détecteur selon un nombre de coups (ou d'intensités) par unité de temps. Tout comme le LA-ICP-MS, une standardisation est nécessaire pour s'affranchir du fractionnement de masse instrumentale.

Durant cette thèse, les analyses à la sonde ionique ont été effectuées au Centre de Recherches Pétrographiques et Chimiques (CRPG, Nancy, France) à l'aide de la sonde ionique IMS 1270. Elles ont permis, via la cartographie des isotopes de l'oxygène, de contraindre l'action des fluides dans la préservation et la perturbation du chronomètre U-Pb dans les minéralisations cuprifères supergènes. Les conditions d'analyse ainsi que le protocole analytique sont reportés dans la section « methodology » du chapitre VI.

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CHAPITRE III :

Caractérisation minéralogique et chimique des minerais
cuprifères supergènes : cas d'étude des districts miniers de
l'Atacama et de Gaoua

Préambule

L'objectif de cette étude est de fournir à la communauté scientifique, une base de données complète sur la caractérisation minéralogique et chimique des minéralisations cuprifères supergènes (MCS) *in situ* et exotiques. Au préalable de toute étude géochronologique, une étude minéralogique et chimique détaillée est indispensable voire primordiale. La caractérisation effectuée dans ce chapitre avait pour but de comprendre la genèse des MCS à la lumière de la minéralogie rencontrée, de la chimie des minéraux et faire un lien avec les conditions géologiques et climatiques déjà connues du fonctionnement de l'altération supergène. Les échantillons ont été prélevés dans des mines à ciel ouvert encore en exploitation (Damiana, Zaldivar, Gaby), dans des mines artisanales abandonnées (El Cobre) et proviennent de la carothèque de mines à ciel ouvert anciennement exploitées (Mina Sur et Gaoua). Cette étude est la première du genre à comparer entre eux dépôts *in situ* et exotiques du désert d'Atacama, et par analogie, comparer les résultats obtenus avec la MCS du porphyre de Gaoua, au sud-ouest du Burkina Faso. La différence d'âge de l'activité magmatique-hydrothermale et les paramètres climatiques et géologiques différents entre ces deux zones ont permis d'apporter des clés supplémentaires à la compréhension de la genèse des MCS.

Les résultats des travaux, présentés dans la section III.1, ont été acceptés pour publication dans la revue « Ore Geology Reviews ». Des données complémentaires, qui discutent des processus d'oxydation-réduction et des fluides impliqués dans la genèse des MCS sont présentés dans le chapitre IV

III.1 Mineralogical and chemical characterization of supergene copper-bearing minerals: examples from Chile and Burkina Faso

Ce chapitre a été accepté pour publication dans la revue Ore Geology Reviews. Les annexes citées dans cet article sont disponibles en libre accès sur la version numérique via le lien suivant (<https://doi.org/10.1016/j.oregeorev.2021.104078>).



Mineralogical and chemical characterization of supergene copper-bearing minerals: Examples from Chile and Burkina Faso

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ABSTRACT

Using optical microscopy, SEM, EPMA and LA-ICP-MS, we analyzed and characterized the textural features of Cenozoic supergene Cu-bearing minerals from three exotic and two *in situ* supergene copper mineralization from the Atacama Desert in northern Chile. In addition, we analyzed their major and rare earth elements compositions. We then compared these data to those obtained from the *in situ* supergene copper mineralization from the Gaoua Cu-Au porphyry district, emplaced during the Cenozoic in a different geodynamic setting in the West African craton. In both the *in situ* and exotic supergene copper mineralization, chrysocolla is the dominant supergene copper-bearing mineral, followed by pseudomalachite with minor amount of copper wad. Chrysocolla and pseudomalachite show distinct textural features. Chrysocolla appears either as black Mn-rich clasts or light-blue to green masses, filling the fractures and coating the non-mineralized clasts. Pseudomalachite occurs as green color bands or thin coatings filling empty spaces. All the deposits share some common features with regard to their major element and REE compositions, i.e. i) same range of chemical compositions suggesting similar conditions of formation and ii) strong Ce anomaly indicative of oxidant conditions during the crystallization of these supergene copper minerals. Our results reflect similar conditions for the formation of both supergene copper minerals in all the mining districts and lead us to propose that both areas (i.e. the Atacama Desert and southwestern Burkina Faso) underwent similar geological and climatic conditions in order to form and preserve supergene copper mineralization, i.e. exhumation of the porphyry copper deposit and weathering of the primary copper sulfides, downward and laterally moving of copper-bearing solutions to form *in situ* and exotic SCM and finally, arid to hyperarid climate to prevent mechanical abrasion and leaching of the newly formed supergene copper mineralization.

1. Introduction

Supergene copper mineralization (SCM) is produced by the interaction between sulfides and supergene processes and was originally defined by Ransome (1912) as *sulfide oxidation and leaching of ore deposits in the weathering environment, and any attendant secondary sulfide enrichment*. In order to form supergene copper mineralization, specific tectonics, climate and geomorphologic conditions are required. Tectonics controls the uplift needed to lower the groundwater table and raise the deep-seated ore deposits towards more oxidizing environments where the oxidation and leaching of sulfides may occur. On the other

hand, climate controls water availability, and therefore the leaching of sulfides and remobilization of copper-bearing solutions in the supergene environment towards the locus where supergene copper-bearing minerals precipitate. Then, favorable geomorphologic conditions prevent major erosion and removal of the supergene mineralized bodies (Hartley and Rice, 2005; Sillitoe, 2005). Two types of SCM have been recognized: 1) *in situ* deposits, which are produced by nearly vertical descending Cu-bearing aqueous solutions and precipitation of SCM within or near the leached cap (Sillitoe, 2005); and 2) exotic deposits, which are originated by lateral migration of Cu-bearing solutions from the parental deposit, without direct link with the original source of metal (Fig. 1,

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Münchmeyer, 1996; Sillitoe, 2005). In order to better understand the genesis of *in situ* and exotic SCM deposits and the parameters controlling their formation, mineralogical and geochemical characterization are required. To the best of our knowledge, apart from the work of Chavez (2000) who described in detail the zoning and distribution of copper oxide minerals in SCM in general, all the previous studies have been focused on the description of single SCM deposits and the characterization of the secondary K-bearing minerals that are genetically linked to the precipitation of copper-bearing minerals (Alpers and Brimhall, 1988; Bouzari and Clark, 2002; Cuadra and Rojas, 2001; Kahou et al., 2020; Marsh et al., 1997; Mote et al., 2001a). Furthermore, most of these studies have been carried out in the Atacama Desert and southwest USA. However, SCM can be observed all around the world (Fig. 2A) and were therefore formed under various climatic and tectonic conditions (e.g. Atacama Desert, SW of U.S.A, northern Mexico, Mongolia, Papua New Guinea, Philippines, western and central Africa, etc...). Here we present a comparison of SCM deposits in two contrasting geological and climatic settings, the Atacama Desert and the southwestern region of Burkina Faso.

For decades, the Atacama Desert represents an ideal location to study SCM because of the presence of world-class examples of both *in situ* (Chuquicamata, Salvador, Cerro Colorado, Zaldivar-Escondida Norte, etc.) and exotic (Mina Sur, Damiana, Tesoro, etc.) SCM formed within an active continental margin under hyperarid climate resulting from the interaction between the uplift of the Andean mountain and the intensification of the Humboldt Current (Garreaud et al., 2010). In this area, we focused our study on Zaldivar and Gaby *in situ* SCM and Mina Sur, Damiana and El Cobre exotic SCM, all formed during the Eocene to Miocene epochs. As a contrasted example, we also studied the *in situ* SCM of Gaoua, in Burkina Faso, emplaced during the Cenozoic, and located in a passive tectonic margin under a much wetter climate (i.e. sub-humid to Sahelian climate).

In more details, we carried out an intensive mineralogical and mineral chemistry studies of the oxidized copper ores using optical microscopy and SEM to describe the textural features together with EPMA and LA-ICPMS analyses for a chemical characterization. All the acquired data were then combined in order to better constrain the main factors controlling the genesis of SCM. The mineralogical characterizations show that Atacama Desert and SW Burkina Faso underwent similar processes during the SCM formation and preservation despite geodynamic differences. Our new chemical study confirms and implements previous ones (Chávez, 2000; Fernández-Mort et al., 2018; Sillitoe, 2005) by pointing out that exotic SCM deposits were formed under uninterrupted oxidizing conditions while *in situ* SCM deposits show changes in the redox conditions during their formation.

2. Geological background

The Atacama Desert is worldwide known to host some of the world's largest porphyry copper deposits, e.g. Escondida, Chuquicamata and Collahuasi. Most of these deposits are located in the Precordillera, a near N-S trending pre-Andean mountain range that extends over 800 km and corresponds to a former magmatic arc formed during the Incaic orogeny (Fig. 2B; Mpodozis and Ramos, 1989; Amilibia et al., 2008; Mpodozis and Cornejo, 2012). This mountain range contains most of Chile's porphyry copper deposit and is made up of Late Paleozoic to Eocene blocks, delimited by inverted normal and strike-slip faults (Scheuber and Reutter, 1992). In the Atacama Desert, the emplacement of hydrothermal alteration and hypogene mineralization was synchronous with the formation of the Precordillera (Sillitoe and Perelló, 2005) while supergene alteration occurred at least ~ 11 m.y. after the last hydrothermal event (Sillitoe and McKee, 1996).

The Mina Sur exotic copper deposit (Fig. 2B) is located within the Chuquicamata mining district, the second biggest Cu producer in the world. Geological, petrological and tectonic features of the Chuquicamata porphyry copper as well as the Mina Sur exotic copper deposits have been discussed in detail by previous authors (Dilles et al., 2011; Mortimer et al., 1977; Mpodozis and Cornejo, 2012; Newberg, 1967; Ossandón et al., 2001; Rivera et al., 2012; Sillitoe and Perelló, 2005) and are only briefly summarized here. In response to the uplift of the Precordillera, several forearc basins were formed during the Late Tertiary (Scheuber et al., 1994) including the Calama basin, which hosts the Mina Sur exotic copper deposit. The basement of this basin is represented by a metamorphic Paleozoic complex, extensively faulted and brecciated and by a Permian to Carboniferous Igneous complex (Ossandón et al., 2001; Rivera et al., 2012). The Calama formation and the El Loa group (Tomlinson et al., 2001), both made of continental sedimentary to volcano-sedimentary erosional gravels (May et al., 2010, 1999) lie above this basement. An ignimbrite flow deposited on top of the gravels was dated at 8.4 ± 0.4 Ma by K/Ar on biotite (Mortimer et al., 1977), which gives a minimum depositional age for these gravels. The exotic copper mineralization, which comprises copper silicates, copper phosphates, copper carbonates and copper halides is observed either filling fractures on the bedrock or the empty spaces available between the gravels.

The Damiana exotic copper deposit originates from the lateral migration of copper solutions from the Salvador porphyry copper deposit, within the El Salvador Mining District (Fig. 2B). This mining district has been well studied by Gustafson and Hunt (1975), Cornejo et al. (1997), Gustafson et al. (2001) and Mote et al. (2001b). The district is located near the Sierra Castillo fault, which represents the southern

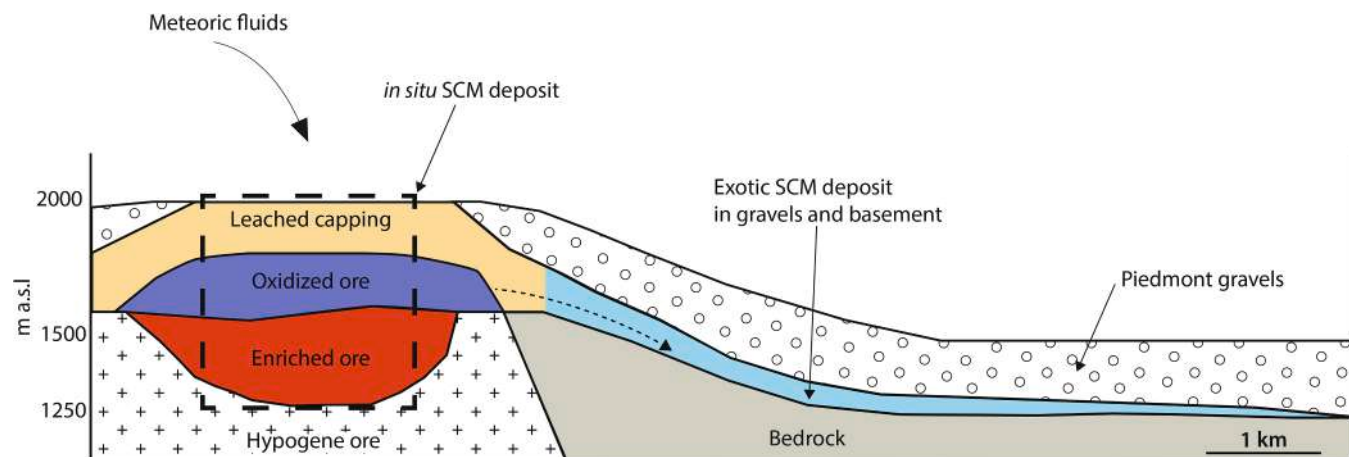


Fig. 1. Schematic representation of the relationships between hypogene porphyry copper mineralization and supergene copper mineralization (SCM) forming *in situ* and exotic copper deposits (modified after Sillitoe, 2005).

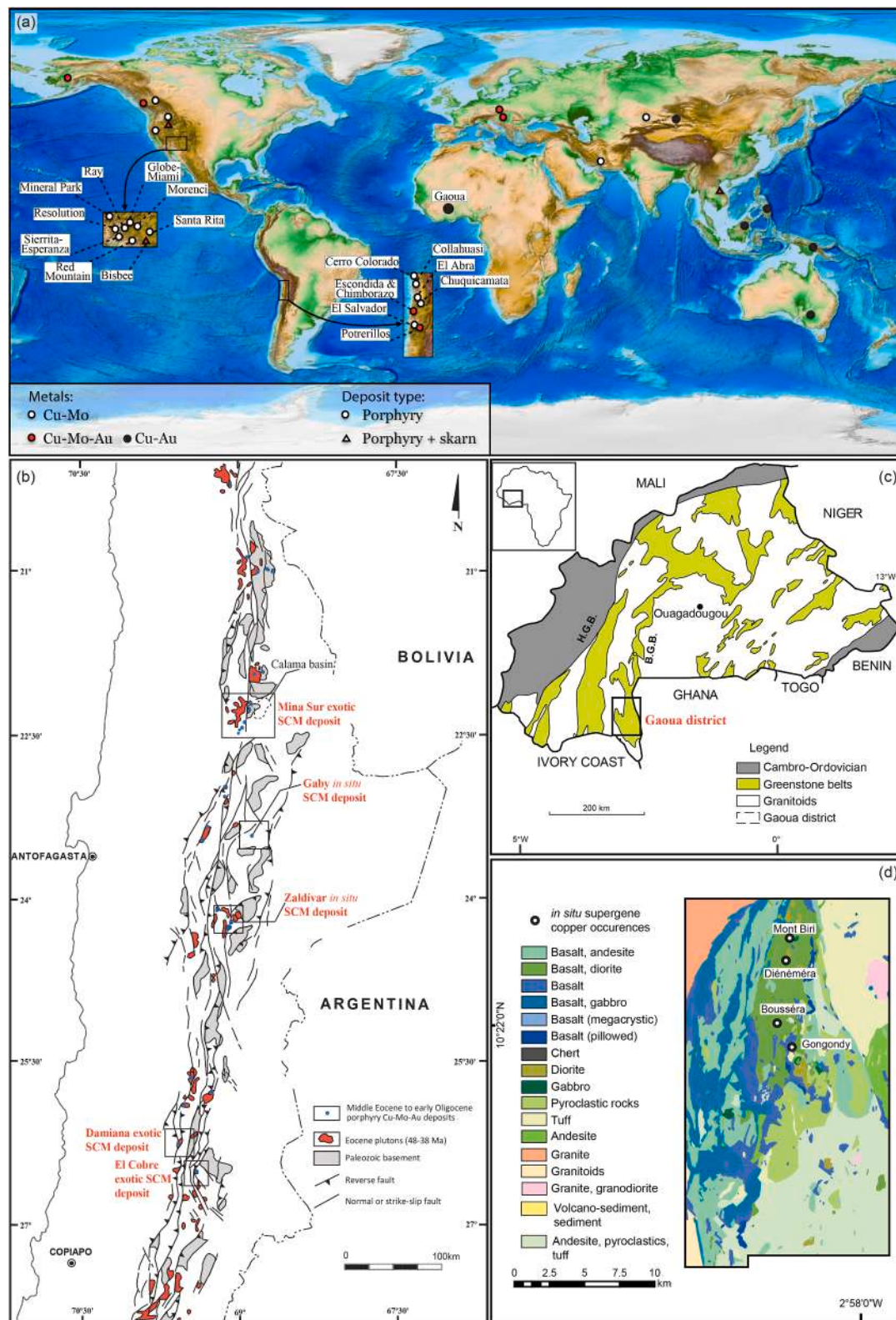


Fig. 2. Location and geological map of the studied areas. a) location of major SCM in the world map, including Atacama Desert of northern Chile and Gaoua Cu-Au district (after Sillitoe, 2010). b) Structural map of the Precordillera of northern Chile (after Mpodozis and Cornejo, 2012) showing the location of the *in situ* and exotic SCM deposit studied. Black squares mark the location of the Chuquicamata, Salvador and Potrerillos mining districts in which the Mina Sur, Damiana and El Cobre exotic SCM deposits are located, respectively c) Location (black square) of the Gaoua Cu-Au district within the simplified geological map of Burkina Faso (BGB: Boromo Greenstone Belt; HGB: Houndé Greenstone Belt after Béziat et al., 2008). d) Detailed geological map of the Gaoua Cu-Au district showing the location of the Mont Biri, Diénémara, Gongondy and Bousséra *in situ* supergene Cu-Au occurrences (Baratoux et al., 2015; Le Mignot et al., 2017).

segment of the Domeyko fault system. The Domeyko fault system is a near N-S trending major zone of deformation in the Precordillera, related to the emplacement of some of the most important porphyry copper deposits in the Atacama Desert (Mpodozis and Cornejo, 2012). The bedrock of the mining district is made of a Paleocene rhyolitic dome complex, named the Cerro Indio Muerto, which has been intruded by hypogene mineralized porphyries (Cornejo et al., 1997). The exotic copper mineralization in the Damiana deposit is filling fractures that are present in the Early Cretaceous volcanoclastic rocks *a.k.a.* the Llanta formation (Bissig and Riquelme, 2010; Rojas and Muller, 1994). This mineralization is also within the gravels (*i.e.* Atacama Pediplain), filling paleochannels around the Cerro Indio Muerto. Finally, ignimbrite flow and tuff, dated at 11.6 ± 0.5 Ma and 12.5 ± 0.5 Ma respectively (Sillitoe et al., 1968), cover the Atacama pediplain and yield a minimum age for the deposition of the pediment.

The El Cobre exotic deposit is linked to the Potrerillos porphyry copper deposit located approximately 30 Km to the southeast of El Salvador deposit, in the Potrerillos mining district (Fig. 2B; Bissig and Riquelme, 2009). Previous studies discussed the geology as well as the structural features of the Potrerillos porphyry copper deposit (Bissig and Riquelme, 2009; Marsh et al., 1997), indicating that this deposit is linked to the Sierra Castillo fault and is hosted by Jurassic to Cretaceous marine and volcano-sedimentary rocks. Hypogene mineralization of the Potrerillos porphyry copper deposit were emplaced during the late Eocene (~ 36 – 35 Ma; Marsh et al., 1997). At El Cobre exotic deposit, copper mineralization was deposited within the fractured and brecciated Paleocene andesitic and rhyolitic volcanic rocks (Bissig and Riquelme, 2009), which provide therefore a maximum age for their deposition.

The Zaldivar and Gaby *in situ* SCM are also located within the Precordillera of northern Chile (Fig. 2B). Zaldivar is part of the Escondida cluster, which represents the biggest copper district in the world whilst Gaby is located ~ 100 Km south of Chuquicamata and ~ 43 Km east of Spence porphyry copper deposit. The formation of both deposits is linked to the compressional and transtensional movements of the Domeyko fault system, related to the Incaic orogenic event (Mpodozis and Cornejo, 2012). Country rocks at Zaldivar is made of the La Tabla formation (Urzua, 2009), a set of Early Permian rhyolite to dacite ignimbrite and volcanic rocks. The latter are intruded by granodiorite to dacite porphyries, related to the Incaic magmatism (between 41 Ma and 30 Ma; Maksaeu and Zentilli, 1999). At Gaby, basement rocks are represented by the Carboniferous Quebrada Escondida metavolcanic-sedimentary rocks and the Permian Pampa Elvira granodiorite complex. This basement is intruded by two Eocene porphyries, the dike-like Gaby and Crowded porphyries. In both deposits, a well-developed supergene alteration profile is observed with a 120–500 m-thick supergene copper orebody at Zaldivar and a 250 m-thick copper oxide orebody at Gaby (Aguilar et al., 2003; Perelló et al., 2018). Both deposits lie beneath thick gravels pediment and comprises copper silicates as predominant Cu-bearing minerals, together with copper sulfates, copper phosphates and black-copper oxides.

The Gaoua porphyry Cu-Au district in southeastern Burkina Faso (Fig. 2C), is located within the West African craton (WAC) which consists of an Archean core, juxtaposed to Paleoproterozoic greenstone belts also known as the Boromo-Goren greenstone belt (Baratoux et al., 2011). The deposition of the Paleoproterozoic greenstone belt of the WAC took place during the Eburnean orogeny, around 2.25 to 2.15 Ga ago (Baratoux et al., 2011). These Boromo-Goren greenstone belt consists of volcanic to plutonic rocks affected by a greenschist facies regional metamorphism. These volcano-plutonic rocks were intruded by granitoids, emplaced from ca. 2250 Ma to 2060 Ma, and deformed successively by three deformation stages (Béziat et al., 2008; Baratoux et al., 2011, 2015). At a local scale, the Gaoua district is located at the southwestern margin of the Boromo Belt (Fig. 2C). The basement of the Gaoua porphyry copper deposit comprises a thick-sequence of mafic rocks (*i.e.* gabbro, basalt, andesite), followed by calc-alkaline intrusive

bodies (diorite, granodiorite, dolerite, granite, rhyolite). All the series underwent a regional greenschist-facies metamorphism (Baratoux et al., 2015). Hypogene copper mineralization is hosted by the greenschist facies volcanic flows and quartz-diorite intrusions (Le Mignot et al., 2017). This mineralization appears as veins, hydrothermal breccia filling or is disseminated within quartz-diorite porphyry stocks at Mont Biri, Diénémara, Gongondy and Bousséra (Fig. 2D; Le Mignot et al., 2017). The supergene copper ore of the Gaoua district is linked to the Tertiary history of the West African craton. During the Cenozoic, the onset of a hot and wet tropical climate, in alternation with dry seasons, in this tectonically stable craton and in addition to the low denudation rates in the region (2 – 20 m Ma^{-1} ; Beauvais and Chardon, 2013) allowed for the formation of large and flat erosion surfaces *a.k.a.* pediplains or regolith. These pediplains, which result from chemical and mechanical alteration of the bedrock (*i.e.* Birimian greenstone belts, Gunnell, 2003), sometimes overlie supergene mineralization of various economic importance, *i.e.* manganese at Tambao, and copper at Gaoua (Beauvais et al., 2008; Chardon et al., 2018). However, to the best of our knowledge no studies have been published about the recognition and/or the characterization of the *in situ* SCM from the Gaoua porphyry Cu-Au district.

3. Analytical procedures

Samples from five Cu-deposits in northern Chile and one Cu-Au deposit in Burkina Faso have been collected during a sampling campaigns in 2018 (*i.e.* Mina Sur, Damiana, El Cobre for exotic SCM) or were provided by mining geologists (*i.e.* Zaldivar, Gaby and Gaoua for *in situ* SCM). Mineralogical studies were carried out at the Géosciences Environnement Toulouse (GET, Université de Toulouse, France) using a polarizing microscope NIKON JLV 500 on polished thin sections. Backscattered electron images (BSE) as well as qualitative data were obtained using the JEOL JSM 6360 LV Scanning Electron Microscope (SEM) coupled to an energy dispersive spectrometry (EDS) analysis system at the GET laboratory. The analytical conditions used were 15kv for the acceleration voltage, 50 μm for the beam size while a tungsten filament was used as the electron source. Quantitative analyses as well as major element distribution maps were carried out at the Centre de Micro-Characterisation Raimond Castaing (Université de Toulouse, France) using the CAMECA SXFive Electron Probe Micro-Analyzer (EPMA) on polished thin sections. The analytical conditions for the profiles were 2 μm for the beam size, 10nA for the current intensity and an acceleration voltage of 15 keV. Data are reported in ESM 1. For the maps, the analytical settings were 100nA for the current intensity, an acceleration voltage of 15 keV, a dwell time of 900 ms and a varying step size of 4 and 5 μm . Chemical studies, *i.e.* REE analyses, were carried out at the GET laboratory using a Thermo-Fisher Element-XR, High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) coupled to an ESI NWR213UC 213 nm laser ablation system (ns-LA). Tuning of the instrument as well as mass calibration were performed on NIST SRM 610 glass reference material, *i.e.* $^{238}\text{U}^{+}/^{232}\text{Th}^{+}$ between 0.95 and 1.05, oxide production $< 0.5\%$ and a sensitivity > 20000 cps/ppm for ^{238}U . Laser ablation were carried out using a laser fluence of $3 \text{ J}/\text{cm}^2$, a repetition rate of 10 Hz and a 20 μm spot size. Ablated materials were transported in helium (450 mL/min) which was used as carrier gas. Each laser spot was ablated during 40 s with 10 s of background collection and 40 s for the “wash-out”. The isotopes monitored are ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu . The internal and external calibration procedure suggested by Longerich et al. (1996) was used. The following standards were used: NIST SRM 610 reference glass as primary standard and 91500 zircon (as a proxy for the black chrysocolla and chrysocolla, see Wiedenbeck et al. 1995) as well as Durango apatite (as a proxy for pseudomalachite, see McDowell et al., 2005) as secondary, quality control standards (see Kahou et al., 2020). External measurement was carried out at the beginning and the end of each analytical session and each 15 spot

analyses. Data reduction was carried out using the Iolite data reduction software (Paton et al., 2011). Operating conditions and REE concentrations obtained on black chrysocolla, chrysocolla and pseudomalachite are reported in ESM 2.

4. Textural and chemical characterization of supergene copper mineralization

4.1. Textural features of SCM

To summarize the following description of the ore samples and the mineralogical assemblages, a synthetic paragenetic sequence is presented in Fig. 3.

4.1.1. The Mina Sur exotic SCM

The ore body at Mina Sur is ca. 2.2 km long, 1.2 km wide with a maximum thickness of about 110 m (Mortimer et al., 1977) and lies 2 Km south of the world-class Chuquicamata porphyry copper deposit. The copper mineralization is mainly composed of chrysocolla and atacamite that fill fractures in the bedrock as well as the porosity in the overlying sedimentary cover (Mortimer et al., 1977; Münchmeyer, 1996). Macroscopic scale observations of the samples selected for this study (Fig. 4A) show that the copper mineralization is mainly composed of chrysocolla either under the form of black Mn-rich angular millimeter size clasts (*a.k.a* black chrysocolla or copper pitch; see Throop and Buseck, 1971), or as millimetric turquoise to pale green Mn-poor bands coating both the black chrysocolla and the sedimentary clasts. Chrysocolla bands are intercalated with green micrometer size thin-bands of pseudomalachite. Atacamite, a copper chloride showing an acicular texture, is also present in small proportion. Under plane polarized light, black chrysocolla appears as black clasts, showing locally a concentric banding texture with black to brownish color variations (Fig. 4B). The chrysocolla bands (Fig. 4B) are made of microcrystalline aggregates with a strong birefringence in plane-polarized light (Campos et al., 2015; Foote and Bradley, 1913; Menzies et al., 2015; Sun, 1963; Thompson, 1980). Pseudomalachite has an emerald-green to dark green color (Fig. 4B) and a low pleochroism in plane-polarized light (Berry, 1950; Shoemaker et al., 1977). Atacamite displays thin black prismatic crystal in cross-polarized light (Fig. 4C) and appears as overgrowths around the chrysocolla and pseudomalachite bands. Backscattered electron imaging (Fig. 4D) shows a more complex textural association between these minerals as chrysocolla and pseudomalachite display intergrowth textures. In some places, crystals of chrysocolla crosscut some

pseudomalachite bands. Such textural relationships have been interpreted as resulting from dissolution-precipitation of pseudomalachite by chrysocolla (Crane et al., 2001). Finally, atacamite is present as prismatic crystals that grew on top of other mineral phases or also as filling available voids. Textural observations clearly shown that atacamite formed after chrysocolla and pseudomalachite.

4.1.2. The Damiana exotic SCM

At the scale of the outcrop, mineralization in both gravels (Fig. 5A) and bedrock fractures (Fig. 5B) appear as a homogeneous, cryptocrystalline blue-greenish mass. In hand specimens, chrysocolla is the most abundant copper mineral, followed, to a lesser extent, by copper wad, a term mainly used by miners to refer to a mixture of Mn, Fe, Cu oxy-hydrates (Fam and Rojas, 1997; Menzies et al., 2015; Mote et al., 2001a; Pincheira et al., 2003).

In the ore found in the Damiana bedrock, optical microscopy observations confirm that chrysocolla predominates over copper wad and pseudomalachite. In the fractures, chrysocolla appears as greenish and heterogenous fillings. Sometimes, chrysocolla appears as micrometric concentric bands (Fig. 5C). Copper wad precedes chrysocolla and appears as thin coatings in fractures with a brown to dark brown color and a low pleochroism. Pseudomalachite was the last mineral to crystallize. It shows a thin coating texture under SEM, indistinguishable under the petrographic microscope and occurs as overgrowths on chrysocolla (Fig. 5D). Backscattered electron imaging shows a clear paragenetic sequence characterized by 1) copper wad showing colloform texture deposited as thin coatings within the bedrock fractures 2) massive chrysocolla is found within fractures in the bedrock usually on top of copper wad and 3) pseudomalachite filling the empty spaces left (Fig. 5D).

In the Damiana gravels, the SCM is deposited in the available empty spaces within the gravels (Fig. 5E). Chrysocolla is the dominant copper phase with lesser amounts of copper wad, pseudomalachite, microcrystalline quartz and apatite. Under plane polarized light, chrysocolla appears as millimetric greenish layers coating the gravels clasts. The texture is relatively homogeneous, with a low pleochroism and a strong relief (Fig. 5E). Pseudomalachite shows green to dark green color in plane polarized light, strong relief with a millimeter crystal size (Fig. 5E). Finally, quartz appears as euhedral micro-crystals, with low relief and birefringence (Fig. 5E). SEM-EDS analyses have shown a precipitation sequence characterized by chrysocolla precipitation coeval with colloform apatite, followed by the crystallization of pseudomalachite and microcrystalline quartz at a later stage (Fig. 5F). BSE images

Mineral	Mina Sur		Damiana		El Cobre		Gaby		Zaldivar		Gaoua	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
Copper wad	—		—		—		—		—			
Black chrysocolla	—											
Chrysocolla		—		—		—		—		—		—
Pseudomalachite		—		—		—		—		—		—
Brochantite												
Cuprite												
Atacamite		—						—				
microcrystalline quartz				—		—						
Apatite				—								
Sulfide relicts							—		—			

Fig. 3. Synthetic paragenetic sequence for the studied exotic and *in situ* SCM deposits. Stage 1 corresponds to the main supergene oxidation while Stage 2 corresponds to the late filling empty spaces.

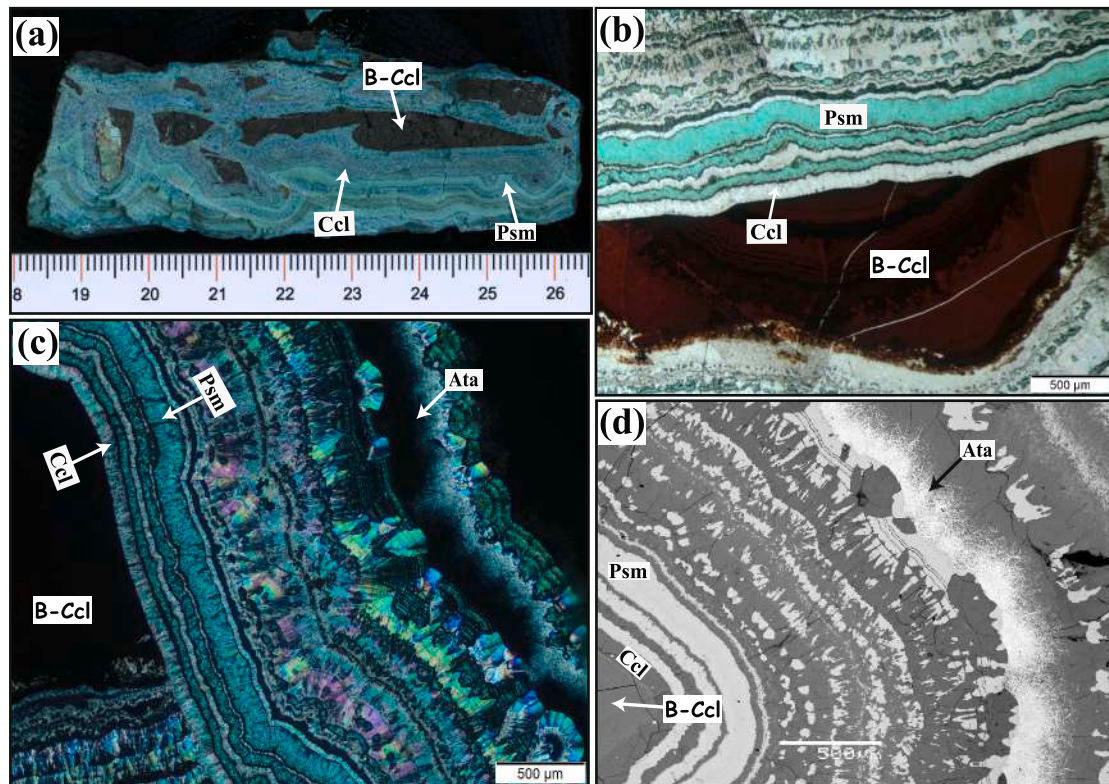


Fig. 4. Sample and thin sections photographs showing the relationships between Mina Sur copper minerals. a) Black chrysocolla (B-Ccl) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. b) Plane-polarized light photograph showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. c) Cross-polarized light and d) SEM photomicrographs showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite needles (Ata) on chrysocolla and pseudomalachite.

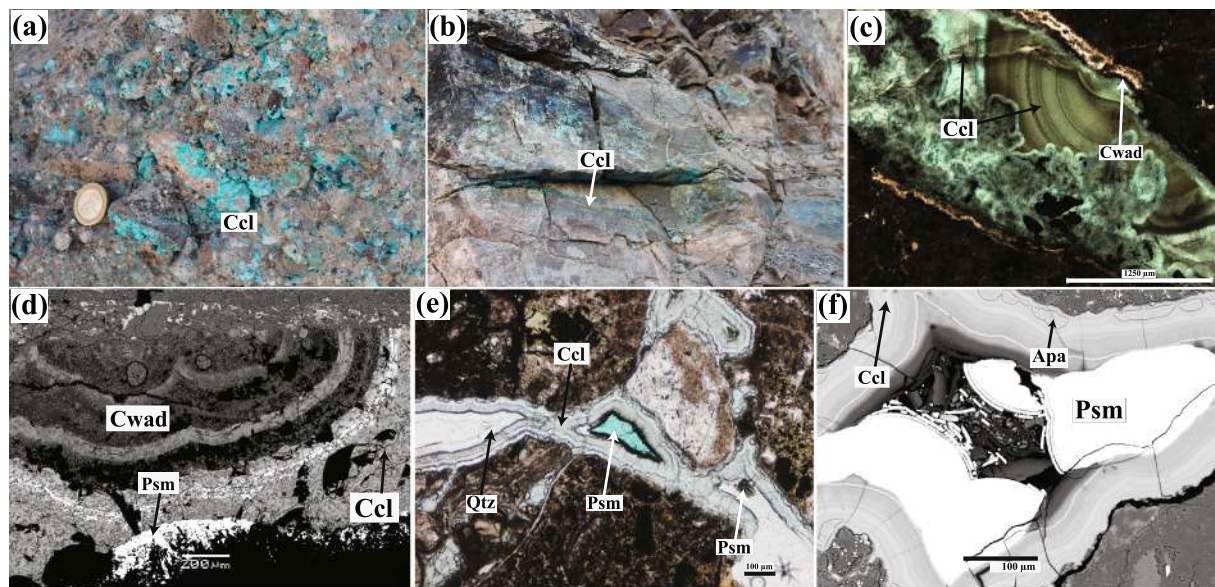


Fig. 5. Sample and thin sections photographs showing the relationships between Damiana copper minerals. Chrysocolla (Ccl) filling empty spaces and porosity of the gravels at a) Damiana gravels and fractures at b) Damiana bedrock. c) Cross-polarized light photograph showing chrysocolla (Ccl) and copper wad (Cwad) filling fractures at Damiana bedrock. d) SEM photomicrographs showing copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl), and pseudomalachite (Psm) coating chrysocolla. e) Plane-polarized light photograph of chrysocolla (Ccl) filling porosity of the gravels at Damiana gravels and pseudomalachite and microcrystalline quartz filling empty spaces. f) SEM photomicrographs showing chrysocolla (Ccl) coeval with apatite (Apa) filling porosity of the gravels and pseudomalachite (Psm) crystallizing in empty spaces.

of chrysocolla displays either homogeneous texture or micrometer-scale banded texture, linked to variable Si/Cu ratios as shown by SEM-EDS analyses.

4.1.3. The El Cobre exotic SCM

At the scale of the outcrop, mineralization appears as massive cryptocrystalline light-blue to dark-blue masses filling the fractures. It

may also be present as thin coating on the edge of some fractures (Fig. 6A,B). Chrysocolla is the most abundant Cu-bearing mineral, followed by minor copper wad and traces of pseudomalachite.

Under a petrographic microscope, a common paragenetic sequence is easily distinguishable for the filling of the fractures: first, copper wad is deposited as thin coatings covering the edges of the fractures, followed by the precipitation of chrysocolla (Fig. 6C). Finally, pseudomalachite and microcrystalline quartz are the last mineral phases to be deposited. At El Cobre, chrysocolla occurs mostly as cluster of concentric micrometer-scale laminae (Fig. 6C). Under SEM, chrysocolla shows a fairly homogeneous texture (Fig. 6D). Pseudomalachite crystallizes as concentric spherulitic and mammillary texture (as shown by SEM images, Fig. 6D) filling open spaces, impregnating bedrock fractures and overgrowing chrysocolla.

4.1.4. Zaldivar *in situ* SCM

The SCM at Zaldivar porphyry copper deposit extends over a thickness of about 500 m under the piedmont gravels (Monroy, 2000). At a macroscopic scale, the *in situ* SCM appears as emerald green to dark-green masses surrounding angular to sub-angular black clasts (Fig. 7A). The green to dark-green masses are made of brochantite and pseudomalachite while the black clasts are made of dark chrysocolla. Brochantite is the most abundant mineral phases whereas pseudomalachite and chrysocolla are less abundant. Under plane polarized light, both types of brochantite show a weak pleochroism (Fig. 7B). Prismatic-crystal shaped brochantite displays zoning characterized by a silica-rich core surrounded by druse crystal growth (Fig. 7B). Pseudomalachite occurs as light-green to green masses filling spaces similarly to brochantite (Fig. 7B). Chrysocolla is observed, under plane polarized light, as light- to dark- brown masses surrounding the clasts and filling the empty spaces or as coating the breccias (Fig. 7B). Chrysocolla displays a strong relief and shows a massive texture with syneresis cracks (Fig. 7C).

SEM images clearly exhibit textural relationship between the copper-bearing minerals. Brochantite displays a markedly druse-crystal shape with micrometer-scale size (Fig. 7C) while pseudomalachite and brochantite show intergrowth textures (Fig. 7C). However, locally, brochantite seems to develop at the expense of a former assemblage of chrysocolla and pseudomalachite (Fig. 7C). Occasionally, pseudomalachite masses display homogeneous texture, without impurities. Copper wad forms micrometer-scale thin concentric bands coating pseudomalachite crystals (Fig. 7D).

4.1.5. Gaby *in situ* SCM

In hand and core-logging samples, copper oxide mineralization appears either as veins (filling fractures) or disseminated within the porphyry (Fig. 8A). Chrysocolla is the most common mineral phases, followed by minor amounts of black copper oxides, brochantite and atacamite. Under the petrographic microscope, chrysocolla appears as light- to dark- green masses filling empty spaces (Fig. 8B). Under plane polarized light, chrysocolla shows a strong relief without cleavage. Chrysocolla presents no outward crystal form, although sometimes crystalline in internal structure (Fig. 8B). Copper wad is observed, under plane polarized light, as dark brown to black amorphous masses. Under SEM, chrysocolla displays a relative homogeneous texture with a lot of internal cracks and/or fractures (Fig. 8C). Copper wad is filling fractures and empty spaces and exhibits a colloform texture (Fig. 8C). Brochantite clearly shows the direct replacement of sulfides (Fig. 8D) displaying impregnations and disseminations within the sulfides relicts and as coatings at the edges of the altered sulfides. Finally, atacamite coats both chrysocolla and brochantite as highlighted by SEM images (Fig. 8D).

4.1.6. Gaoua *in situ* SCM

SCM is disseminated inside the porphyries or fills some veins in association with primary sulfides. In hand samples, oxidized copper ore

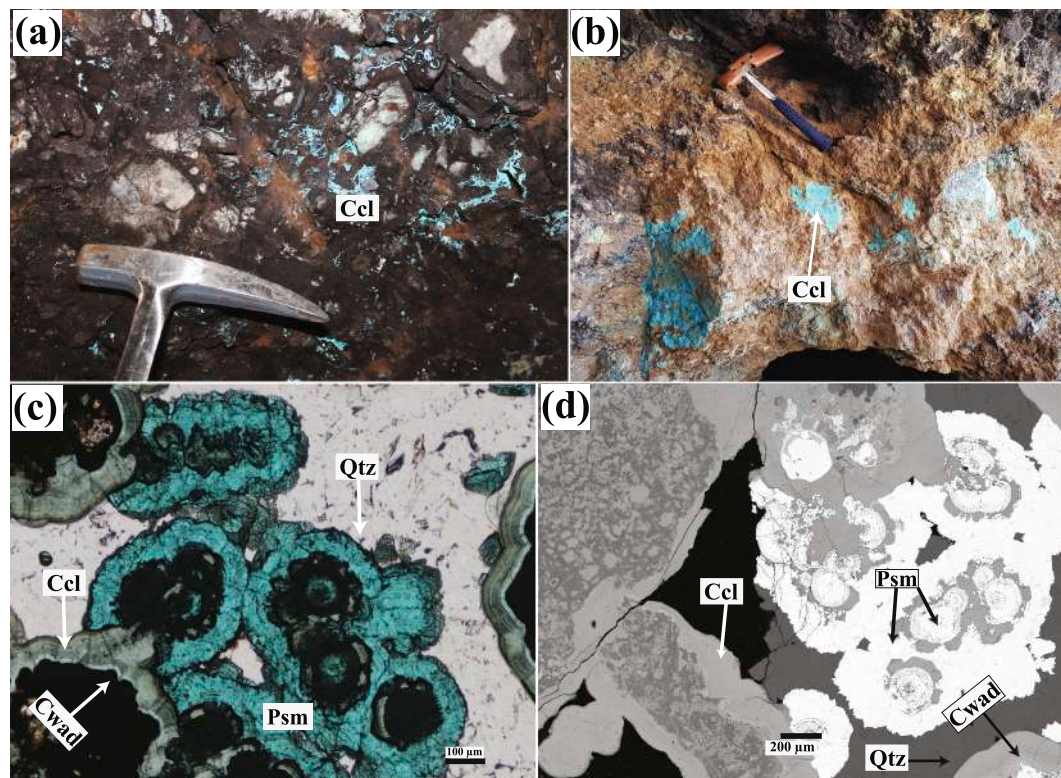


Fig. 6. Sample and thin sections photographs showing the relationships between El Cobre copper minerals. a, b) Chrysocolla (Ccl) filling fractures of the altered andesite bedrock. c) Plane-polarized light photograph showing copper wad (Cwad), chrysocolla (Ccl) and pseudomalachite filling fractures of the andesite bedrock. d) SEM photomicrograph showing chrysocolla (Ccl) coating on copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl) and pseudomalachite (Psm) and amorphous quartz filling empty spaces.

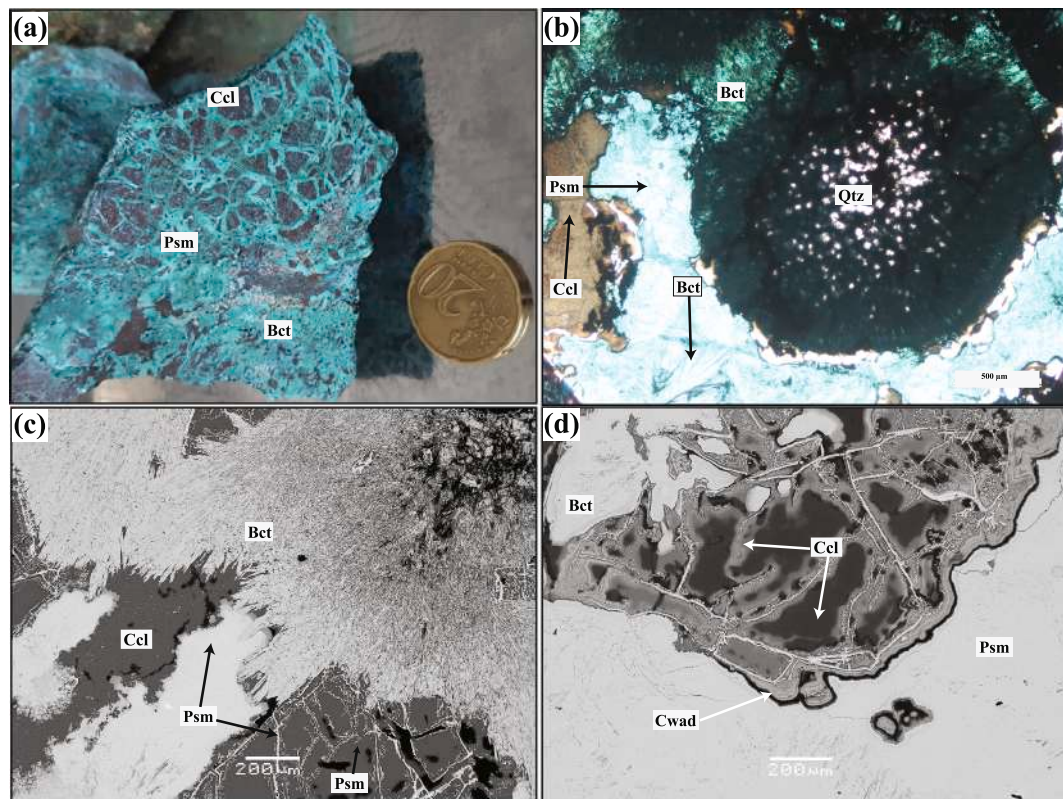


Fig. 7. Sample and thin sections photographs showing the relationships between Zaldivar copper minerals. a) Hand-samples of Zaldivar supergene copper minerals. b) Plane-polarized light photograph showing relicts of altered sulfides replaced by brochantite and brown chrysocolla and pseudomalachite gradually replacing brochantite. c, d) SEM photomicrographs showing a complex textural relationship between brochantite, copper wad (Cwad) thin band, chrysocolla and pseudomalachite.

displays homogeneous light- to dark- blue masses filling veins (Fig. 9A). Under the petrographic microscope, these light to dark blue masses can be identified as chrysocolla, which is the most abundant oxidized Cu-bearing minerals (Fig. 9B). Under plane polarized light, chrysocolla appears as green to dark-green heterogeneous masses mainly found within fractures or as coating (Fig. 9B). Pseudomalachite and copper oxides (i.e. cuprite) are present in lesser amounts while no copper wad and atacamite have been found (Fig. 9C). Pseudomalachite is found as inclusions within the chrysocolla internal texture (Fig. 9D) while copper oxides exhibit a square granular shape due to corrosion and occurs as thin coatings as well as impregnating silica clasts as illustrated in Fig. 9D. Chrysocolla seems to replace cuprite and fills the empty spaces between the quartz crystals (Fig. 9D).

4.2. Chemical compositions of the main Cu-bearing minerals

4.2.1. Mineral chemistry

Quantitative major and minor element distributions of the studied SCM are reported in ESM 1.

In the exotic deposits (i.e. Mina Sur, Damiana or El Cobre), chrysocolla shows slightly variable proportion of CuO (~between 50 and 55 wt% at Mina Sur, 35–45 wt% at Damiana and ~ 52 wt% at El Cobre) and SiO₂ (values between ~ 40–50 wt% at Mina Sur, 45–50 wt% at Damiana and ~ 35–45 wt% at El Cobre) as well as a variable proportion of H₂O (average between 0 and 10 wt%). Al₂O₃, CaO, K₂O, MgO, FeO are also found as trace elements (Fig. 10A). Black chrysocolla (Fig. 10B), which is only found at Mina Sur, is distinguished from chrysocolla by a higher amount of MnO (up to 6 wt%) and H₂O (10–20 wt%) and a lower content in SiO₂ (20–40 wt%) and CuO (~45–50 wt%). Pseudomalachite displays more homogeneous composition with high CuO (~68.4 wt% at Mina Sur, between 63 and 70 wt% at Damiana and ~ 67 wt% at El

Cobre) and P₂O₅ contents (average 24.2 wt% at Mina Sur, 23–27 wt% at Damiana and 27–28 wt% at El Cobre) and low H₂O contents (5–10 wt%) in all exotic deposits (Fig. 10C). Silica, aluminum, iron and calcium are also present as trace elements.

The compositional data obtained for the *in situ* SCM (i.e. Zaldivar, Gaby and Gaoua) are listed in ESM 1 and displayed in Fig. 10D for chrysocolla. At Zaldivar, the chemical composition of chrysocolla is consistent with previously published analyses (Newberg, 1967; Pinget, 2016) and display high SiO₂ (~43 wt%) and CuO (~51 wt%) contents with a low water content (~4 wt%). Brochantite contains high proportion of Cu (CuO ~ 78 wt% and 84 wt%), and sulfate (SO₃ ~ 11–20 wt%) while water was below the detection limits. Pseudomalachite shows CuO contents between 21 and 24 wt%, P₂O₅ between 67 and 69 wt% and H₂O contents between 5 and 8 wt%. Chrysocolla is composed of CuO (~50 wt%), SiO₂ (average between 39 and 47 wt%) and variable water contents (average between 0 and 15 wt%).

At Gaby, chrysocolla presents high CuO (~between 45 and 58 wt%) and SiO₂ contents (~between 28 and 42 wt%) and a varying proportion of H₂O (~between 3 and 12 wt%). Low concentrations of CaO (<1 wt%) is also found in chrysocolla. Brochantite, which replaces ancient sulfides, reveals high CuO (~between 76 and 100 wt%) and SO₃ (~between 17 and 40 wt%) contents. These wide range of values does not agree with the published values for brochantite (Mrose and Reichen, 1965) but rather highlights the ongoing replacement of sulfides relicts by brochantite and other Cu-phosphate minerals. EPMA-analyses carried out on atacamite show homogeneous Cl (~12–15 wt%) and CuO concentrations (74–77 wt%) and significant quantities of SiO₂ (up to 5 wt%), emphasizing the presence of chrysocolla or silica impurities within the atacamite.

Finally, for the Gaoua deposit, EPMA analyses reveal that chrysocolla presents chemical compositions that are similar to those of the Atacama

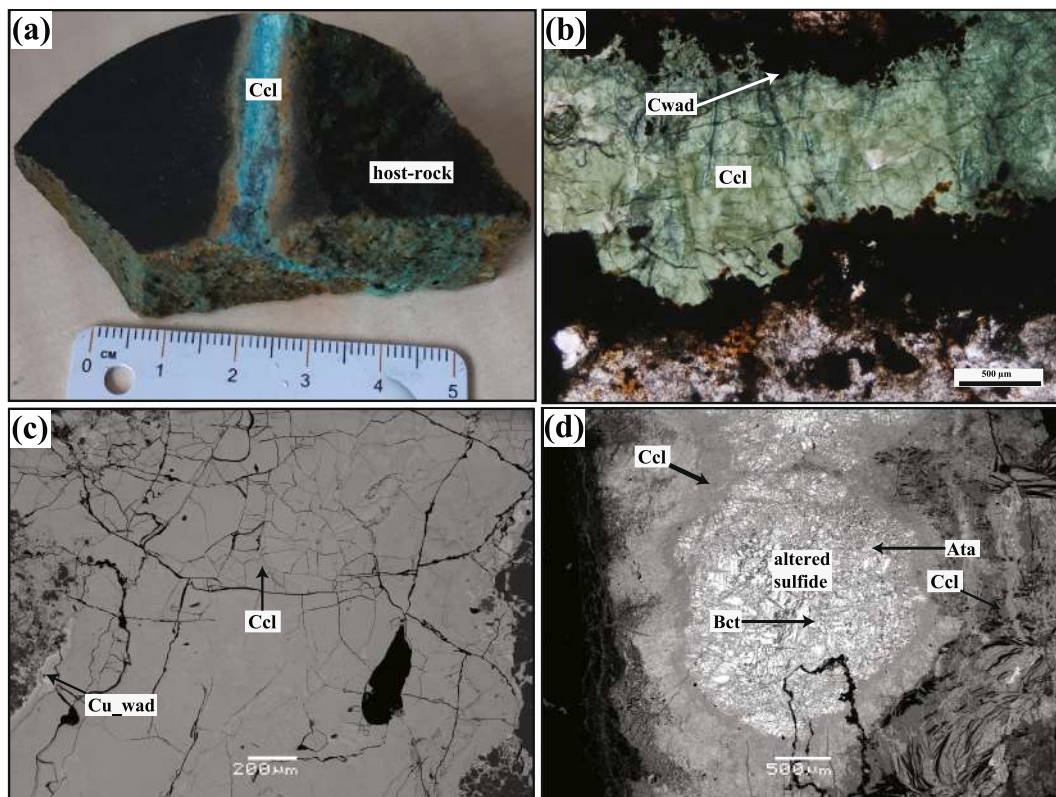


Fig. 8. Sample and thin sections photographs showing the relationships between Gaby copper minerals. a) Hand-samples of Gaby showing chrysocolla (Ccl) filling fractures in the Gaby micro-diorite host-rock. b) Plane-polarized light photograph showing copper wad (Cwad) and chrysocolla filling fractures of the host-rock. c, d) SEM photomicrographs showing c) copper wad thin band and fractured and homogeneous texture of chrysocolla, crystallizing within host-rock veins and d) an altered sulfide replaced by brochantite and chrysocolla, and atacamite (Ata) overgrowing on brochantite.

Desert. The SiO_2 and CuO contents vary from 35 wt% to 48 wt% (average ~ 41 wt%) and from 41 wt% to 51 wt% (average ~ 46 wt%) respectively while the Al_2O_3 contents can reach ~ 1.5 wt%. In Gaoua, intra-layer compositional profiles of chrysocolla show a relatively homogeneous chemical composition with SiO_2 and CuO ranging from 35 wt% to 45 wt% and 43 wt% to 51 wt%, respectively. Low K_2O , CaO and Na_2O contents have also been detected. Pseudomalachite chemical analyses show high CuO (~ 67 wt%) and P_2O_5 (~ 21 wt%) contents with minor amounts of SiO_2 ($\sim$ up to 2 wt%). Aluminum, calcium and magnesium are present as trace elements.

In order to better characterize the chemical homogeneity of the Cu-bearing minerals (i.e. chrysocolla and pseudomalachite), distribution maps of Si, Cu and P were built for both type of deposits (i.e. exotic and *in situ*). At Mina Sur, silica, copper and phosphorous show a fairly homogeneous distribution in both minerals (Fig. 11A–C) although low-Cu and high-Si spots demonstrate the presence of impurities and/or mineral inclusions. At Damiana and El Cobre, elemental distribution maps show that the distribution of Si, Cu and P are rather homogenous in both chrysocolla and pseudomalachite with the exception of the micro-cracks as seen in Fig. 12A–F. Nevertheless, a faint concentric zoning can be observed in pseudomalachite at El Cobre (as shown in Fig. 12B, D, F), which underlines concentric mineral layering and reveals the crosscutting relationship between chrysocolla and pseudomalachite. For chrysocolla and pseudomalachite from Zaldivar, elemental distribution maps are homogeneous for P, Si and Cu and show a faint zoning for Si, Cu and P in the copper wad (Fig. 13A, C, E). Finally, for the Gaby deposit, distribution maps for Si and Cu at the boundaries between chrysocolla and copper wad, show growth bands within the copper wad contrasting with the homogenous distributions within the chrysocolla (Fig. 13B, D).

4.2.2. Rare earth elements

Results are presented in [ESM 2](#) for REE and in [Fig. 14](#). Except for Damiana and El Cobre, all the chrysocolla and pseudomalachite samples have REE concentrations above the detection limits.

REE data of chrysocolla from exotic (Fig. 14A) and *in situ* (Fig. 14B) SCM have been plotted in a chondrite-normalized spider diagram (McDonough and Sun, 1995). Most of the chrysocolla from both exotic and *in situ* deposits, show a flat pattern for all the REE with a slightly depleted spectrum for HREE, a strong negative Ce-anomaly and a small negative Eu-anomaly. Chrysocolla from the *in situ* SCM of Zaldivar appears as an outlier, with notably lower REE contents and a strong positive Ce-anomaly. Chrysocolla from Gaby and Gaoua has REE contents that are ten times higher than those from Zaldivar, with a strong negative Ce-anomaly. REE contents of chrysocolla from Mina Sur are ten times lower than any other exotic deposits without a markedly negative Ce-anomaly. Chrysocolla from Damiana displays LREE contents ten times higher than those from Mina Sur and El Cobre. Black chrysocolla from Mina Sur show a strong negative Ce-anomaly, a flat HREE spectrum with HREE contents that are ten times higher than chrysocolla from the same deposit.

With the exception of Damiana, the REE patterns for pseudomalachite found in the exotic and *in situ* SCM show high LREE and HREE concentrations when compared to REE contents of chrysocolla and black chrysocolla (Fig. 14C, D). The REE spectrum at El Cobre shows concentrations up to ten times higher than those obtained at Damiana and Mina Sur, especially for LREE. For Mina Sur and El Cobre, LREE spectrum show a strong negative Ce-anomaly while LREE data at Damiana show an almost flat spectrum without any noticeable negative Ce-anomaly. In spite of their distinct, negative Ce-anomaly, REE contents from El Cobre are more Ce-rich than those from Damiana and Mina Sur. Compared to the LREE spectrum, the HREE spectrum from Mina Sur and

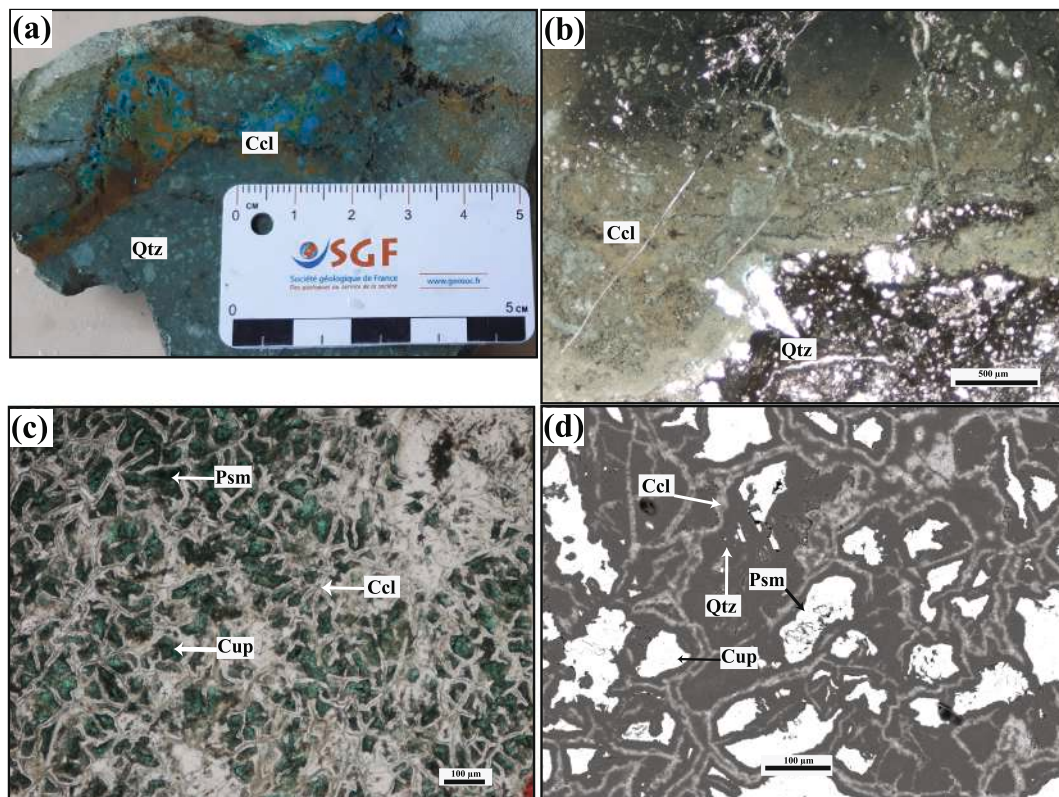


Fig. 9. Sample and thin sections photographs showing the relationships between Gaoua copper minerals. a) Hand-samples of Gaoua showing chrysocolla (Ccl) filling fractures in the Gaoua quartz-andesite host-rock. b) Plane-polarized light photograph showing chrysocolla (Ccl) filling fractures of the host-rock. c) Plane-polarized light and d) SEM photographs showing thin green crystals of cuprite (Cup) and pseudomalachite (Psm) coating on quartz crystals and chrysocolla filling empty spaces and corrodes cuprite.

Damiana shows a slight enrichment while at El Cobre, the HREE displays a slight depleted spectrum (Fig. 4C). The notable exception is the pseudomalachite REE pattern from the Zaldivar deposit (Fig. 14D), which shows a HREE depleted spectra compared to LREE and a weak negative Eu-anomaly. We also note that the LREE contents in pseudomalachite from Zaldivar are systematically an order of magnitude higher than pseudomalachite from Mina Sur and Damiana.

5. Discussion

5.1. Physicochemical controls for the SCM formation

In all the studied *in situ* and exotic SCM, chrysocolla is by far the most abundant copper-bearing mineral and predominates over copper wad, atacamite and pseudomalachite.

In the *in situ* SCM deposits, the mineral parageneses are almost similar with minor copper wad at Zaldivar and Gaby, which precedes abundant chrysocolla in the three deposits, followed by lesser amount of pseudomalachite at Zaldivar. At Gaoua, cuprite is the main second stage mineral followed by pseudomalachite. This paragenetic sequence suggests that all these deposits have undergone the similar processes of *in situ* supergene oxidation. In detail, at Zaldivar and Gaby, textural and mineralogical features show that copper sulfides were replaced by oxidized sulfate-Cu minerals (Figs. 7C and 8C). The oxidation process is accompanied by a lower pH (Anderson, 1982) and a loss of copper (i.e. by downward or lateral migration) as shown by the lower copper contents in sulfate minerals compared to supergene sulfides. The main thermodynamic constraints for abundant chrysocolla precipitation are pH and H_4SiO_4^0 (aq) activity (Crane et al., 2001; Yates et al., 1998). Chrysocolla precipitates when the pH exceed ~ 5 (Yates et al., 1998). Precipitation of chrysocolla is thus commonly explained by changing

conditions from acid ($\text{pH} < 5$) to neutral or low-alkaline ($\text{pH} < 9$) due to the neutralization of the acidic copper solutions during fluid-rock interaction (Newberg, 1967). It also means that most of the minerals that contributes to lowers the pH (i.e. pyrite and chalcopryrite) are leached or do not have the capacity to increase the pH. As suggested by Crane et al. (2001), when H_4SiO_4^0 (aq) is the dominant species in the copper solution, chrysocolla will precipitate at a $\text{pH} \sim 7$. Inversely, when H_2PO_4 (aq) is the dominant species in the copper solutions, pseudomalachite will precipitate. This can explain the precipitation of pseudomalachite at Zaldivar and Gaoua. Generally, cuprite crystallizes as replacement of the primary sulfides (Schwartz, 1934) and is rapidly oxidized to hydrate the copper phases. In Fig. 9D, chrysocolla seems to replace cuprite which confirms the assumption of Schwartz (1934).

In the exotic SCM (i.e. Mina Sur, Damiana, El Cobre), the same paragenetic sequence is clearly observed: small amount of copper wad, followed by abundant precipitation of chrysocolla and pseudomalachite. At Mina Sur atacamite appears as overgrowths on chrysocolla. At Damiana, apatite growth is coeval to the first phase of chrysocolla. At Damiana and El Cobre, pseudomalachite and microcrystalline quartz are linked to the second crystallization stage event. Except for Mina Sur characterized by the presence of reworked angular clasts of black chrysocolla linked to mechanical transportation or *in situ* breaking, all three deposits show mineral textures resulting from the deposition of copper transported in solution from a source (i.e. porphyry copper deposits) to a sink (i.e. the adjacent basins). This requires a progressive neutralization of the mineralizing fluids originating from the upstream oxidizing ore from porphyry copper deposits (Münchmeyer, 1996; Sil-litoe, 2005). According to Newberg (1967) and Fernández-Mort et al. (2018), chrysocolla can precipitate as soon as the pH reaches value between ~ 5 and 9 with an optimum value of ~ 7 . Chrysocolla is formed by the interaction between a copper-rich fluid and SiO_2 (Yates et al.,

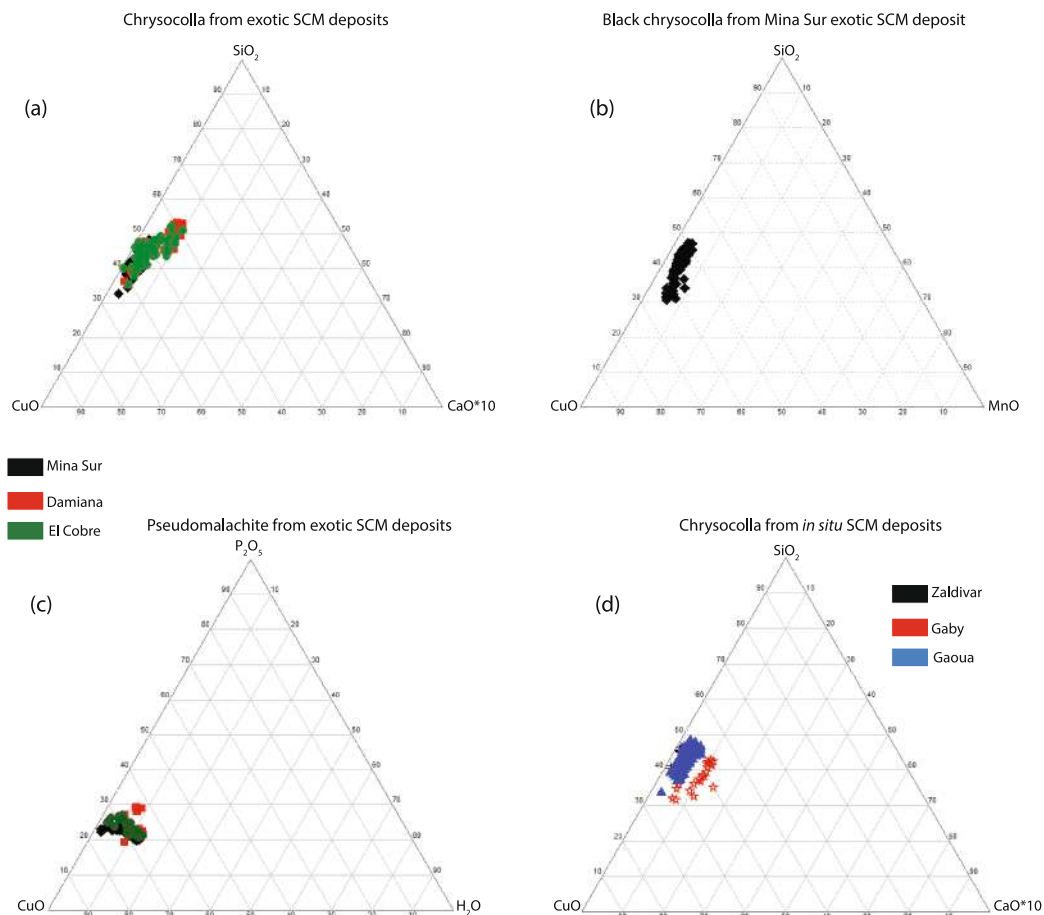


Fig. 10. Representative diagrams of oxidized supergene copper mineralization chemical analyses showing in Triplot diagrams. a) Chrysocolla chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM deposits. b) black chrysocolla chemical analyses from Mina Sur exotic SCM deposit. c) Pseudomalachite chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM deposits. d) Chrysocolla chemical analyses from Zaldivar, Gaby and Gaoua *in situ* SCM deposits.

1998). Copper comes from the porphyry while SiO_2 can come from either the porphyry host rocks or from the gravels present in the basins (e.g. altered feldspars). Finally, the good porosity and permeability of the host gravels will favor the precipitation of chrysocolla.

The paragenetic relationship between chrysocolla and pseudomalachite records pH variation. Fig. 7 from Crane et al. (2001) and Fig. 10 from Fernández-Mort et al. (2018) have shown that a slight variation of the pH in copper-rich solutions can lead to the saturation of either chrysocolla or pseudomalachite together with the H_4SiO_4^0 (aq) activity. This could explain the alternation of chrysocolla and pseudomalachite observed at Mina Sur and the presence of second stage pseudomalachite at Damiana and El Cobre. The fact that, in both *in situ* or exotic SCM, pseudomalachite has been found as thin bands or as thin coatings around chrysocolla, implies that the chemistry of copper-rich solutions from the parental porphyry is not constant but has changed according to the pH variation and the H_4SiO_4^0 (aq) and H_2PO_4^- (aq) ions activity.

At Damiana and El Cobre, the last mineral to precipitate was the microcrystalline quartz. Bustillo (2010) has shown that microcrystalline quartz is stable at $\text{pH} < 9$ whereas at $\text{pH} > 9$, calcite is broadly stable. At pH between 5 and 9, chrysocolla and pseudomalachite tend to co-precipitate. When the mineralizing fluids is depleted in copper, microcrystalline quartz can precipitate (Dold, 2006). The meaning of microcrystalline quartz precipitation can be discussed in terms of a silicification process (Bustillo, 2010), favored by the silica content, temperature, host-rock permeability and pH. Highly silica oversaturated solutions will lead to poorly-ordered silica phases (e.g. opal and amorphous silica) while slightly saturated solutions conduct to more ordered forms (i.e. quartz and chalcedony). This transition may reflect a

dilution of the silicification process as shown by Thiry et al. (2006) and highlighted by Fernández-Mort et al. (2018) at Tesoro Central exotic copper deposit. Indeed, the transition from chrysocolla to microcrystalline quartz, observed in our samples, could be a proof of a silicification process.

The fact that no copper carbonates were observed in both type of deposits could be explained by either the combination of high H_4SiO_4^0 (aq) activity and a pH maximum value of ~ 9 for the copper-rich solutions or by the fact that the fluid was too depleted in copper after chrysocolla and pseudomalachite formation to promote copper carbonates precipitation.

Ultimately, when the climate become more arid (or hyperarid), atacamite, a copper salt highly soluble in fresh water, started to crystallize. This is well exemplified by the atacamite needles overgrowing pseudomalachite at Mina Sur (Fig. 5D) linked to salt-rich water circulation in the hyperarid conditions of the Atacama Desert (Reich et al., 2008). The fact that atacamite was not found at Gaoua can be explained either by the absence of saline fluids which could have promoted the formation of atacamite or salt minerals (e.g. gypsum, anhydrite), or by their late destabilization in the context of modern semi-arid climatic conditions (the West African Craton never experienced a hyperarid climate; Séranne, 1999).

As observed in most of the deposits, chrysocolla and copper wad show concentric banding texture which suggests chemical variations of the mineralizing fluids as already mentioned by Nelson et al. (2007) and Campos et al. (2015). The banding textures observed within chrysocolla have also been explained by Nelson et al. (2007) as the result of biogenic processes, suggesting bacterial involvement in the formation of *in situ* (i.

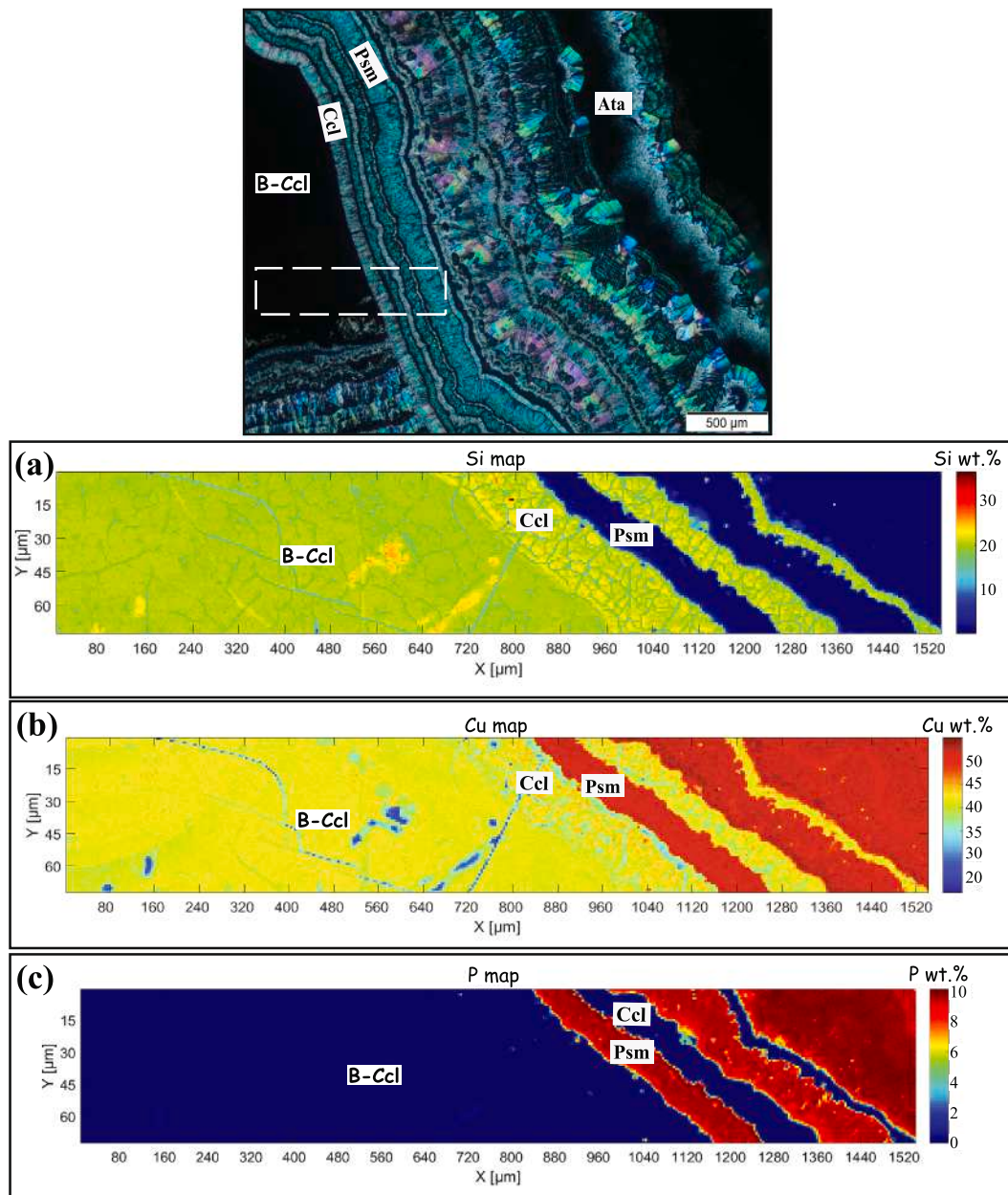


Fig. 11. EPMA chemical characterization of supergene copper minerals from Mina Sur exotic SCM deposit. a) Si map b) Cu map and c) P map at the transition between black chrysocolla (B-Ccl), chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the homogeneity/heterogeneity distribution of silicon, copper and phosphorus. Dotted square represents the area analyzed.

e. at Gaby) and exotic (i.e. at Mina Sur, Damiana and El Cobre) SCM.

5.2. REE concentration in supergene copper minerals

Beside the presence of oxidized copper rich minerals such as silicates, phosphates and sulfates, the existence of oxidizing conditions in the studied localities is supported by the geochemical characterization of the supergene copper minerals (chrysocolla and pseudomalachite) where REE spectra (Fig. 14) are characterized by Ce-anomalies. As shown by Goldschmidt (1937) and Braun et al. (1990), Ce is the only LREE to present two oxidation states (Ce^{3+} and Ce^{4+}) in a low-T environment. This makes Ce highly sensitive to redox processes. In fact, the oxidation state of Ce is mainly controlled by the pH. At low pH, water could reduce Ce^{4+} to Ce^{3+} whereas if the pH value increases, Ce^{3+} is oxidized to Ce^{4+} (Bouchaud et al., 2012). Bouchaud et al. (2012) have also shown, by experimental studies, that Ce^{3+} and Ce^{4+} are soluble in

meteoric water at neutral to alkaline pH values. Additionally, Estrade et al. (2019) and references therein, have shown that the precipitation of Ce, either as Ce^{4+} or Ce^{3+} , within supergene environments, is linked to the depth of the supergene column. In the upper part of the column, within more oxidizing and higher pH, Ce^{4+} precipitates in Ce-rich minerals such as cerianite (CeO_2) or associated with Mn- and Fe- oxyhydroxides. Consequently, the supergene copper minerals will display negative Ce-anomaly due to the Ce^{4+} consumption by cerianite or Mn-Fe oxyhydroxides. This is the case for chrysocolla and pseudomalachite presented in this study who recorded negative Ce-anomaly, except for chrysocolla from Zaldivar. Conversely, in the lower part of the supergene column, under low pH and reduced conditions, Ce^{3+} predominates over Ce^{4+} and no Ce-rich minerals such as cerianite or Mn-Fe oxyhydroxides can precipitate. Therefore, Ce will be available in the environment and captured by Cu-rich supergene minerals that will consequently display positive Ce-anomaly as seen for example for

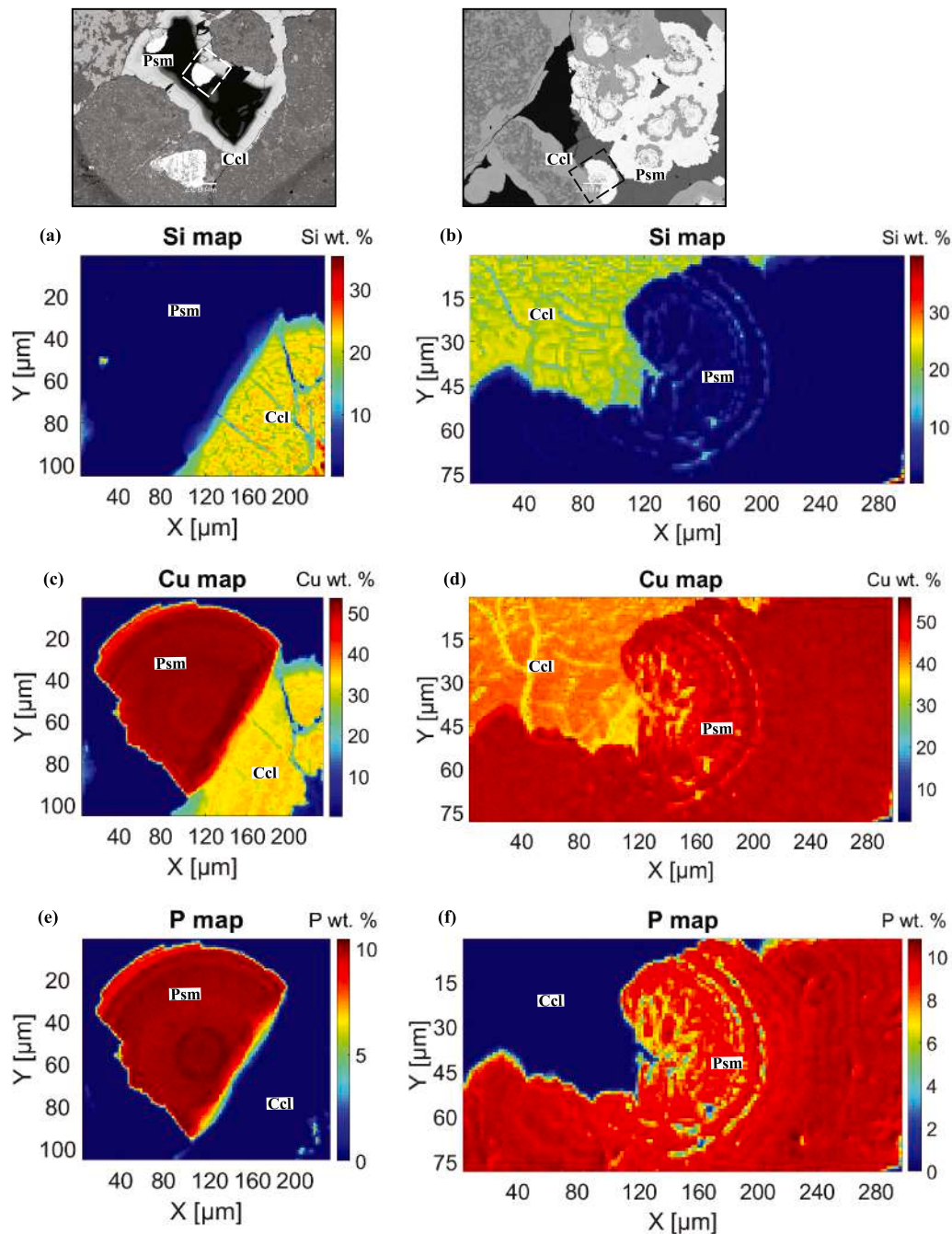


Fig. 12. EPMA chemical characterization of supergene copper minerals from a, c, e) Damiana and b, d, f) El Cobre exotic SCM deposits. a, b) Si map c, d) Cu map and e, f) P map at the transition between chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analyzed.

chrysocolla at Zaldivar. Similarly, [Decrée et al. \(2015\)](#) have shown that REE spectrum in heterogenite (a supergene cobalt mineral, CoOOH) can display negative Ce-anomaly when this mineral co-precipitates with Mn- and Fe-oxides in the upper part of the oxidation profile and positive Ce-anomaly when heterogenite forms in the deeper part of the oxidation profile. The negative Ce-anomalies in exotic copper deposits will further support continuous oxidizing conditions. By contrast, the REE patterns from *in situ* supergene copper minerals (i.e. chrysocolla and pseudomalachite), which show both positive and negative Ce-anomalies, might reflect changes in the redox conditions during the leaching process, above the porphyry, both in time (reducing to oxidizing conditions) and space, i.e. from oxidizing conditions at the top (with Ce^{4+} predominates) toward reducing conditions at depth (with Ce^{3+} predominates).

If we focus on the REE concentration processes for both *in situ* and exotic deposits, the REE distribution within chrysocolla and pseudomalachite are heterogeneous. Pseudomalachite from El Cobre and Zaldivar contains ten times more REE than those from the other deposits. Furthermore, REE patterns of chrysocolla are contrasted, as the REE contents in Damiana are ten times higher compared to those from Mina Sur, while the REE contents of Zaldivar are ten times lower than those from Gaby and Gaoua. Indeed, in supergene environments, the REE-bearing minerals control the budget and the distribution of the REE. The weathering of the primary REE-bearing minerals (i.e. zircon, monazite and xenotime) will induce either the redistribution of the REE within the newly formed supergene copper minerals (e.g. chrysocolla and pseudomalachite) or the consumption of the REE by secondary REE-

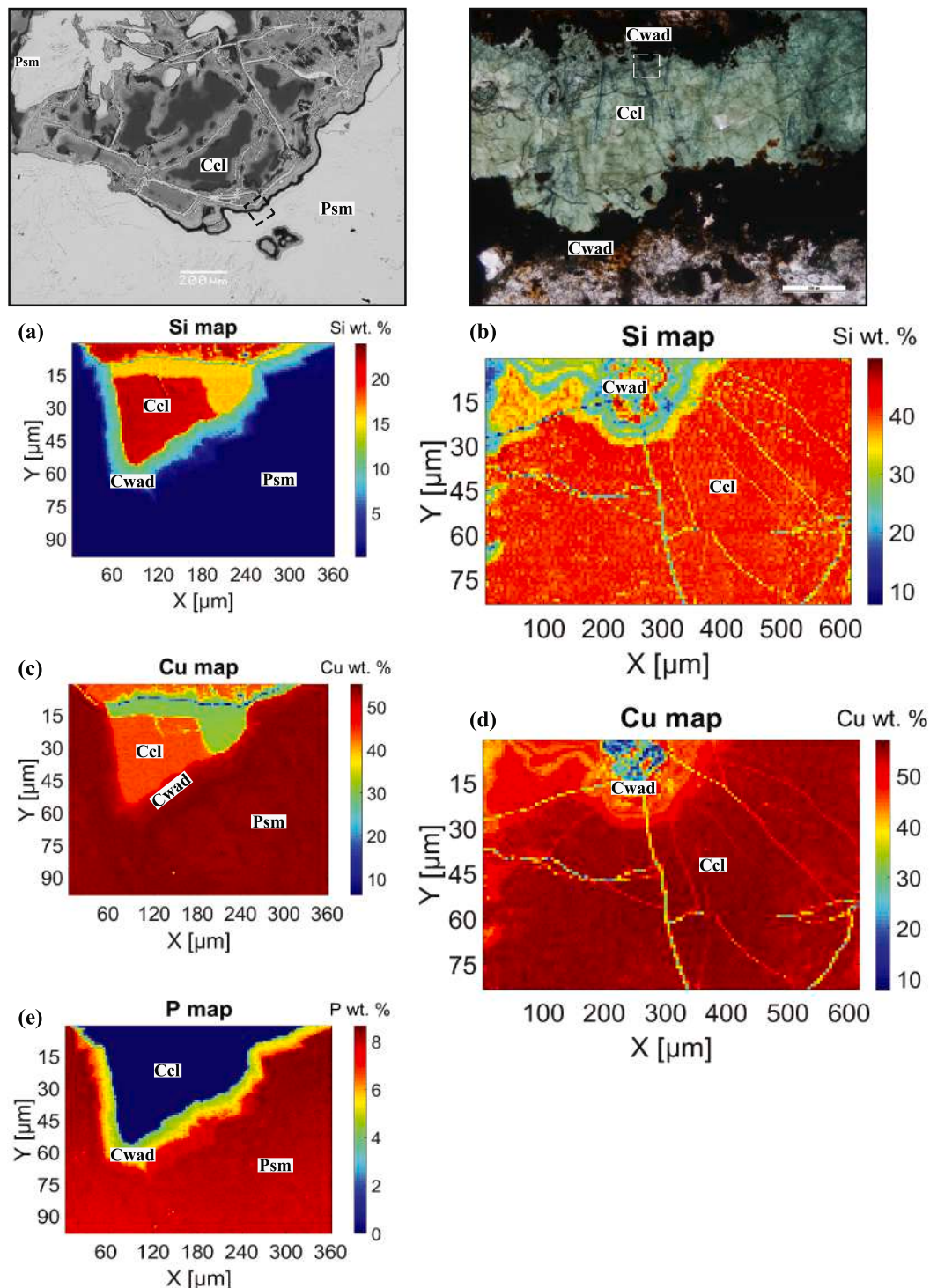


Fig. 13. EPMA chemical characterization of supergene copper minerals from Zaldivar and Gaby *in situ* SCM deposit. a, b) Si c, d) Cu and e) P maps at the transition between chrysocolla (Ccl), copper wad (Cwad) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analyzed.

bearing minerals (i.e. allanite, bastnesite, rhabdophane; Braun et al., 2018). For instance, the absence of secondary REE-bearing minerals at El Cobre and Zaldivar could explain the high REE concentrations found in pseudomalachite from both deposits whereas possible precipitation of apatite and rhabdophane (i.e. two secondary phosphate REE-bearing minerals) in the other deposits (i.e. at Mina Sur and Damiana) could explain the low REE contents in pseudomalachite. Similarly, the low REE content in chrysocolla at Mina Sur and Zaldivar (Fig. 14A, B) could

be explained by the precipitation of secondary REE-bearing silicates minerals (e.g. allanite, bastnesite) that trapped the REE.

5.3. Necessary conditions for the genesis and preservation of oxidized SCM

In the Atacama Desert of northern Chile and in southwestern Burkina Faso, tectonics (i.e. Incaic orogeny in Northern Chili and Eburnean

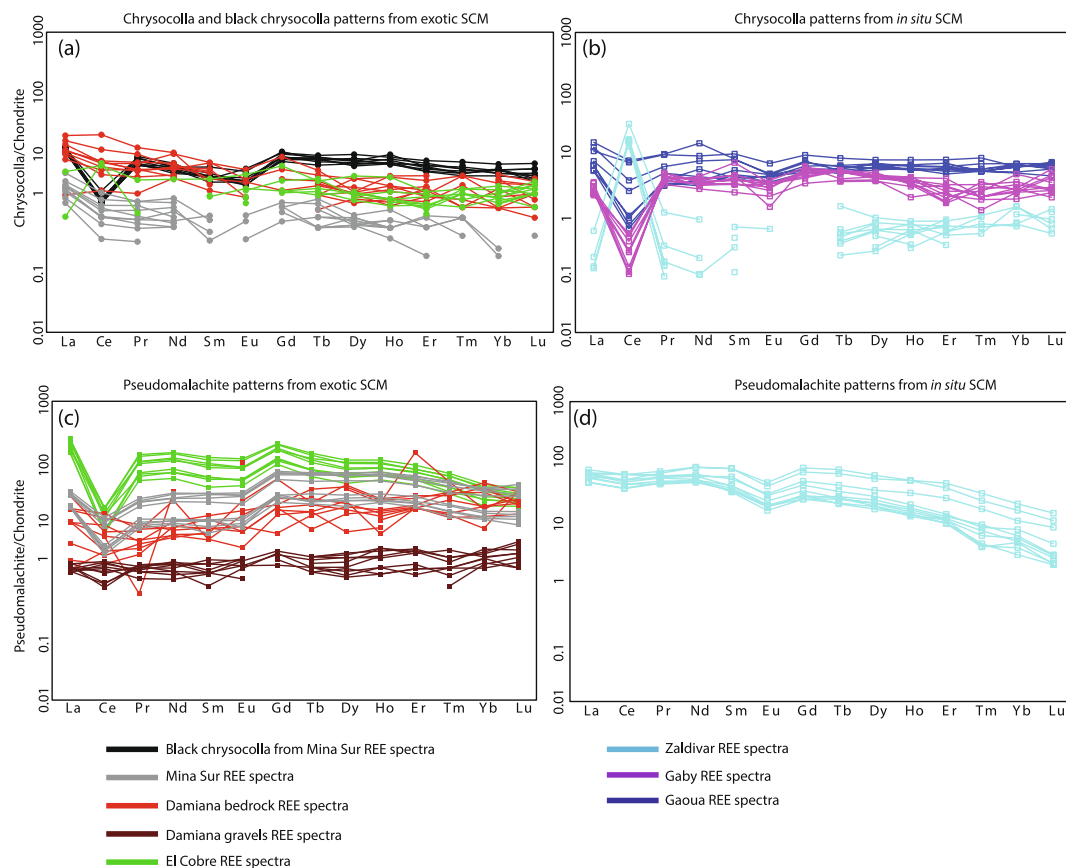


Fig. 14. Chondrite normalized REE patterns for oxidized supergene copper minerals. a, b) REE patterns of chrysocolla and black chrysocolla from exotic and *in situ* SCM deposits. c, d) REE patterns of pseudomalachite from exotic and *in situ* SCM deposits. Chondrite normalizing values are taken from McDonough and Sun (1995).

orogeny in Burkina Faso) and climatic (i.e. semi-arid to arid climate) settings were combined to favor supergene alteration of porphyries and the formation of thick *in situ* supergene copper orebodies (Sillitoe, 2005; Sillitoe and McKee, 1996) and/or exotic-Cu deposits (Fernández-Mort et al., 2018; Hartley and Rice, 2005; Münchmeyer, 1996; Riquelme et al., 2017; Sillitoe, 2005). To produce an oxidized supergene copper mineralization, three conditions are necessary. First, tectonic uplift will bring the primary porphyry stock and hypogene sulfides close to the earth surface where oxidizing conditions, controlled by the level of water table, prevail. Second, under favorable climatic conditions, the oxidation of sulfides will produce acidic solutions which will transport copper down and laterally, in the subjacent area, to form an oxidized copper ores when copper solution reach saturation (Fernández-Mort et al., 2018; Reich and Vasconcelos, 2015). Finally, once the supergene column is formed, favorable climatic conditions as well as moderate erosion rate can favor SCM preservation. The fact that, although both areas have experienced different tectonic styles, the supergene copper minerals from northern Chile and SW Burkina Faso are identical and share the same chemical compositions implies that they both underwent similar climatic evolutions, i.e. from semi-arid to arid, during the mineralization processes. However, if Northern Chile has evolved towards a hyperarid climate for the past ~ 10 m.y., responsible for the formation of atacamite, the SW Burkina Faso area has only experienced a semi-arid climate since the Eocene (Monsels, 2016). According to Hartley and Rice (2005), who published a compilation of supergene copper deposits ages in the Atacama Desert, the formation of *in situ* SCM took place between 36 Ma and 6 Ma. More recently, Riquelme et al., (2017) and Kahou et al., (2020) have published ages between ca. 25–12 Ma and ca. 19 Ma for the formation of the Centinela and Mina Sur exotic copper deposits respectively, i.e. ages that are within the range found for the *in situ* SCM. As stated by Sillitoe (2005) and Sanchez et al. (2018), in

Chile, the processes necessary for the formation of well-developed oxidized SCM profile can take anything from a million to ten millions of years and ceased at the onset of hyperaridity. In SW Burkina Faso, the age of the SCM deposit is unknown but the phases responsible for the exhumation of the porphyry towards oxidizing conditions were contemporaneous with lateritization/bauxitisation processes, i.e. between 59 Ma and 3 Ma (Beauvais et al., 2008; Beauvais and Chardon, 2013). These exhumation phases were controlled by evolving weathering conditions and took place at rates lower than 20 m/m.y. (Beauvais and Chardon, 2013). The comparison between Chilean and African SCM suggest that the preservation of the supergene deposits is due to a favorable combination of slow erosion rates and aridity.

Another necessary factor for the genesis of oxidized SCM can be related to evaporation process. In the southern part of the Atacama Desert, a stable isotope study by Bissig and Riquelme (2010) has shown that meteoric waters were affected by high evaporation rates to favor the deposition of supergene alunite. In the same manner, Fernández-Mort et al. (2018) also highlighted that evapoconcentration was the main parameter to form the exotic SCM of Tesoro Central. Although no isotope studies have been carried out in this study, this evaporation process can be involved in the formation of both *in situ* and exotic SCM deposits from Chile but also in the *in situ* SCM from Burkina Faso.

5.4. Oxidized SCM characterization: Key for an exploration success

Oxidized SCM are the result of supergene alteration of hypogene sulfides, namely pyrite and chalcopyrite from any sulfide-rich deposit. This supergene alteration produces a vertical zonation consisting on a Fe- and Al-rich leached cap depleted in Cu, followed by an oxidized horizon moderately enriched in copper (up to 1 wt% of Cu) and at the bottom a secondary sulfide enrichment zone, highly enriched in copper

(up to 2 wt% of Cu) formed below the paleo water table (Chávez, 2000; Sillitoe, 2005). As stated by Chavez (2000), the distribution of oxidized copper minerals can be used as exploration keys. For example, as shown by our study, the broad distribution of chrysocolla within *in situ* SCM are interpreted as characteristic of a geochemically mature supergene system and the formation of a well-developed *in situ* oxidized SCM. In fact, both types of oxidized SCM represent an important target for numerous exploration and mining companies as their exploitation is environmentally friendly compare to process required for the recovery of copper from sulfide ore. As a result, mineralogical characterization of SCM can provides some useful keys to better improve the metallurgical treatment.

To date, mapping exploration program combined with geophysical and geochemical studies, successfully located oxidized and enriched porphyry copper deposits buried beneath piedmonts gravels. Moreover, geomorphological and sedimentological studies are powerful tools to discover new *in situ* and exotic SCM. As proposed by Riquelme et al. (2017), the exploration of these deposits, buried under gravels and ignimbrite, needs to take into consideration both the landscape evolution and the depositional history of the piedmont gravels. The study of the landscape and the piedmont evolution has also been presented as a major guide for the exploration of supergene ore by Chardon et al. (2018) in Burkina Faso. When the conditions are favorable, supergene alteration of porphyry copper deposit also leads to the deposition of exotic SCM, hosted within piedmont gravels or underlying bedrock fractures. The presence of exotic copper deposits is indicative of the existence of primary copper porphyry deposits somewhere upstream and can be used as exploration tool. Although in some cases, the source of these deposits are known (e.g. Chuquicamata porphyry for Mina Sur and Salvador porphyry for Damiana, see Munchmeyer, 1996), the sources of some exotic-Cu deposits remain unknown (e.g. Tesoro and Lagarto exotic-Cu deposits; Munchmeyer, 1996; Sillitoe, 2005). Therefore, the mineralogical and geochemical characterization of the supergene copper minerals should be implemented during exploration strategies. For instance, the predominance of chrysocolla over copper wad in an exotic-Cu deposit is indicative of a lateral migration of copper-rich solutions within a radius of 2 to 6 km around the primary porphyry copper deposit. When combined with mass-balance calculation model and geomorphology, mineralogical studies can assess the geochemical maturity of the oxidized ore of the porphyry copper deposit and the directions followed by the copper solutions from the primary copper deposits to the sink (Alpers and Brimhall, 1989; Mote et al., 2001b). Consequently, an integrated study involving geomorphology, sedimentology and geochronological together with a mineralogical and geochemical characterization of the oxidized SCM must be taken into account for enhanced exploration success.

6. Conclusions

Supergene copper mineralization from three exotic and two *in situ* Cu-deposits from the Atacama Desert in Northern Chile and the Gaoua *in situ* Cu-Au district in Burkina Faso have been studied in details. Mineralogical and chemical characterization of these SCM provide new insights on the genesis of these deposits. Chrysocolla, which precipitates after copper wad, is the main Cu-bearing minerals and shows similar textures and chemical compositions in both *in situ* and exotic SCM. Precipitation of chrysocolla reflects the progressive evolution of the mineralizing fluids from acidic (pH < 5) to neutral or low-alkaline (pH < 9) conditions during fluid-rock interaction. Chrysocolla is then followed by the crystallization of pseudomalachite in exotic deposits due to changes of both pH and H_2PO_4 activity of the Cu-bearings fluids (i.e.). Geochemical analyses emphasize the strong oxidizing conditions required for the formation of oxidized SCM and show that REE distribution and Ce-anomaly are linked to the pH evolution, the depth of the supergene column and the presence of primary and secondary REE-bearing minerals. The fact that almost the same mineralogy and geochemical patterns are observed on six different deposits, on different

location and geodynamic context, point out the fact that the processes involve in the formation of these deposits are very similar, i.e. progressive neutralization of the acidic copper solutions that lead to chrysocolla precipitation at neutral pH, high H_2PO_4 (aq) activity together with low $H_4SiO_4^0$ (aq) activity that permit pseudomalachite formation, and silicification process that lead to the late crystallization of microcrystalline quartz.

The role of regional and local controls on the formation and preservation of supergene mineralization is now well-understood and requires a subtle balance between tectonics, climate and geomorphology. The formation of such deposits requires several steps with first the exhumation and weathering of the primary porphyry deposit to ensure surface oxidizing processes and a preservation favored by an environment characterized by moderate erosion and rain fall to prevent mechanical abrasion and leaching of the newly formed deposits and finally, a possible key role played by evaporation processes. This equilibrium has been achieved in both Northern Chile and SW Burkina Faso where similar mineralization processes have been involved to form SCM.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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CHAPITRE IV :

Apport des isotopes du cuivre dans la compréhension de l'altération supergène des porphyres cuprifères

Dans le chapitre III, nous discutons de la genèse des minéralisations cuprifères supergènes (MCS) du désert d'Atacama à la lumière de la caractérisation texturale, chimique et géochimique. Cette caractérisation s'est heurtée cependant à l'absence de données sur les fluides minéralisateurs. L'absence d'inclusions fluides et l'incapacité d'obtenir des données quantitatives sur les isotopes de l'oxygène dans les minéraux étudiés (i.e. la chrysocolle et la pseudomalachite) nous a poussé à explorer la voie des isotopes du cuivre pour contraindre le rôle des fluides et des processus d'oxydation-réduction dans la genèse des MCS. De plus, la signature isotopique du cuivre dans les minéraux supergènes renseigne sur le degré d'altération supergène et constitue de fait un métallotecte (Mathur et al., 2015, 2009).

Dans le désert d'Atacama, mais aussi dans d'autres districts métallogéniques, de nombreuses études se sont focalisées sur la caractérisation isotopique de la colonne supergène *in situ*. Par contre, aucunes données n'existent sur la minéralisation exotique de cuivre. La caractérisation isotopique de cette dernière pourrait cependant nous renseigner sur la nature des fluides ayant permis leur formation, i.e. fluides météoriques ayant lessivé tardivement la colonne supergène *in situ* et migré en aval pour former le dépôt exotique ($0 < \delta^{65}\text{Cu} < 2 \text{ ‰}$; Vance et al., 2008) et/ou des fluides oxydants ayant lessivé le cuivre au cours du principal processus d'altération supergène ($0 < \delta^{65}\text{Cu} < 10 \text{ ‰}$; Mathur et al., 2009).

Dans la section IV.1, nous présentons, sous la forme d'un article en préparation, les résultats de la caractérisation isotopique de trois minéralisations cuprifères exotiques du district minier de l'Atacama. L'objectif est de comprendre comment les processus d'oxydation-réduction affectent la genèse des dépôts de cuivre et obtenir ainsi un set complet de données sur le fractionnement isotopique du cuivre depuis la colonne supergène *in situ* jusqu'au dépôt exotique en aval.

Dans la section IV.2, une discussion complémentaire présentera des données sur les isotopes du cuivre de la chrysocolle des mines de Zaldivar (district minier d'Escondida, désert d'Atacama chilien) et de Gaoua (district Cu-Au de Gaoua, sud-ouest du Burkina Faso). Les contextes géologiques de ces deux districts miniers ont été présentés dans le chapitre III de ce manuscrit. L'objectif étant de comprendre si des contextes géologiques différents (climat, vitesse d'exhumation, durée de l'altération supergène, etc.) pourraient influencer sur le degré de fractionnement des isotopes du cuivre. Toujours dans

cette section, une attention est portée sur les résultats analytiques et la valeur du standard BHVO-2 obtenue, anormalement élevée pour un basalte.

IV.1 Understanding reduction-oxidation processes in supergene exotic copper deposits from Atacama Desert, northern Chile: what Cu isotope can tell us ?

Ce chapitre est présenté sous la forme d'un article en préparation pour une soumission prochaine à une revue scientifique. Les annexes citées sont disponibles dans la section annexe du manuscrit.

Understanding reduction-oxidation processes in supergene exotic copper deposits from Atacama Desert, northern Chile: what Cu isotope can tell us?

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Abstract

Reduction-oxidation processes that lead to exotic copper deposits can be better understood thanks to the natural copper isotope fractionation which occur during supergene alteration of porphyry copper deposits. Here, we present copper isotope data obtained by MC-ICP-MS on chrysocolla and pseudomalachite from three exotic copper deposits from Atacama Desert, northern Chile. Chrysocolla and pseudomalachite display positive $\delta^{65}\text{Cu}$ values ranging between 2.46 ‰ to 6.85 ‰ and are in agreement with $\delta^{65}\text{Cu}$ values reported for newly-formed oxidized copper minerals and secondary sulfides from supergene alteration of porphyry copper deposits from Atacama Desert. Conversely, our data yield higher $\delta^{65}\text{Cu}$ values than those reported for iron oxides from the leached cap ($< -0\text{‰}$) and the hypogene protore ($-1\text{‰} < \delta^{65}\text{Cu} < +1\text{‰}$). Our findings suggest that the same mineralizing fluids, that comes from the leaching of the unroofed protore during supergene alteration, has led to the formation of the ^{65}Cu -rich oxidized area, the secondary sulfides enrichment zone and, laterally, the exotic copper mineralization. The heavier ^{65}Cu values ($+6.85\text{‰}$) found at El Cobre exotic copper deposit, located at 4000 m a.s.l, suggest a multiple and intense redox reworking of copper, enhanced by the long-termed tectonic activity in this area which lower the phreatic level and the high altitudes which capture moisture even under the prevailing hyperarid conditions in the Atacama Desert. For exploration purpose, the high ^{65}Cu values found for exotic copper minerals are indicative of significant and multiple

alteration cycles of the primary copper sulfides and constitutes a proxy for an unrecognized mature supergene column of a porphyry copper deposit, hidden upstream.

Keywords: copper isotope fractionation; supergene alteration; porphyry copper deposit; exotic copper deposit; chrysocolla; pseudomalachite

Introduction

Copper stable isotopes are a powerful tool to study supergene processes and recycling of primary copper sulfides within the Earth crust but also in sea-floor. In Atacama Desert of northern Chile, it is now well-established that the supergene alteration of porphyry copper deposits (PCD) took place from ~ 44 Ma down to 14 Ma (Hartley and Rice, 2005) and possibly lasted until 7-6 Ma in the southern part of the Atacama Desert (Bissig and Riquelme, 2010; Marsh et al., 1997). Supergene alteration affects the primary porphyry copper deposits and favors the formation of *in situ* hundred meter-width supergene column and, in a distal part of the porphyry copper, a supergene exotic copper deposit (Fig. 1; Münchmeyer, 1996; Sillitoe, 2005). Exotic copper deposits result from the lateral migration of the parent copper solution from an upstream porphyry copper and constitute a prime exploration target due to the high tonnage and grade (Mortimer et al., 1977; Münchmeyer, 1996; Sillitoe, 2005). Both *in situ* and exotic supergene copper deposits occurred during arid climatic conditions when sufficient meteoric water have percolated through the primary porphyry copper deposits and favored *in situ* supergene alteration of these PCD and the formation of exotic copper deposit. Then, supergene alteration seems to have ceased during climatic dessication of Atacama Desert, the exact timing of which is still a matter of debate (Hartley and Rice, 2005; Marsh et al., 1997; Reich et al., 2009; Sillitoe and McKee, 1996). Exotic copper deposits are mainly composed, in Atacama Desert, of copper silicates (e.g. chrysocolla), followed by minor copper phosphates (e.g. pseudomalachite), copper wad (a copper, iron, manganese and cobalt oxy- and hydroxy-hydrates; term commonly used by miners) and copper salts (e.g. atacamite and paratacamite), formed during arid conditions and preserved under presently hyperarid climate (Chávez, 2000; Münchmeyer, 1996; Newberg, 1967; Sillitoe, 2005).

In the last two decades, many studies have focused on the understanding of Cu isotopic fractionation (^{65}Cu and ^{63}Cu , the two natural stable isotopes of Cu) during supergene alteration of porphyry copper deposits (Braxton and Mathur, 2011; Mathur et al., 2009, 2005; Palacios et al., 2011) and applied to black smokers and sedimentary copper deposits (Asael et al., 2007; Borrok et al., 2008; Maréchal, 1998; Markl et al., 2006; Rouxel et al., 2004). The aim of these previous studies was to identify the copper isotope reservoirs during supergene alteration and the extent of supergene

enrichment zone in the porphyry copper deposit in order to better constrain the cycling of copper during supergene alteration and its potential for exploration purpose. These studies suggest that supergene alteration of porphyry copper deposits leads to the formation of an isotopically light Fe-oxides leached capping, an isotopically heavy supergene chalcocite-rich supergene enrichment zone and a narrow copper isotopic range ($\sim$ near 0‰) for the primary sulfides (Fig. 1).

Except the work of Braxton and Mathur (2011), who studied both supergene *in situ* and proximal-exotic chalcocite, no data have yet been published (to the best of our knowledge) to characterize copper isotopic fractionation during the formation of exotic copper minerals (i.e. chrysocolla, pseudomalachite, etc.) in the Chilean Atacama Desert. Yet, these data are of prime importance to know what is the copper isotopic reservoir of these exotic copper deposits and understand what controls the copper isotopic signature of exotic copper minerals, e.g. the nature and the temperature of the fluids, the lateral transport, the distance from the parental porphyry source, etc.

Maréchal and Sheppard (2002) demonstrated that there is no significant isotope fractionation ($\delta^{65}\text{Cu} < 0.5 \text{ ‰}$) during the formation of exotic copper deposits because only reactions involving a change in copper valence (i.e. sulfide leaching, precipitation of secondary copper sulfides and oxidized minerals) are accompanied by isotope fractionation. $\delta^{65}\text{Cu}$ signature of exotic copper minerals must therefore reflect the signature of the mineralizing fluids or the meteoric fluids that leached the copper deposit later. Meteoric fluids have a light $\delta^{65}\text{Cu}$ signature ($0 < \delta^{65}\text{Cu} < 2 \text{ ‰}$; Vance et al., 2008) while the mineralizing fluids resulting from the leaching of primary sulfides during the oxidation process are enriched in ^{65}Cu ($0 < \delta^{65}\text{Cu} < 10 \text{ ‰}$; Markl et al., 2006; Mathur et al., 2009; Viers et al., 2019).

This study reports, for the first time, the copper stable isotope data of chrysocolla, black chrysocolla and pseudomalachite from three exotic copper deposits from the Atacama Desert of northern Chile, i.e. Mina Sur in the Chuquicamata mining district and Damiana and El Cobre within the Salvador and Potrerillos mining districts, respectively. The main goals of this study are to i) report the isotopic composition of exotic copper minerals and compare it to the previous data obtained on *in situ* supergene copper minerals, ii) identify the isotopic reservoirs of the mineralizing fluids, iii) obtain a complete Cu isotope dataset from the upstream supergene column to the downstream oxidized exotic copper mineralization. The results obtained, when compared with previous published studies, indicate

that the same ^{65}Cu -rich mineralizing fluids at the origin of the upstream ^{65}Cu -rich enrichment zone and oxidized area has migrated laterally to promote exotic copper mineralization. They also militate for a multiple episode of redox recycling copper during supergene alteration, from Eocene-Oligocene boundary until Quaternary times.

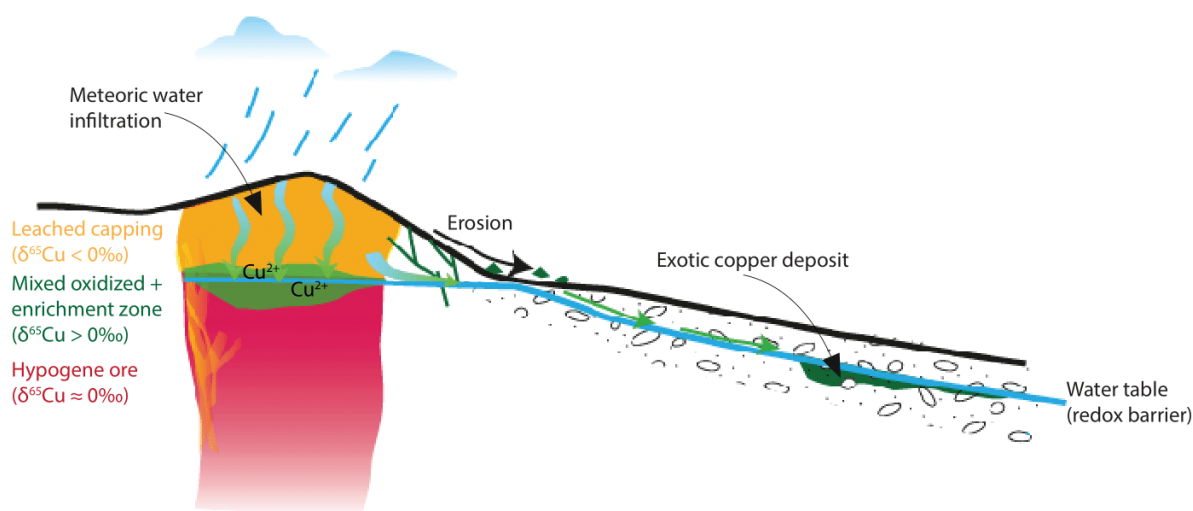


Figure 1: Schematic representation of an in situ supergene column from a porphyry copper deposit showing its typical copper isotopic signatures and its relationship with a downstream exotic copper deposit

Geological setting of the areas sampled

The main supergene deposits are located between $18^{\circ}30'\text{S}$ and 26°S in the Atacama Desert of northern Chile. All the four morpho-tectonic units of Atacama Desert comprise supergene PCD but the most important and economically belt are the 800 km-long late Eocene to early Oligocene belt a.k.a. Domeyko Cordillera (Fig. 2; Sillitoe and Perelló 2005; Mpodozis and Cornejo 2012). The Domeyko Cordillera is made up of several late Carboniferous to Permian volcanic and plutonic basement rocks overlain by Mesozoic and Cenozoic sedimentary sequences (Mpodozis and Cornejo, 2012; Sillitoe and Perelló, 2005). The samples of this study have been collected within the Mina Sur, Damiana and El Cobre exotic copper deposits which results of the lateral migration of copper solutions from Chuquicamata, Salvador and Potrerillos porphyry copper, respectively. The geological features of each deposit and mining district has been extensively described in previous studies (Bissig and Riquelme,

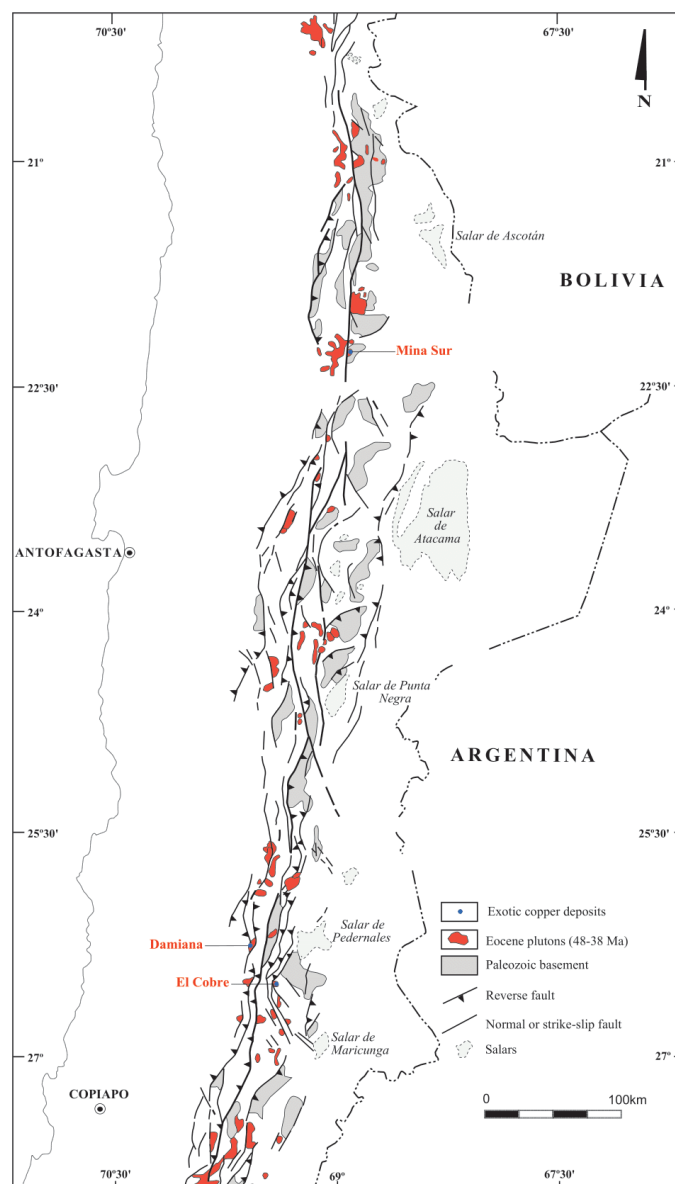
2009; Gustafson et al., 2001; Marsh et al., 1997; Mote et al., 2001; Münchmeyer, 1996; Ossandón et al., 2001; Rivera et al., 2012) and will be summarized in the following.

The basement of the *Mina Sur* exotic copper deposit is made up of Paleozoic metamorphic and granitic rocks covered by Mesozoic andesite to rhyolite volcanic rocks and volcanic-sedimentary sequences (see Fig. 1 from Kahou et al. 2020). Covered all the sequences, the Eocene piedmont gravels host the lenticular orebody of Mina Sur (Kahou et al., 2020; Mortimer et al., 1977; Münchmeyer, 1996; Newberg, 1967).

Within the Salvador mining district, *Damiana* exotic copper deposit lies about ~ 3 km away from the Cerro Indio Muerto (Gustafson et al., 2001; Gustafson and Hunt, 1975; Mote et al., 2001). The Paleozoic plutonic basement is covered by Cretaceous volcanoclastic and andesitic rocks a.k.a. Llanta formation (Rojas and Muller, 1994). The exotic copper orebody is hosted in both Cretaceous bedrock and Miocene pediments gravels which cover the entire area (see Fig. 2 from Mote et al. 2001).

About ~ 35 km further south of the Salvador mining district, the *El Cobre* exotic copper deposit, a small-scale artisanal mined, lies directly in the fractured and brecciated Paleocene andesitic and rhyolitic volcanic rocks within the Potrerillos mining district (Bissig and Riquelme, 2009).

Figure 2: Location of the mining district studied within the Eocene-Oligocene Precordillera belt of the Atacama Desert of Chile



Textural features of the samples collected

Thin and polished sections were prepared at Géosciences Environnement Toulouse (GET, Université de Toulouse, France) and studied under a Nikon Eclipse E100 optical microscope. Qualitative data as well as backscattered electron images were obtained using the JEOL JSM 6360LV scanning electron microscope (SEM) coupled to an energy dispersive spectrometry (EDS) analysis system at the GET laboratory, working at 15 kV and 50 μm .

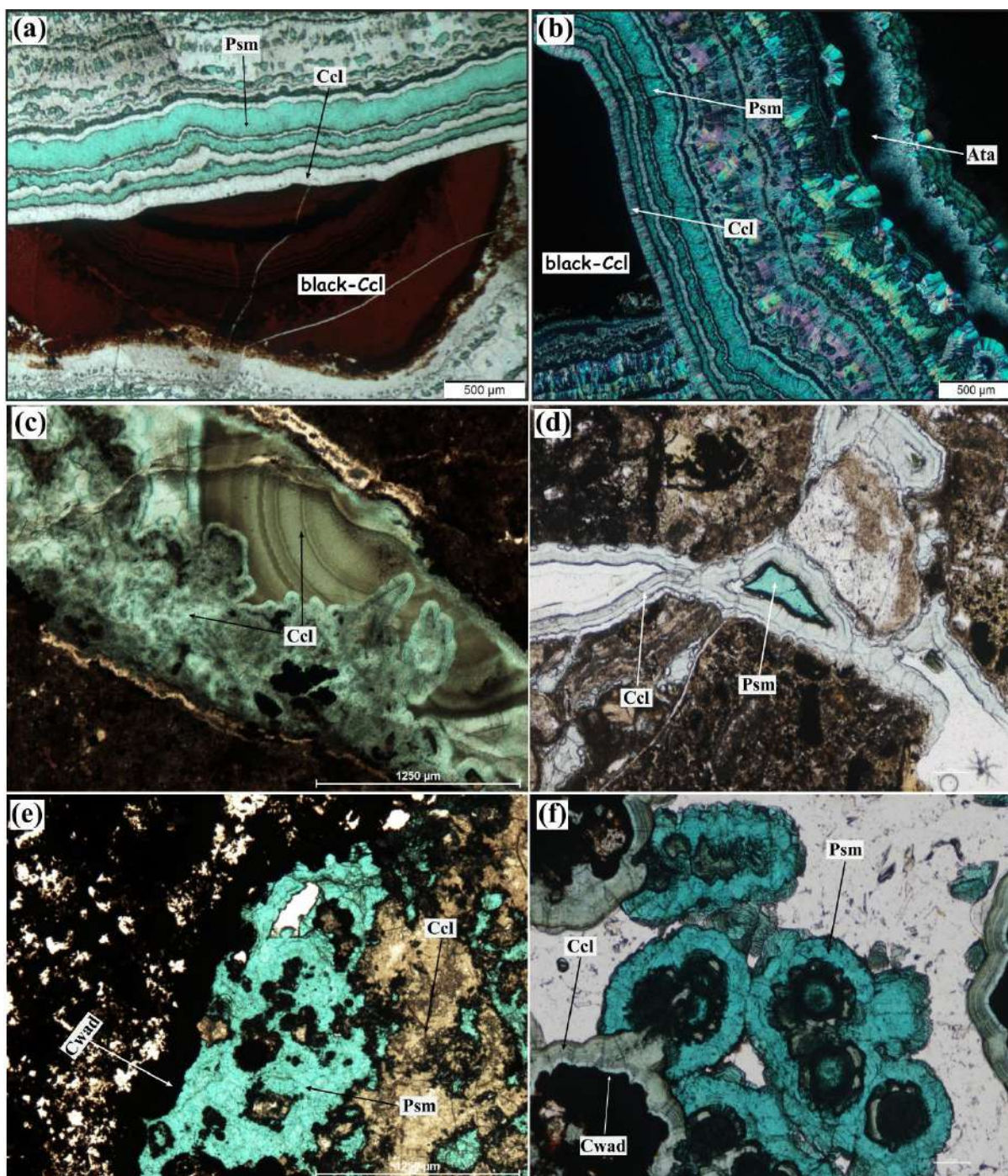
At *Mina Sur*, the copper orebody is mainly composed of chrysocollas, *sensu lato*, including black Mn-rich angular clasts of chrysocolla (*a.k.a* black chrysocolla or copper pitch), and thin-size bands of chrysocolla, *sensu stricto*, turquoise to green color (Fig. 3a), coating black Mn-rich chrysocolla clasts.

Black chrysocolla is also coated by pseudomalachite bands, with a pale-green to dark-green color (Fig. 3a, b). Finally, atacamite appears as thin-size black prismatic crystals overgrowing on chrysocolla and pseudomalachite bands (Fig. 3b).

At *Damiana*, the copper minerals are characterized by abundant chrysocolla and minor pseudomalachite and copper wad. Chrysocolla appears both as filling bedrock fractures and the porosity and empty spaces of the gravels above the bedrock (Fig. 3c, d). Chrysocolla displays a millimetric green-color banding coating the gravels clast and appears as greenish heterogenous masses, filling the bedrock fractures (Fig. 3c, d). Pseudomalachite appears as a late-crystallized phase, filling the empty spaces of the gravels (Fig. 3d).

At *El Cobre*, the copper ore shows chrysocolla as the most abundant Cu-bearing mineral, followed by lesser amount of pseudomalachite and copper wad. Under the microscope, chrysocolla appears as brownish massive material as well as patina filling the fractures of the bedrock (Fig. 3e, f). Pseudomalachite displays concentric spherule texture, filling empty spaces and overgrowing on chrysocolla (Fig. 3f).

Figure 3: Sample and thin sections photographs showing the textural relationships of the exotic copper minerals from the Mina Sur, Damiana and El Cobre deposits. a) Plane-polarized light photograph showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. b) Cross-polarized light showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite needles (Ata) on chrysocolla and pseudomalachite. c) Plane-polarized light showing chrysocolla filling fractures of the andesite bedrock. d) Plane-polarized light showing chrysocolla (Ccl), with a banding mammillary texture, filling porosity of the gravels and pseudomalachite (Psm) filling empty spaces. e) Plane-polarized light photograph showing copper wad (Cwad), chrysocolla (Ccl) and pseudomalachite (Psm) filling fractures of the andesite bedrock. f) Plane-polarized light photograph showing chrysocolla (Ccl), with a banding mammillary texture, coating on copper wad (Cwad) and pseudomalachite (Psm) filling empty spaces



Material and analytical methods

Samples preparation

In all the three exotic copper deposits, only chrysocolla and pseudomalachite have been sampled to copper isotopic analyses purpose. At Mina Sur, one black chrysocolla clast as well as pseudomalachite band have been collected for analyses. At Damiana and El Cobre, only chrysocolla, the most abundant phase, has been collected. All the copper minerals have been collected from hand

specimens using a DREMEL electric rotary tool, separated carefully under a binocular microscope and crushed into powder with an agate mortar at GET laboratory.

Cu purification method

To purify the samples and isolate Cu, we used the modified Borrok et al. (2007) anion-exchange column chromatography protocol. Chrysocollas (i.e. black chrysocolla and chrysocolla) and pseudomalachite were digested in concentrated HNO₃ (15.2 N) and HF (28 N) in a closed beaker on a hot plate during 24H. After evaporation, the samples were reworked in 3 mL of HCl 6N (except BHV-O2 dissolved in HCl-F) and put in a closed beaker on a hot plate at 120°C for 24H. An aliquot of each solution has been taken for Cu separation so that a minimum of 800 ng of Cu was available for analyses (corresponding to a total mass of sample of ca. 0.03 to 0.1 µg for chrysocolla, 0.15 µg for black chrysocolla and 0.3 µg for pseudomalachite), and evaporated to dryness. Copper was purified with AG1-MP1 anion-exchange resin (Biorad) following the elution sequence of Borrok et al. (2007). After conditioning with 3 ml of HCl 9N, samples were loaded in 1 ml of HCL 9N. The matrix was eluted with 4 ml of HCl 9N, then copper was eluted with 5.5 mL of HCl 9N and evaporated to dryness at 80°C. After the elution, the samples were dissolved in HNO₃ 0.09N and doped with a Zn solution (Borrok et al., 2007) so that the final Cu and Zn concentration, ready for isotopic analyses, was 250 ppb for both copper and zinc. The yield of column separation was checked for each sample and was consistently found to be in range 100±10%.

MC-ICP-MS analytical method

All copper stable isotope analyses have been carried out at GET laboratory using a multi-collector (MC)-ICP-MS Neptune plus, Thermo-finnigan. The materials were transported to the MC-ICP-MS with a PFA nebulizer at a flow rate of 75 µL/min and a make-up gas flow (Argon) of 1.071L/min, operated at low resolution. The copper isotopic ratios are reported as a deviation relative to the standard NIST 976 according to the following equation:

$$\delta^{65}\text{Cu} = \left\{ \left[\frac{\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{sample}}}{\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{standard}}} \right] - 1 \right\} * 1000$$

Each analytical session begins with a 1-hour session run on the NIST 976 standard and then follows the sequence outlined below: 1- Blank 2- NIST 976 standard 3- NIST 976 standard 4- Blank 5- NIST 976 standard 6- NIST 976 standard 7- Sample 8- Sample 9- NIST 976 standard 10- Blank 11- NIST 976 standard. Each sample was analyzed three times and the sequence was bracketed with NIST 976 standard. Cu isotopes (^{63}Cu and ^{65}Cu) and Ni isotope (^{62}Ni) as well as Zn isotopes (^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn) were measured simultaneously. The possible isobaric interference between ^{64}Ni and ^{64}Zn was corrected by the measurement of ^{62}Ni signal. To correct the instrumental mass bias, a Zn solution JMC 3-0749-L was added to the samples and the standard using the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio. One external standard, the BHVO-2 glass, was processed throughout the analytical sessions as an unknown sample to control the reproducibility and accuracy of the analyses and yield $\delta^{65}\text{Cu} = 14.80$ (n=3).

Results and discussion

Isotopic composition of exotic copper minerals from the Atacama Desert

The $\delta^{65}\text{Cu}$ data obtained are reported in Table 1. All the exotic copper minerals analyzed have a positive $\delta^{65}\text{Cu}$ values and displays a broad range from 2.42‰ to 6.83‰. At Mina Sur, black chrysocolla and pseudomalachite show $\delta^{65}\text{Cu}$ values average of 2.57‰ and 2.46‰, respectively. At Damiana, chrysocolla from the bedrock fractures and from the gravels show $\delta^{65}\text{Cu}$ isotopic signature of 3.66‰ and 4.09‰, respectively. Chrysocolla from El Cobre show the heaviest $\delta^{65}\text{Cu}$ isotopic signature with average 6.83‰. Three main observations can be extracted from the data set: 1) $\delta^{65}\text{Cu}$ values of the exotic copper minerals exceed zero and are highly fractionated with respect to the primary sulfide minerals, 2) $\delta^{65}\text{Cu}$ values from each single deposit are rather homogenous whatever the mineral, 3) the $\delta^{65}\text{Cu}$ values of chrysocollas between each single deposit are significantly different and range from ca. 2.60‰ at Mina Sur to ca. 4.11‰ at Damiana and to ca. 6.87‰ at El Cobre.

These results are in agreement with previous studies and confirm the $\delta^{65}\text{Cu}$ enrichment between reduced copper sulfide minerals and secondary copper minerals (i.e. chrysocollas and pseudomalachite). The $\delta^{65}\text{Cu}$ results for the primary sulfides from porphyry copper deposits in Chili, southwestern America and Philippines have shown values from -1 ‰ to 1 ‰ (from Chili and southwestern America; Mathur et al., 2009, 2005), from 0.28 ‰ to 0.34 ‰ (from Chili; Palacios et al.,

2011) and from -0.6 ‰ to 1 ‰ (from Philippines; Braxton and Mathur, 2011). The supergene column, which are the products of the pyrite-chalcopyrite weathering, have heterogeneous values between the leached cap at the top, the oxidized ore in the vadose zone and the enrichment zone below the water table (Fig. 4). Despite this heterogeneity, according to the literature (Braxton and Mathur, 2011; Maréchal, 1998; Mathur et al., 2009; Palacios et al., 2011), a clear tendency can be drawn. The leached cap (i.e. iron oxides) exhibits negative $\delta^{65}\text{Cu}$ values despite heterogeneities within this zone. The oxidized ore display, in average, positive $\delta^{65}\text{Cu}$ values even if, a single mineral can display both negative and positive $\delta^{65}\text{Cu}$ values within the same deposit (e.g. chrysocolla at Collahuasi porphyry copper deposit; see Mathur et al., 2009). The enrichment zone (mainly chalcocite), in all the deposit, from different region (Chile, NW America, Philippines) show a positive and broad range of $\delta^{65}\text{Cu}$ values, in agreement with $\delta^{65}\text{Cu}$ of secondary sulfides found in hydrothermal deposits (Graham et al., 2004; Larson et al., 2003; Rouxel et al., 2004).

Chrysocollas and pseudomalachite from this study, both oxidized copper minerals, display positive $\delta^{65}\text{Cu}$ values within the three different exotic copper deposit, although located at different latitude and elevation. The $\delta^{65}\text{Cu}$ values from Mina Sur and Damiana are in the same range than $\delta^{65}\text{Cu}$ values reported in the unpublished thesis of Maréchal (1998) for chrysocolla from Chuquicamata in Chile (3.30 ‰ and 2.46 ‰), slightly higher than those obtained by Palacios et al. (2011) at Spence deposit in Chile (average 1.34 ‰ for chrysocolla) and higher than $\delta^{65}\text{Cu}$ values reported by Mathur et al. (2009) for chrysocolla from the Collahuasi copper district in Chile (from -4.54 ‰ to + 0.79 ‰) and from the Bayugo Cu-Au gold deposit in Philippines (-3.4 ‰ for chrysocolla; Braxton and Mathur, 2011). However, at El Cobre, located at 4000 m a.s.l, the $\delta^{65}\text{Cu}$ value is the heaviest reported in Chile for a silicate copper mineral, suggesting a possible control of the elevation on copper isotope fractionation due to multiple copper recycling caused by moisture capture at high elevation. This data compilation shows that there is a significant fractionation during supergene alteration of the porphyry copper deposit that lead to the formation of three distinct isotopic reservoirs, i.e. a leached capping at the top of the supergene column, an oxidized ore above the phreatic level, and a secondary sulfides enrichment zone below the phreatic level.

Sample	Location	Elevation	Mineral type	$\delta^{65}\text{Cu}$ results (‰)
<i>Mina Sur deposit</i>				
C-Mn 1	samples from the gravels	2500 m	Black chrysocolla	2.60
C-Mn 2	samples from the gravels	2500 m	Black chrysocolla	2.55
C-Mn 3	samples from the gravels	2500 m	Black chrysocolla	2.56
P-CQ 1	samples from the gravels	2500 m	Pseudomalachite	2.48
P-CQ 2	samples from the gravels	2500 m	Pseudomalachite	2.42
P-CQ 3	samples from the gravels	2500 m	Pseudomalachite	2.49
<i>Damiana deposit</i>				
DW9-1	samples from the bedrock fractures	2287 m	chrysocolla	3.68
DW9-2	samples from the bedrock fractures	2287 m	chrysocolla	3.65
DW9-3	samples from the bedrock fractures	2287 m	chrysocolla	3.68
DG18-1	samples from the gravels	2426 m	chrysocolla	4.11
DG18-2	samples from the gravels	2426 m	chrysocolla	4.09
DG18-3	samples from the gravels	2426 m	chrysocolla	4.11
<i>El Cobre deposit</i>				
CO18-1	Samples from the bedrock fractures	3766 m	Chrysocolla	6.87
CO18-2	Samples from the bedrock fractures	3800 m	Chrysocolla	6.84
CO18-3	Samples from the bedrock fractures	3806 m	Chrysocolla	6.83

Table 1: Copper isotope composition results from chrysocolla and pseudomalachite from the exotic copper deposits studied

Models of copper isotopic fractionation in supergene environments

In porphyry copper environments, tectonic uplift leads to the unroofing of the primary copper mineralization (i.e. pyrite-chalcopyrite) and induce the lowering of the phreatic level. Infiltration of meteoric water oxidizes and leaches the copper and transports it downward below the phreatic level, where it precipitates in a reduced form as the secondary sulfides (chalcocite $\pm$ covellite) in the so-called enrichment zone. This “supergene” fluid-rock interaction therefore generates copper isotope fractionation (Ehrlich et al., 2004; Maréchal, 1998; Mathur et al., 2005) due to two levels of oxidation-reduction reaction. Isotopic analyses and laboratory experiments (Ehrlich et al., 2004; Maréchal and Sheppard, 2002; Zhu et al., 2002) have shown that aqueous copper solutions from the leached cap are isotopically heavier than the leached products. Consequently, the precipitation of these copper solutions below the water table, under reduced conditions, will generate a heavy isotopic reservoir, i.e. the chalcocite-rich enrichment zone. At the surface, the remained products, i.e. the leached capping, will be depleted in ^{65}Cu due to the fluid-rock interaction. Hence, the iron-oxides minerals, within the leached cap will display negative $\delta^{65}\text{Cu}$ values as illustrated by previous studies (Braxton and Mathur, 2011; Mathur et al., 2009, 2005). When the enrichment zone is saturated, the mineralizing fluids, enriched in

^{65}Cu , will precipitate the copper above the phreatic level and produce an oxidized copper ore, isotopically heavier than the starting material. Successive leaching events will therefore favor the increase of the ^{65}Cu depletion in the leached cap and the ^{65}Cu enrichment within the enrichment zone and the oxidized ore (Fig. 4).

As it has been shown by Kahou et al. (2020), supergene alteration of porphyry copper deposits and formation of exotic copper mineralization occur simultaneously in the Atacama Desert of northern Chile. It means that during the pyrite-chalcopyrite leaching event, the isotopically-heavier copper solutions migrate downward and also laterally and lead to the precipitation of ^{65}Cu -enriched exotic copper minerals (Fig. 4). This assumption is supported by the study of Shields et al. (1965) who showed that copper isotopic fractionation is related to low-temperature supergene processes when copper is oxidized, transported and re-precipitated.

If we focus in the Chuquicamata porphyry complex, the unpublished thesis of Maréchal (1998) and the work of Mathur et al. (2009) have reported $\delta^{65}\text{Cu}$ values of chalcocite at 2.86‰ (Mathur et al., 2009) while chrysocolla from the oxidized ore displays $\delta^{65}\text{Cu}$ values at 3.30‰ and 2.46‰ (Maréchal, 1998). Both studies display $\delta^{65}\text{Cu}$ values in range of those obtained at Mina Sur exotic copper deposit in this study, i.e. 2.57‰ on black chrysocolla and 2.46‰ on pseudomalachite.

At the El Salvador mining district, the $\delta^{65}\text{Cu}$ values of both secondary chalcocite and Cu-oxides displays 3.37‰ (n=4) and 2.20‰ (n=2), respectively (Mathur et al., 2009). Those values are in agreement with the results obtained at Damiana exotic copper deposit for chrysocolla (average 3.89‰). All the results stated above suggest that lateral migration of copper solutions does not generate sizable copper isotope fractionation and confirms the fact that the primary mineralizing fluids, isotopically ^{65}Cu heavier, are the isotopic reservoir of the exotic copper mineralization.

At the El Cobre exotic copper deposit, within the Potrerillos mining district, the absence of $\delta^{65}\text{Cu}$ data prevented us to characterize the isotopic fractionation of the supergene column from the parental porphyry. Consequently, it is difficult to obtain a complete overview of the parental porphyry source and the exotic copper sink. However, when comparing data obtained on chrysocolla from all the deposits of the present study, we can observe a difference of $\sim 3.18\text{‰}$ between the $\delta^{65}\text{Cu}$ values of chrysocolla from Mina Sur and Damiana compared to El Cobre. If the $\delta^{65}\text{Cu}$ values of black chrysocolla

from Mina Sur as well as chrysocolla from Damiana are in agreement with previous studies of copper isotopic composition of chrysocolla from porphyry copper deposits in Chile and elsewhere (Maréchal, 1998; Markl et al., 2006; Mathur et al., 2009; Palacios et al., 2011) and define a narrow range of values (2.46-3.89‰), the $\delta^{65}\text{Cu}$ values of chrysocolla from El Cobre is relatively high (6.85‰, this study). This high $\delta^{65}\text{Cu}$ value may highlight the presence of an isotopically heavy primary Cu reservoir or a local geological control modifying the fractionation processes that controls the isotopic composition of the mineralizing fluids, e.g. the duration of the supergene alteration and/or location of El Cobre at high elevation. Due to the lack of $\delta^{65}\text{Cu}$ data from the Potrerillos porphyry copper source, the first hypothesis cannot be discussed at the moment. The second hypothesis is sustained by the fact that the hyperarid climatic conditions have been established later in the Potrerillos mining district and all the southern part of the Chilean Atacama Desert than in other areas (Bissig and Riquelme, 2009; Marsh et al., 1997; Mortimer, 1973). Bissig and Riquelme (2010, 2009) have shown that supergene alteration was thus active in this area from Oligocene to Pleistocene due to multiple uplift episodes which have lowered the phreatic level and increased the elevation of this area at 4000 m a.s.l, sufficiently to capture orographic moisture. Increasing the duration and intensity of the leaching process would then have enriched the fluid in ^{65}Cu (Braxton and Mathur, 2011; Mathur et al., 2005). Therefore, the multiple leaching event, since Oligocene until Pleistocene times, will favor multiple recycling of copper due to the reworking of initial chrysocolla precipitation. This multiple reworking will generate a ^{65}Cu -enriched fluid which might explain the high $\delta^{65}\text{Cu}$ values of chrysocolla obtained at El Cobre.

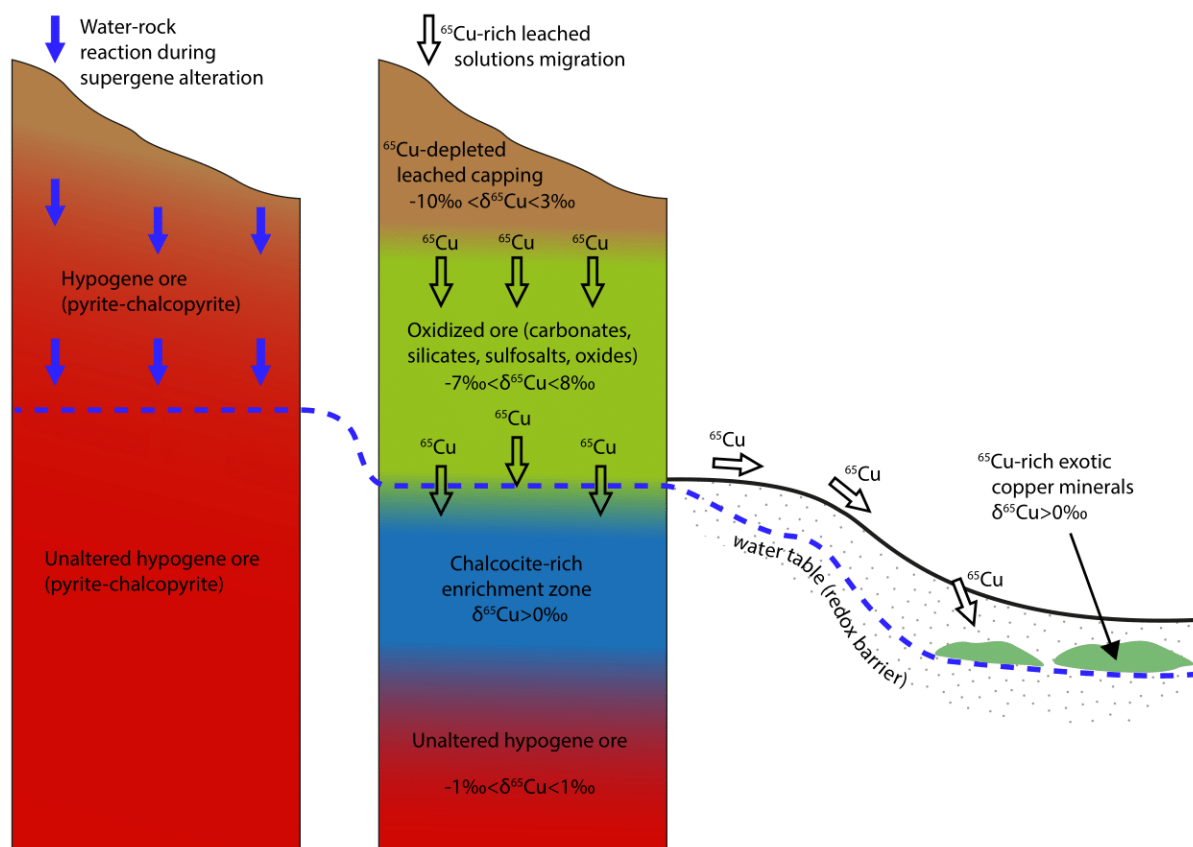


Figure 4: Schematic model displaying the development of three copper isotope reservoirs during the in situ supergene alteration of a porphyry copper deposit and the contemporaneous migration of the heavy copper solutions to create an isotopically enriched exotic copper deposit. During supergene alteration, the leached cap is progressively depleted in heavy ^{65}Cu . The ^{65}Cu -rich aqueous solutions migrate downward and generate the chalcocite-rich enrichment zone and the oxidized area, both ^{65}Cu -rich realm. The hypogene ore keeps the $\delta^{65}\text{Cu}$ values near $\sim 0\text{‰}$. The values are reported from this study and from the literature (Braxton and Mathur, 2011; Mathur et al., 2009; Palacios et al., 2011)

Microbial involvement on the copper isotopic fractionation in exotic copper deposit

As an alternative, the high ^{65}Cu values of copper in exotic copper minerals may come from the microbial activity. It has been shown by Sillitoe et al. (1996) and Nelson et al. (2007a) that nanobacteria can promote and favor the supergene enrichment of porphyry copper deposit (Sillitoe et al., 1996) and are involved in the formation of the exotic copper deposits of Huiniquintipa and Mina Sur (Nelson et al., 2007). These microbes, widespread in the copper deposits of Atacama Desert, could therefore promote the copper isotopic fractionation during the precipitation of the exotic copper minerals. Mathur et al. (2005), in a comparative study on copper isotopic fractionation in the supergene environment with

and without bacteria (i.e. *Thiobacillus ferrooxidans*), have shown that the copper isotopic fractionation is lighter during biotic oxidation compared to abiotic oxidation during the *in situ* supergene alteration. This lighter isotopic fractionation during biotic experiments is due to the formation of the isotopically heavy copper cells within *Thiobacillus ferrooxidans* bacteria which can be a sink of ^{65}Cu during supergene alteration (Mathur et al., 2005). The $\delta^{65}\text{Cu}$ values obtained from the exotic copper minerals in this study (2.42-8.87‰) are in range with the results found by Mathur et al. (2005) for abiotic experiments and support a precipitation from a heavy-rich ^{65}Cu mineralizing fluid without bacteria mediation ($\delta^{65}\text{Cu} = 5.34\text{‰}$ for aqueous copper in leach fluids). Although Nelson et al. (2007) have shown the involvement of anaerobic methanogenic microbes in the formation of exotic copper deposits in northern Chile, we can argue that those microbes were not able to promote the formation of the isotopically heavy exotic copper minerals, at least, in the three exotic copper deposits studied. However, since Münchmeyer (1996) and Sillitoe (2005) militate for a possible bacterial involvement in the formation of exotic copper deposits in northern Chile, especially *Thiobacillus ferrooxidans*, further studies should be undertaken to better understand the role of bacteria in the ^{65}Cu -enrichment of exotic copper minerals.

Implications for exploration strategies

Such as many other tools, copper isotopic signatures can serve as a proxy to discover hidden porphyry copper deposit localized upstream and associated exotic copper deposits downstream. Mathur et al. (2009) and Braxton and Mathur (2011) were the first authors to explore the potential of copper isotope fractionation for exploration of porphyry copper and related deposits. The firsts have shown that the copper isotope signature of the supergene column could indicate the degree of the supergene alteration and therefore the maturity of the supergene column. Braxton and Mathur (2011) have revealed, for the Bayugo porphyry Cu-Au deposit (Philippines), that the positive $\delta^{65}\text{Cu}$ values of the iron oxides of the leached cap suggest an oxidative reworking of a former enrichment zone where copper is remobilized and therefore militate for a mature supergene enrichment zone below the leached cap. In contrast, they argue that negative $\delta^{65}\text{Cu}$ values of iron oxides can be interpreted as the result of the leaching of an unenriched hypogene protore. Braxton and Mathur (2011) have also shown that, in

the exotic copper deposit located downstream of the Bayugo porphyry, proximal chalcocite is highly fractionated ($> +3\text{‰}$) compared to distal chalcocite ($< +1\text{‰}$). Therefore, they propose that isotopic signature of exotic chalcocite can be a proxy to unravel the direction and the proximity of an upstream porphyry copper deposit.

Our study goes further and shows, for the first time, the $\delta^{65}\text{Cu}$ values of oxidized exotic copper minerals (i.e. chrysocolla and pseudomalachite). Compare to the chalcocite-rich enrichment zone and the oxidized ore of the supergene column, the $\delta^{65}\text{Cu}$ values of the exotic copper minerals display the same positive $\delta^{65}\text{Cu}$ values. This demonstrates that oxidized exotic copper minerals originate from the same ^{65}Cu -rich leaching solution. The high $\delta^{65}\text{Cu}$ values ($> + 2.5\text{‰}$) encountered in chrysocolla and pseudomalachite reflect a high degree of fractionation and could therefore suggest a multiple cycle of *in situ* supergene alteration of an upstream porphyry copper deposit which is an indicator of the maturity of the supergene column. A mature supergene column which constitutes a prime target for many mining exploration companies.

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IV.2 Discussions complémentaires

IV.2.1 Rôle des paramètres géologiques et climatiques sur le fractionnement isotopique du cuivre

A Zaldivar, dans le district minier d'Escondida (désert d'Atacama), tout comme à Gaoua, au sud-ouest du Burkina Faso, les données $\delta^{65}\text{Cu}$ réalisées sur la chrysocolle (Annexe 1, Table 1) de l'horizon oxydé de la colonne supergène montrent des valeurs moyennes positives avec, à Zaldivar, $\delta^{65}\text{Cu} = 1.48$ ‰ (n=4) et à Gaoua, $\delta^{65}\text{Cu} = 3.14$ (n=3). Comparées à la bibliographie, ces résultats sont dans la même gamme de valeurs que celles connues des chrysocolles et des minéraux de l'horizon oxydé bien que ces dernières présentent des hétérogénéités (Braxton and Mathur, 2011; Mathur et al., 2009; Palacios et al., 2011).

Les résultats obtenus montrent que le fractionnement isotopique du cuivre n'est que peu contraint par la différence de contextes géologiques et climatiques. A Zaldivar, l'altération supergène est liée à l'exhumation rapide des porphyres cuprifères entre le tardi Eocène et le début de l'Oligocène. Dans ce district minier, l'altération supergène s'est déroulée entre ca. 18 Ma et ca. 14 Ma. Dans le district minier de Gaoua, l'exhumation du porphyre a été très lente et l'altération supergène a été continue tout au long du Cénozoïque au gré de la lente exhumation du porphyre et du climat humide à aride qui y règne depuis l'ouverture de l'Atlantique. Bien que jamais reporté dans la littérature, cette légère différence des valeurs du $\delta^{65}\text{Cu}$ entre Gaoua et Zaldivar pourrait être le crédit d'une altération supergène plus longue à Gaoua qu'à Zaldivar, impliquant de fait une altération complète voire continue des sulfures primaires riches en ^{65}Cu . Cependant, comme discuté par Young (2003) et Wall et al. (2006), la signature isotopique du cuivre est fortement dépendante de facteurs locaux tels que le pH, Eh, la température des fluides et l'état du réseau cristallin des minéraux. La légère différence du degré de fractionnement entre les valeurs reportées à Zaldivar et à Gaoua pourrait donc être le reflet de conditions chimiques différentes durant l'altération supergène de ces porphyres.

IV.2.2 Contrôle analytique

Pour contrôler la précision et la reproductibilité des analyses, nous avons utilisé un standard de basalte communément utilisé dans les analyses des isotopes du Cu, le BHVO-2 (Little et al., 2017; Moynier et al., 2017). Ce standard secondaire, à matrice silicaté, a subi la même procédure de purification que les échantillons, à savoir un seul stade de passage à travers les colonnes. Les résultats (Annexe 1 Table 2) ont donné des valeurs très élevées par rapport à la bibliographie, ces dernières se situant autour de 0 ‰. Ces résultats soulèvent par conséquent un possible artefact analytique. Cependant, le standard secondaire n'ayant subi qu'un seul passage à la résine contre deux ou trois comme cela est communément fait, la différence entre nos résultats et les données de la littérature se situeraient donc autour de la méthode de purification.

Les résultats obtenus sur nos échantillons, similaires à la littérature, sont considérés comme robustes, nonobstant les valeurs du standard secondaire. Cependant, des investigations sont en cours pour obtenir une meilleure purification du standard secondaire via un triple passage à travers les colonnes de purification.

CHAPITRE V :

Première datation U-Pb de la minéralisation cuprifère
supergène : cas d'étude dans le district minier de
Chuquicamata

Avant-propos

L'âge et la durée de l'altération supergène représentent une donnée fondamentale d'une part, pour la compréhension du fonctionnement global de l'altération supergène et d'autre part pour comprendre la relation entre la formation de la minéralisation cuprifère supergène et l'évolution du relief et du climat. Avant cette étude, la contrainte de l'âge et de la durée de l'altération supergène des porphyres cuprifères reposaient sur la présence ou non de minéraux d'altération (e.g. alunite, jarosite, cryptomélane) pas toujours ubiquistes dans les minéralisations supergènes *in situ* et exotiques. Dans le district minier de Chuquicamata, des échantillons de cuivre ont été prélevés dans le dépôt exotique de Mina Sur, située 6 km plus en aval du porphyre géant de Chuquicamata.

Les datations U-Pb effectuées sur la pseudomalachite Mina Sur ont donné un âge de formation à ca. 19 Ma, dans la même gamme d'âge que celles obtenues sur les minéraux d'altération, au-dessus du porphyre de Chuquicamata, par Sillitoe and McKee (1996), entre ca. 19 Ma et ca. 15 Ma. Les données acquises montrent qu'il est possible de dater directement la minéralisation cuprifère supergène et ainsi contraindre directement l'âge et la durée de fonctionnement de l'altération supergène.

V.1 First U-Pb LA-ICP-MS *in situ* dating of supergene copper mineralization: case study in the Chuquicamata mining district, Atacama Desert, Chile

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First U-Pb LA-ICP-MS in situ dating of supergene copper mineralization: case study in the Chuquicamata mining district, Atacama Desert, Chile

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Abstract

Since the second half of the twentieth century, exotic copper mineralization represents a prime target for many mining exploration companies operating in the hyperarid Atacama Desert, in northern Chile. Although there is evidence that the emplacement of such deposits took place during specific Tertiary climatic periods and relief formation, many uncertainties remain regarding the exact timing for their deposition and/or the genetic link between the exotic deposits and the primary porphyry copper deposits. We present a first attempt of U-Pb dating of copper-rich minerals from the Mina Sur exotic deposit from the Chuquicamata mining district. A suite of Mn-rich black chrysocolla clasts surrounded by pseudomalachite bands has been characterized and dated in petrographic context using both nanosecond and femtosecond in situ laser ablation ICP-MS analyses. U-Pb dating on pseudomalachite bands yields a crystallization age of 18.4 ± 1.0 Ma. For the Mn-rich chrysocolla clasts, the $^{206}\text{Pb}/^{238}\text{U}$ apparent ages range from 19.7 ± 5.0 Ma to 6.1 ± 0.3 Ma, a spread interpreted as the result of U and/or Pb mobility linked to fluid circulation following crystallization. This study demonstrates that supergene copper mineralization can be directly dated by the U-Th-Pb method on pseudomalachite. Furthermore, the age obtained on pseudomalachite indicates that Mina Sur copper deposition took place at ca. 19 Ma, about 11 m.y. after the unroofing and hydrothermal alteration of the Chuquicamata deposit, a result that is consistent with the supergene ages already known in the Atacama Desert.

Keywords Mina Sur deposit · Supergene copper minerals · U-Th-Pb LA-ICP-MS dating · Pseudomalachite · Mn-rich Chrysocolla

Introduction

Supergene copper mineralization (SCM) are important for the economic viability of several porphyry copper deposits worldwide. SCM imply secondary alteration related to sulfide oxidation and leaching of ore deposits in the weathering environment, and associated secondary sulfide enrichment (Ransome 1912). Two types of SCM have been recognized: (1) in situ SCM, derived from descending meteoric water that affect the porphyry copper without lateral migration of copper (Chavez 2000; Sillitoe 2005) and (2) exotic supergene copper mineralization, which are the products of lateral migration of supergene copper from a parental porphyry copper deposit (Munchmeyer 1996; Sillitoe 2005). The latter type of SCM forms from copper leached in the supergene oxide zone of porphyry copper deposits, is transported laterally in acidic fluids, and precipitated downstream when fluids are neutralized or copper saturated (Newberg 1967; Munchmeyer 1996; Chavez 2000; Sillitoe 2005; Nelson et al. 2007; Fernández-

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Mort et al. 2018). For exotic copper deposits to form, favorable tectonic, climate, nature of the bedrock, and sediment cover are required. Tectonics control the uplift needed to induce groundwater table lowering and leaching of sulfides from a porphyry copper deposit. In the case of exotic SCM, semi-arid to arid climatic conditions favor copper leaching in the supergene environment and groundwater migration towards the locus where copper-bearing minerals precipitate, but prevent major erosion and removal of the mineralized bodies. Finally, the nature of the bedrock and sediments contributes to the neutralization of the circulating fluids and the precipitation of copper minerals (Alpers and Brimhall 1988; Munchmeyer 1996; Sillitoe 2005; Hartley and Rice 2005; Riquelme et al. 2017; Fernández-Mort et al. 2018). To understand the specific climatic and geomorphologic conditions favorable for exotic copper deposit formation, good age constraints are required. Currently, the available supergene copper mineralization ages largely rely on secondary K-rich minerals that crystallized near or within the copper mineralization (Sillitoe and McKee 1996; Mote et al. 2001; Bouzari and Clark 2002; Quang et al. 2003; Hartley and Rice 2005; Reich et al. 2009; Bissig and Riquelme 2010). The precipitation of the K-rich minerals may however not be synchronous with the copper-bearing minerals and more problematic; they are not ubiquitous in all exotic deposits. This results in significant uncertainties with respect to the formation ages for exotic deposits and/or the genetic link between the deposits and the hypogene porphyry copper mineralization. Defining the timing of copper mineralization in an exotic deposit is, thus, of prime importance for the definition of the metallogenic model and to elaborate new exploration strategies for the discovery of new deposits in Chile and other regions with similar climatic and tectonic conditions (such as parts of Peru, Iran, Mexico, China, and Mongolia).

In the Atacama Desert, the Chuquicamata mining district represents an ideal location for the study of different types of copper mineralization (Mortimer et al. 1977; Fam and Rojas 1997; Ossandon et al. 2001; Rivera et al. 2012) because of the presence of several world class examples of supergene (Chuquicamata, Radomiro Tomic, Toki Cluster, Ministro Hales) and exotic (Mina Sur, Radomiro Tomic) copper mineralization (Fig. 1). In exotic deposits within this mining district, chrysocolla is, by far, the most important copper-bearing mineral that may be found together with copper phosphates (pseudomalachite, libethenite), copper chlorides (atacamite, paratacamite), copper oxides (cuprite, tenorite), and carbonates (malachite, azurite). While there is to date no direct dating of supergene copper mineralization in the Atacama Desert, previous studies have been carried out to date the supergene oxidation and enrichment using the K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods mostly on K-rich minerals (e.g., cryptomelane, jarosite, alunite: Gustafson and Hunt 1975; Alpers and Brimhall 1988; Sillitoe and McKee 1996; Marsh et al. 1997;

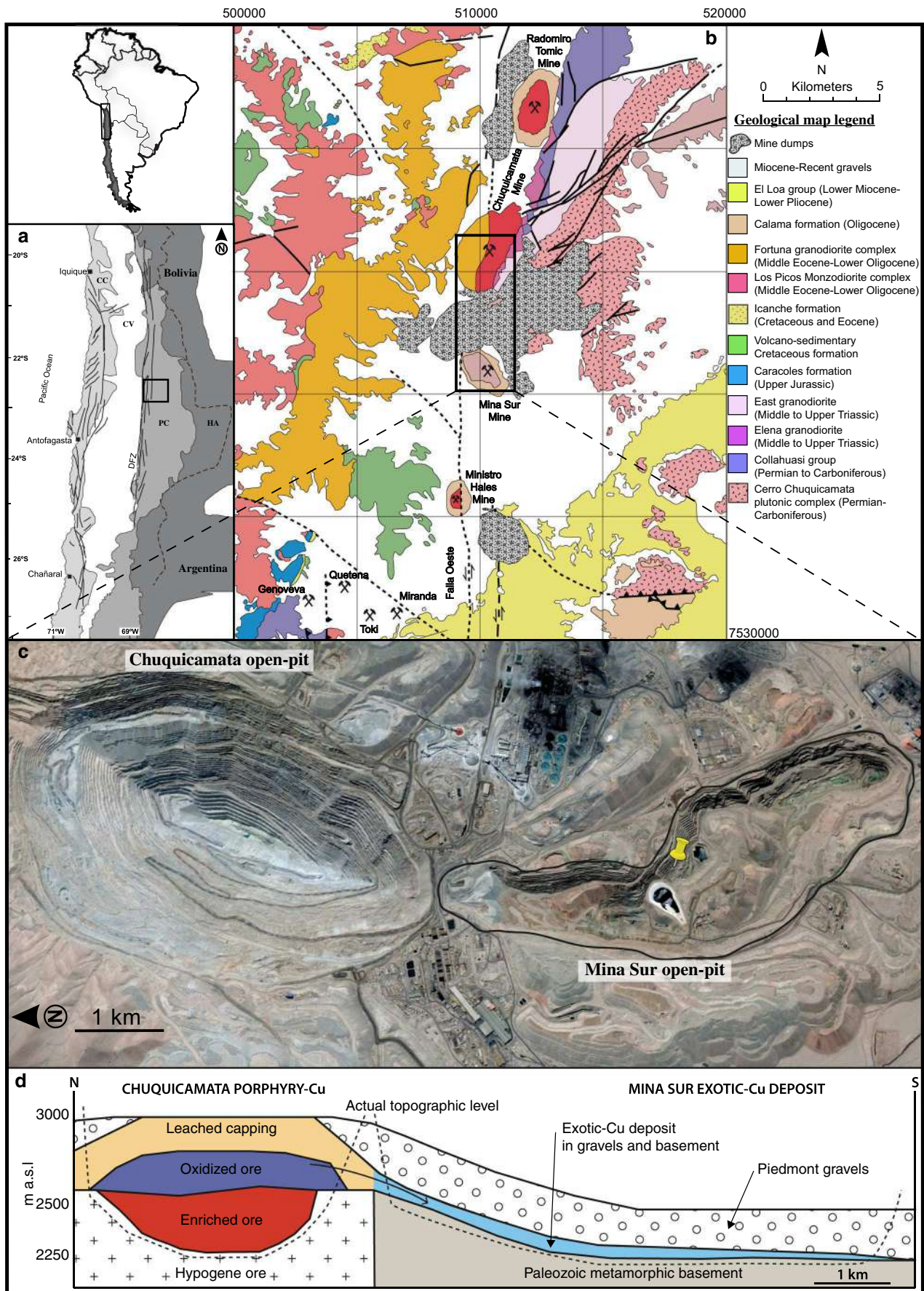
Fig. 1 Location and geological map of the studied area. **a** Physiographic setting of the Atacama Desert of northern Chile (CC, Coastal Cordillera; CV, Central Valley; PC, Precordillera; HA, High Andes; DFZ, Domeyko Fault Zone; from Arancibia et al. 2006). **b** Detailed geological map of the Chuquicamata mining district after Zentilli et al. (2018). **c** Google Earth aerial photography of the Chuquicamata porphyry copper deposit and Mina Sur exotic copper mines and **d** its schematic geological cross-section. Yellow pushpin represents the location of the collected samples

Mote et al. 2001; Bouzari and Clark 2002; Arancibia et al. 2006; Bissig and Riquelme 2010; Riquelme et al. 2017). These studies suggest that supergene alteration of porphyry copper and the formation of exotic copper deposits in the Atacama Desert occurred mainly between 34 and 9 Ma. However, Reich et al. (2009) suggest that a second enrichment stage happened later during the Pleistocene and modified the pre-existing supergene copper oxide minerals. The main goal of the present study is to test, for the first time, the potential of the LA-ICP-MS in situ U-Pb technique to date the deposition of this type of ore deposits. For this purpose, we selected several samples from the largest exotic copper deposit of the Atacama Desert, Mina Sur, located in the Chuquicamata Mining District. Prior to dating, we carried out a complete mineralogical and chemical characterization of the mineralized samples using scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA). All these data are then interpreted in the framework of the well-characterized geological evolution of this mining district.

Geological background

The exotic mineralization of Mina Sur is within the Chuquicamata Mining District (CMD) in the hyperarid Atacama Desert of northern Chile (Fig. 1a). The district is located in the northern section of the Domeyko Cordillera, a pre-Andean mountain range that extends over 800 km from north to south and corresponds to a former magmatic arc formed during the Incaic orogeny (Mpodozis and Ramos 1989; Amilibia et al. 2008; Mpodozis and Cornejo 2012; Fig. 1a). This mountain range, which contains the majority of Chile's porphyry copper deposits, is formed by blocks, Late Paleozoic to Eocene in age, delimited by inverted normal and strike-slip faults (Scheuber and Reutter 1992). At a local scale (Fig. 1b), the "Falla Oeste" is one of these faults, which divides the district into two parts. This fault acted as a plumbing system that facilitated the formation of hypogene sulfide mineralization (Lindsay et al. 1995; Reutter et al. 1996; Tomlinson and Blanco 1997).

The geology of the CMD has previously been described in detail (Reynolds et al. 1998; Ballard et al. 2001; Ossandon et al. 2001; Sillitoe and Perelló 2005; Campbell et al. 2006; Dilles et al. 2011; Mpodozis and Cornejo 2012; Rivera et al. 2012; Barra et al. 2013) and is only briefly summarized



herein. The basement of the CMD is represented by the Igneous-Metamorphic Paleozoic Complex comprising mainly faulted and brecciated amphibolites and micaschists (Paleozoic Metamorphic Complex) and granites, diorites and migmatitic metadiorites related to Cerros de Chuquicamata Igneous Complex (Permian-Carboniferous: Ossandon et al. 2001; Rivera et al. 2012). Volcanic and volcanoclastic rocks (andesite and dacite) from the Collahuasi Group (Carboniferous to Permian) overlain the basement (Tomlinson and Blanco 2008; Munizaga et al. 2008). The Paleozoic complex and the Collahuasi Group are unconformably overlain by Lower to Upper Jurassic marine sediments of the Caracoles Formation (Zentilli et al. 2018), previously named Quehuíta Formation (Rivera et al. 2012). Northwest of the Chuquicamata mine, the Elena and East granodiorites (Middle to Upper Triassic) intrude rocks from the Igneous-Metamorphic Paleozoic Complex and the Collahuasi Formation (Tomlinson and Blanco 2008). Above the Jurassic sequence lie Cretaceous and Eocene volcanic (andesite and dacite) and sedimentary rocks from Quebrada Mala and Icanche Formations (Rivera et al. 2012). To the west of the Chuquicamata mine and of the Falla Oeste, crop out the middle Eocene-Lower Oligocene Los Picos Diorite and the Fortuna Granodiorite (Rivera et al. 2012). South of the Chuquicamata mine, covering the older igneous and volcano-sedimentary rocks, lie the Calama Formation (a.k.a. old gravels; Tomlinson and Blanco 2008) and the El Loa Group. These formations are made up of continental sedimentary to volcano-sedimentary angular to sub-angular erosional clasts, formed in response to the uplift and erosion of the Domeyko Cordillera (May et al. 1999, 2010). Several forearc basins formed in the Domeyko Cordillera range during the Oligocene have been preserved, including the Calama basin which hosts the Mina Sur exotic copper deposit. Detailed studies have previously described the geology and the sedimentary infill of this basin (May et al. 1999; Rech et al. 2006).

Hypogene mineralization and hydrothermal alteration occurred contemporaneously with the formation of the Domeyko Precordillera (Sillitoe and Perelló 2005; Mpodozis and Cornejo 2012). This precordillera has served as a drain and trap for the circulation of the mineralizing fluids. The CMD includes the Chuquicamata porphyry copper complex, emplaced between 35 and 33 Ma (Ballard et al. 2001); the Radomiro Tomic porphyry copper deposit was emplaced around 32 Ma (Cuadra et al. 1997); the 38–36 Ma old Toki Cluster porphyry copper (Barra et al. 2013) and the Ministro Hales mine (35.0 ± 0.3 Ma, Zentilli et al. 2018; Fig. 1b). Hypogene mineralization in these deposits typically consists of chalcopyrite, bornite, enargite, sphalerite, molybdenite, covellite, and chalcocite (Ossandon et al. 2001). This mineralization was affected by supergene alteration, which initiated at least ~ 11 Ma after the last hydrothermal alteration event (Sillitoe and McKee 1996). The supergene alteration

produced enriched ore blankets rich in supergene chalcocite and covellite, as well as an oxidized column with silicates (chrysocolla, diopside), phosphates (pseudomalachite, libethenite, turquoise), carbonates (azurite, malachite), oxides (cuprite, tenorite), and copper halides (atacamite, paratacamite) and a leached cap rich in iron and aluminum minerals (alunite, goethite, hematite, jarosite). In addition, in the Chuquicamata porphyry, copper-bearing supergene fluids migrated laterally southward into the gravels of the Calama Basin to form the Mina Sur exotic mineralization that extends 6 km to the southwest of the source deposit (Fig. 1c, d; Mortimer et al. 1977). This exotic deposit is mainly composed of chrysocolla, copper wad, atacamite, and pseudomalachite filling the fractures of the Paleozoic bedrock and cementing the overlying gravels (Mortimer et al. 1977; Munchmeyer 1996; Sillitoe 2005; Pinget 2016). Finally, ignimbrite flows, dated at 8.4 ± 0.4 Ma (Mortimer et al. 1977), cover the entire district area. Accordingly, some authors consider that this ignimbrite flow marks the end of supergene alteration and erosive processes and the onset of hyperaridity in this area (Sillitoe and McKee 1996; Hartley and Rice 2005; Rech et al. 2006, 2019). However, many authors estimate the onset of the hyperaridity in Atacama Desert more around 10–12 Ma, based on K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ on K-rich minerals (Alpers and Brimhall 1988; Mote et al. 2001; Bouzari and Clark 2002; Quang et al. 2003; Arancibia et al. 2006; Bissig and Riquelme 2010; Riquelme et al. 2017).

Sampling and petrography results

Sampling and analytical procedures

Samples from the central part of the Mina Sur open-pit exotic mineralization were selected at $22^\circ 19' 32''$ S and $68^\circ 54' 12''$ W (Fig. 1c). They are hosted in the sedimentary cover which overlies the bedrock. After induration, due to the friable texture, polished and thin sections were prepared at Géosciences Environnement Toulouse (GET, Université de Toulouse, France). Qualitative and semi-quantitative data as well as backscattered electron images were obtained using the JEOL JSM 6360LV scanning electron microscope (SEM) coupled to an energy dispersive spectrometry (EDS) analysis system at the GET. The analytical conditions were 15 kV for the acceleration voltage and 50 μm for the beam size while a tungsten filament was used as the electron source. Quantitative analyses were carried out at the Centre de MicroCaractérisation Raimond Castaing (Université de Toulouse, France) using the CAMECA SXFive electron probe micro-analyzer (EPMA) on both thin and polished sections. The analytical conditions for the profiles were 2 μm for the beam size, 10 nA for the current intensity, and an acceleration voltage of 15 keV. The standards used were pure metals as well as

natural and synthetic minerals (Al on corundum, Si and Ca on wollastonite, K on sanidine, Cl on tugtupite, Cu on copper metal, Mn on pyrophanite, Fe on hematite, Na on albite, P on monazite, Mg on periclase, U on uraninite, Ba on barytine, S on celestine, Zn on sphalerite, Pb on a glass of lead, and Th on thorianite). The results are reported in Table 1.

Textural and chemical characterization of the exotic copper mineralization from Mina Sur

The mineralized body at Mina Sur has a lenticular shape 1.2 km wide and 6.5 km long with a maximum thickness of about 110 m. The copper mineralization is mainly composed of chrysocolla and atacamite that fill fractures in the bedrock and porosity in the overlying sedimentary cover (Mortimer

et al. 1977; Munchmeyer 1996). Observation at the macroscopic scale of samples selected for this study (Fig. 2a) shows that the copper mineralization is mainly composed of chrysocolla $[(\text{Cu}_{2-x}\text{Al}_x)\text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}]$, sensu lato, present in the form of black Mn-rich angular clasts (also known as copper pitch or black chrysocolla; Throop and Buseck 1971), variable in size, as well as millimetric turquoise to pale green Mn-poor bands coating both the copper pitch and sedimentary clasts. Chrysocolla bands are intercalated with green micrometer to millimeter thick-bands of pseudomalachite $[\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4]$. A copper chloride, atacamite $[\text{Cu}_2\text{Cl}(\text{OH})_3]$, with an acicular texture, is also present in small proportion. Under the microscope, Mn-rich chrysocolla appears as black clasts (Fig. 2b, c), in some cases showing a concentric banding texture with a black to

Table 1 Chemical compositions of Mn-rich chrysocolla clasts, chrysocolla and pseudomalachite bands carried out with EPMA. Structural formula has been calculated for 6 oxygens (chrysocolla) and 7 oxygens (pseudomalachite). *N*, number of analyses

Facies Number of analyses	Mn-rich chrysocolla clasts 105	Chrysocolla 79	Pseudomalachite 123
wt. %			
Al ₂ O ₃	0.057	2.159	0.09
SiO ₂	32.177	36.78	0.221
K ₂ O	0	0.05	0
CaO	0.42	0.442	0.124
Cl	0.153	0.119	0.016
MnO	6.385	0.038	0.014
FeO	0.066	0.049	0.011
Na ₂ O	0.000	0.063	0.000
MgO	0.152	0.121	0.005
BaO	0.179	0.077	0.032
P ₂ O ₅	0.08	0.03	24.189
SO ₃	0.341	0.099	1.327
CuO	49.047	50.782	68.441
Total	89.057	90.809	94.47
Structural formula on the basis of 7 oxygens (chrysocolla) and 10 oxygens (pseudomalachite)			
Al	0.003	0.109	0.008
Si	2.068	2.199	0.017
K	0.000	0.003	0.000
Ca	0.021	0.020	0.010
Cl	0.012	0.009	0.002
Mn	0.348	0.001	0.001
Fe	0.003	0.002	0.001
Na	0.000	0.005	0.000
Mg	0.010	0.008	0.001
Ba	0.003	0.001	0.001
P	0.004	0.001	1.920
S	0.015	0.012	0.280
Cu	2.381	2.293	4.846
Σ Cations	4.868	4.663	7.085
Cu/Si	1.151	1.043	—

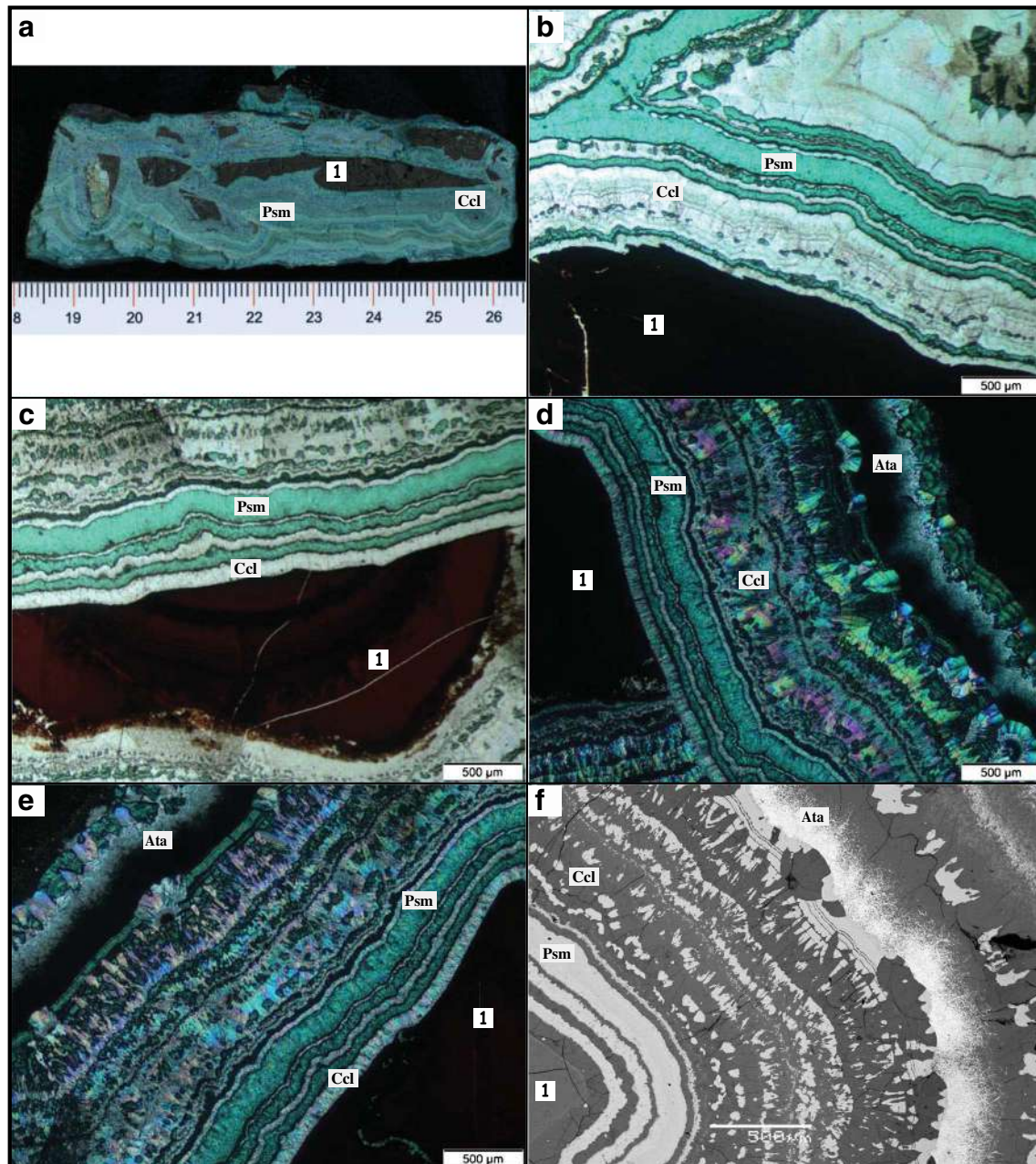


Fig. 2 Sample and thin sections photographs showing the relationships between Mina Sur main copper minerals. **a** Black chrysocolla (1) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands at Mina Sur mine. **b, c** Plane-polarized light photomicrograph showing Mn-rich chrysocolla clast (1) coated by chrysocolla (Ccl) and pseudomalachite

(Psm) bands. **d, e** Cross-polarized light and **f** photomicrographs showing Mn-rich chrysocolla clast (1) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite (Ata) on chrysocolla and pseudomalachite

brownish color variation observed in plane-polarized light. These clasts were fractured prior to or during their coating. The chrysocolla bands (Fig. 2d, e) form microcrystalline aggregates with a strong birefringence in cross-polarized light (Foote and Bradley 1913; Sun 1963; Thompson 1980; Campos et al. 2015; Menzies et al. 2015). They are thought to have formed by the interaction between copper-rich solutions and siliceous sediments (Yates et al. 1998). Pseudomalachite has an emerald-green to dark green color

in transmitted light (Fig. 2b, c) and a low pleochroism in plane-polarized light (Berry 1950; Shoemaker et al. 1977). Atacamite displays thin black prismatic crystal in cross-polarized light (Fig. 2d, e) and appears as overgrowths on both the chrysocolla and pseudomalachite bands. Backscattered electron imaging (Fig. 2f) shows a more complex textural association between the different minerals and chrysocolla and pseudomalachite present intergrowth textures. In places, crystals of chrysocolla crosscut some pseudomalachite bands.

Such textural relationships have been interpreted as resulting from dissolution-precipitation of pseudomalachite by chrysocolla (or vice versa: Crane et al. 2001). Finally, atacamite, which appears as white prismatic crystals that nucleate at the mineral interfaces, clearly crystallized late when compared with all the other minerals. EPMA chemical analyses show that chrysocolla contains mainly CuO (~50–55 wt.%), SiO₂ (~40–50 wt.%), and variable proportion of H₂O (~5–10 wt.%). Other oxides such as ZnO, P₂O₅, MgO, CaO, K₂O, and Al₂O₃ are also present as traces. Copper pitch is distinguished from chrysocolla by a higher amount of MnO (up to 6 wt.%) and H₂O (10–20 wt.%) and a lower content in SiO₂ (20–40 wt.%) and CuO (~45–50 wt.%). Chemical compositions of the pseudomalachite bands show a significant proportion of CuO (~68.4 wt.%) and P₂O₅ (~24.2 wt.%), a quantity of H₂O (~5–10 wt.%) similar to that observed in chrysocolla and a very small amount of SiO₂ (~0.2 wt.%). In addition, intra-layer analysis profiles revealed a relatively good homogeneity of the chemical composition with small variations between 67 wt.% and 70 wt.% and 22 wt.% and 24 wt.% for CuO and P₂O₅ respectively.

U-Th-Pb LA-ICP-MS dating

Materials and methods

Laser ablation ICP-MS technique requires the use of a standard in order to correct for the instruments drift and mass-bias during the course of the analyses. Ideally, this standard should be a “matrix-matching” one, as it is well known that this technique is highly affected by matrix effects (Sylvester 2008). As this is a pioneering study, no pre-established chrysocolla and pseudomalachite standards are available for U-Th-Pb dating. We therefore followed the procedure outlined below.

U-Th-Pb in situ dating was first carried out at the Géosciences Rennes laboratory (University of Rennes, France) using an Agilent 7700x quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS) coupled to an Excimer ESI NWR193UC 193 nm nanosecond laser ablation (ns-LA) system with a two-volume ablation cell. The analyses were performed with an ultra-short pulse duration (< 5 ns), an energy of 5.2 J/cm², spot diameters of 40 µm, and a repetition rate of 4 Hz. Tuning of the instrument and mass calibration were performed on NIST SRM 612 reference glass. The duration of a laser shot is 80 s with 20 s of background noise collection, and 60 s of laser ablation followed by 10 s for the “wash-out”. The isotopes measured are ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁸U, and ²⁰⁴(Hg+Pb). ²³⁵U abundance was calculated on the basis of ²³⁸U/²³⁵U = 137.818 (Hiess et al. 2012). Chrysocolla and pseudomalachite samples (thin sections) were ablated in a helium stream and transported to

Q-ICP-MS by a gas mixture of helium (0.75 l/min), argon (0.87 l/min), and nitrogen (3 ml/min). The analytical standards, used to control the reproducibility and accuracy of analyses on chrysocolla, instrumental mass bias and correct matrix effects, are zircon GJ1 (Jackson et al. 2004) as primary standard and Plešovice zircon (Sláma et al. 2008) as secondary, quality control, material. Since no chrysocolla standard exists, we considered zircon, a silicate, the best proxy to use as standard. Accordingly, for pseudomalachite, we used apatite (another phosphate mineral) as our analytical standard: Madagascar apatite (Thomson et al. 2012) was used as the primary reference material and Durango apatite (McDowell et al. 2005) as secondary, quality control standard. Additional information on the analytical protocol is provided in ESM 1.

To assess the potential elemental fractionation related to the use of non-matrix-matched standards as reference materials, additional analyses were carried out at the Observatoire Midi Pyrénées (Toulouse) using an Element HR-ICP-MS coupled to a femtosecond laser (fs-LA). The femtosecond laser presents the advantage to minimize the isotopic fractionation and to reduce the bias introduced by the use of a standard that does not exactly match the sample matrix (Russo et al. 2002). Ablation was carried out with a frequency of 6 Hz on pseudomalachite and 4 Hz on Mn-rich chrysocolla, a fluence of 2.14 J/cm² and ablation spot diameter of 40 µm on pseudomalachite and 35 µm on Mn-rich chrysocolla. Instrumental mass calibration tuning was performed using NIST SRM 610 reference glass. Raw data were corrected for laser-induced elemental fractionation and instrumental mass discrimination using the same reference materials as those in Rennes, i.e., zircon for Mn-rich chrysocolla and apatite for pseudomalachite. More information about instrumental conditions are reported in ESM 1.

Durango apatite and Plešovice zircon were used as secondary standards, measured as unknown to monitor the reproducibility and accuracy of the analytical procedures in both laboratories. For the Durango apatite, we obtained weighted average ²⁰⁷Pb-corrected ages of 32.2 ± 0.5 Ma (MSWD = 0.69) and 32.9 ± 0.7 Ma (MSWD = 0.50) for ns-LA-Q-ICP-MS in Rennes and fs-LA-HR-ICP-MS in Toulouse, respectively (ESM 2). For Plešovice, ²⁰⁶Pb/²³⁸U weighted average ages provided 336.0 ± 3.3 Ma (MSWD = 0.10) and 338.2 ± 2.6 Ma (MSWD = 0.27) for ns- and fs-LA-ICP-MS, respectively (ESM 2).

Data reduction, for pseudomalachite and Mn-rich chrysocolla, was carried out using VizualAge_Ucompbine, a set of Iolite procedures that work with Igor Pro (Chew et al. 2014). Tera-Wasserburg and density plot diagrams were produced by Isoplot/Ex version 4 (Ludwig 2008) and Density Plotter (Vermeesch 2012), respectively. Uranium-Thorium-Lead values were calculated in relation to the primary reference standards.

Results

Samples

At Mina Sur, only Mn-rich chrysocolla clasts and pseudomalachite bands were found to host enough U and Pb for U-Pb analysis. Isotopic ratios, contents, ages, and associated uncertainties are listed in ESM 2.

Pseudomalachite U-Pb dating

In the pseudomalachite bands, 36 ns-LA-Q-ICP-MS and 90 fs-LA-HR-ICP-MS analyses were performed, relatively close to each other on large and homogeneous bands selected according to SEM images. The analyses revealed high U concentrations (~800–1100 ppm) and low but measurable Pb concentrations (~0.04 ppm) while thorium is not detected. The presence of a small amount of common Pb has been evidenced by the presence of a low counts of ^{208}Pb whereas ^{232}Th is not detected (Andersen 2002).

In a Tera-Wasserburg concordia diagram, the ns-LA-Q-ICP-MS data plot in a concordant position and define a concordant age of 19.5 ± 0.2 Ma (MSWD = 2.5; $N = 36$; Fig. 3a). This age is consistent with the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 19.5 ± 0.3 Ma (MSWD = 2; Fig. 3b).

In addition, the fs-LA-HR-ICP-MS data plot in a slightly discordant position (Fig. 3c). If the isochron is forced to a $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.837 calculated using the Stacey and Kramers Pb evolution model at 19 Ma (Stacey and Kramers 1975), the lower intercept yields an age of 18.0 ± 0.1 Ma (MSWD = 2.3, $N = 90$; Fig. 3c). This age is equivalent within error with the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 18.1 ± 0.1 Ma (MSWD = 2.2; Fig. 3d).

Plotted together (ns- and fs-LA-ICP-MS data) in a Tera-Wasserburg concordia diagram, the data yield a lower intercept age of 18.4 ± 0.2 Ma (MSWD = 4.1, $N = 126$; Fig. 3e) and define a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 18.4 ± 0.2 Ma (MSWD = 3.6; Fig. 3f).

Mn-rich chrysocolla U-Pb dating

In Mn-rich chrysocolla clasts, a total of 96 ns-LA-Q-ICP-MS and 133 fs-LA-HR-ICP-MS analyses were performed within a relatively small area. SEM imaging has revealed that these clasts are generally homogeneous although, in some places, they can display a botryoidal texture. Uranium (~1200–1600 ppm) and Pb (1 to 9 ppm) contents exceed the detection limit and allow for chronometric analysis. No ^{208}Pb nor ^{232}Th have been detected indicating a negligible common Pb contribution. In a Tera-Wasserburg concordia diagram (Fig. 4a), the data obtained by ns-LA-Q-ICP-MS are concordant to slightly discordant and spread over a range of isotopic ratios and apparent $^{206}\text{Pb}/^{238}\text{U}$ ages from 13.7 ± 0.5 Ma down to $6.1 \pm$

0.3 Ma. If the data are reported in a density plot diagram, we obtained one main peak at 10.6 Ma and one secondary peak at 7.7 Ma (Fig. 4b).

In a Tera-Wasserburg concordia diagram, the data obtained by fs-LA-HR-ICP-MS show all the spots in a concordant to slightly discordant position with apparent $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 19.7 ± 5.0 Ma to 8.5 ± 2.0 Ma (Fig. 4c). Plotting the data in a density plot diagram, we obtained one main peak at 13.6 Ma (Fig. 4d).

If we combine data obtained with both the ns-Laser and fs-Laser in a Tera-Wasserburg concordia diagram (Fig. 4e), they all plot in a concordant to slightly discordant position with apparent $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 19.7 ± 5.0 Ma to 6.1 ± 0.3 Ma. Plotting the data in a density plot diagram (Fig. 4f), we obtained one main peak at 12.3 Ma and two secondary peaks around 10 Ma and 7 Ma. Therefore, it was not possible to define a single age due to this apparent age dispersion.

Discussion

In situ U-Pb dating of supergene copper minerals

In the Mina Sur open-pit exotic mineralization, only the Mn-rich chrysocolla clasts and the pseudomalachite bands contained enough U and Pb to be dated by in situ LA-ICP-MS. Common Pb content is negligible for both minerals. For pseudomalachite, using ns- and fs-LA-ICP-MS, the analyses yielded a concordia age of 19.5 ± 0.2 Ma and a lower intercept age of 18.0 ± 0.1 Ma, respectively. For Mn-rich chrysocolla, using ns- and fs-LA-ICP-MS, the data are spread along the concordia with $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 13.7 ± 0.5 Ma to 6.1 ± 0.3 Ma and 19.7 ± 5.0 Ma to 8.5 ± 2.0 Ma, respectively. The difference in age observed between both analytical procedures could be due to laboratory conditions or a slight “matrix effect.” The hypothesis of inter-laboratories bias can be discarded since secondary standard ages are similar within error for Durango apatite and Plešovice zircon. Consequently, we attribute the small age differences to a slight “matrix effect” highlighted by the use of two different types of laser. To evaluate in what extent the “matrix effect” affects the results obtained, a comparison of the downhole fractionation for ns-LA and fs-LA ICP-MS was carried out (ESMs 3 and 4, respectively). The raw $^{206}\text{Pb}/^{238}\text{U}$ was plotted for the different type of matrix (GJ1, Plešovice and FCT zircons, NIST 610 glass and Mn-rich chrysocolla) analyzed with both laser. For the conditions used during the analytical sessions, no significant fractionation was observed for the different types of matrix analyzed. Therefore, for ns- and fs-LA ICP-MS analyses, it is not necessary to have a matrix-match standard as demonstrated in ESMs 3 and 4. Although the existence of a matrix effect is negligible, we still observe a slight dispersion of about 8% for the pseudomalachite individual spot ages.

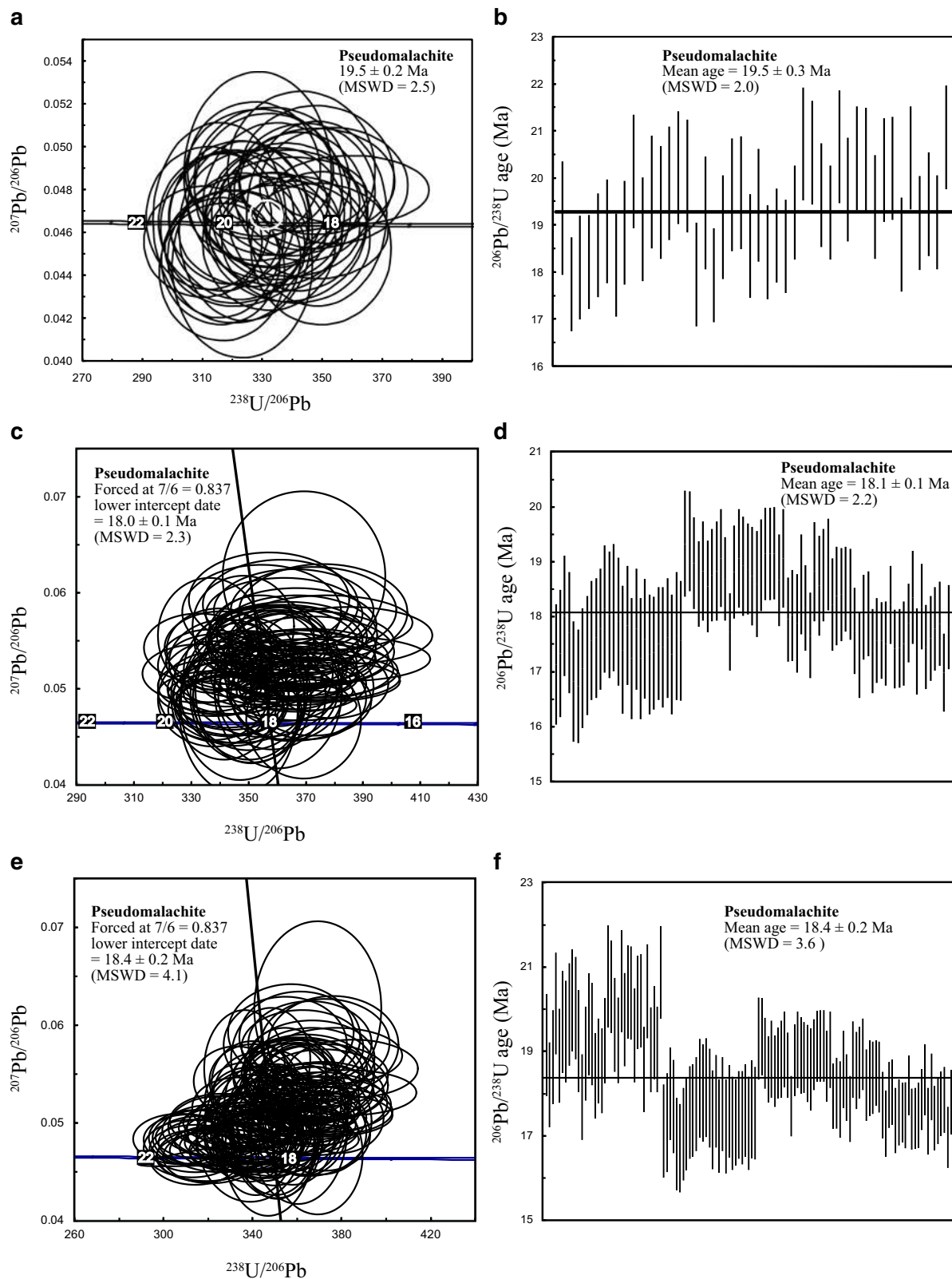


Fig. 3 Tera-Wasserburg and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagrams displaying the analyses made on pseudomalachite bands. The white circle corresponds to the concordia ages calculated using Isoplot. Errors ellipses and age calculations are reported with 2σ errors. **a–d** Tera-Wasserburg concordia diagram and corresponding weighted mean

$^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite with common Pb corrected made on ns-LA-Q-ICP-MS (**a, b**) and on fs-LA-HR-ICP-MS (**c, d, e, f**) Tera-Wasserburg concordia diagram and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram showing data obtained on both ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS

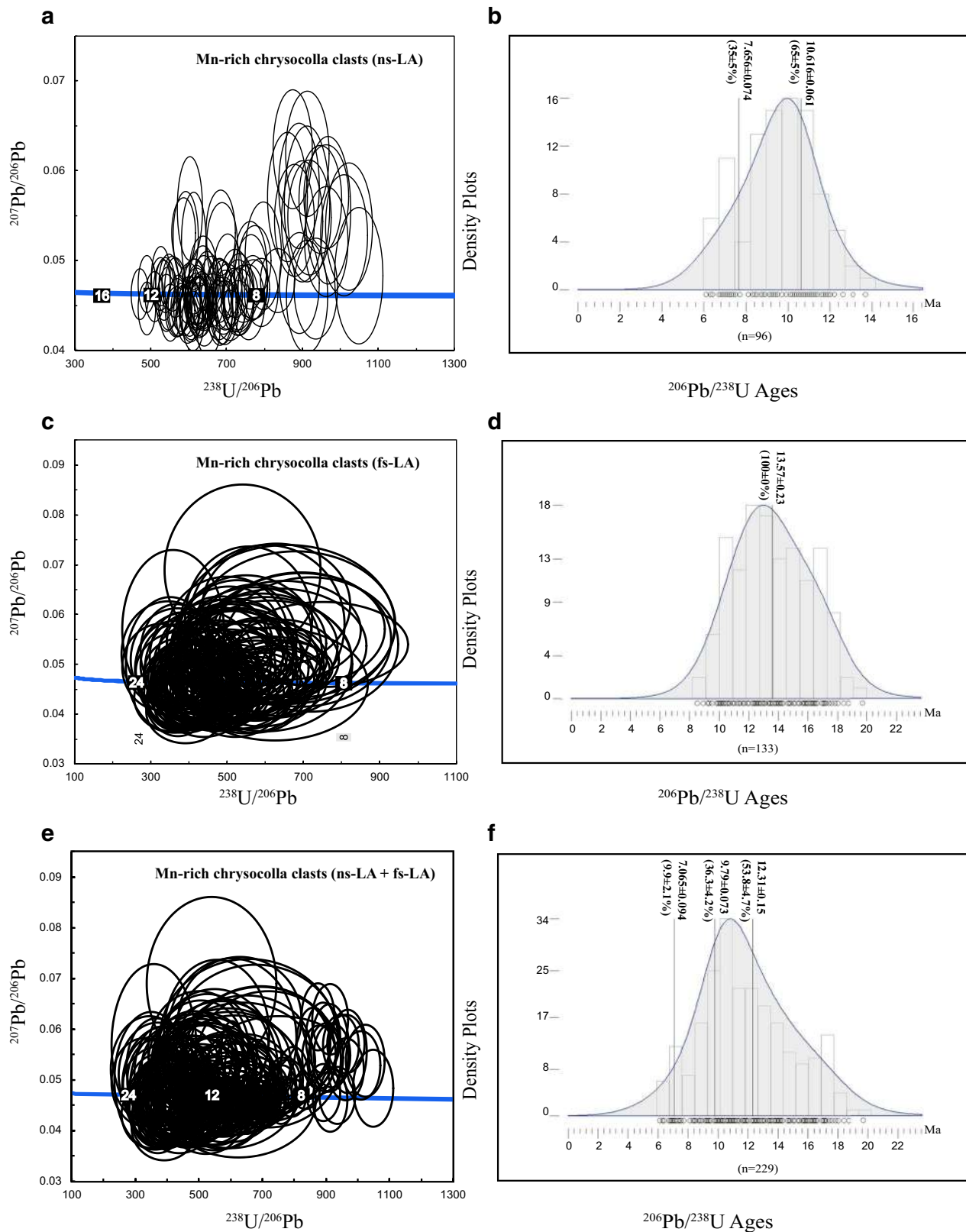


Fig. 4 Tera-Wasserburg concordia diagram and density plot of $^{206}\text{Pb}/^{238}\text{U}$ dates displaying the analyses on Mn-rich chrysocolla clasts. **a, b** Tera-Wasserburg concordia diagram and density plot for Mn-rich chrysocolla of $^{206}\text{Pb}/^{238}\text{U}$ ages by ns-LA-Q-ICP-MS. **c, d** Tera-Wasserburg concordia diagram and density plots for Mn-rich chrysocolla

of $^{206}\text{Pb}/^{238}\text{U}$ ages by fs-LA-HR-ICP-MS. **e, f** Tera-Wasserburg concordia diagram and density plot for Mn-rich chrysocolla of $^{206}\text{Pb}/^{238}\text{U}$ ages by both ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS. In all the diagrams, data point error ellipses are 2σ

Furthermore, if all the data are plotted together (see Fig. 3e), the resulting MSWD of 4.1 for the calculated concordia age of 18.4 ± 0.2 Ma is greater than unity and is probably related to an underestimated analytical error (Ludwig 2008). Consequently, we rather estimate the error from the standard deviation of all the concordant fs-LA-ICPMS and ns-LA-ICPMS ages to be around 1 Ma. This study shows, for the first time, that pseudomalachite is a potentially reliable U-Pb chronometer for supergene copper deposits. The concordant U-Pb dates obtained with both laser systems as well as the chemical homogeneity evidenced by SEM and EPMA suggest that pseudomalachite growth took place in a single stage. Furthermore, the U-Pb system in this mineral is probably resistant to late weathering and/or alteration as the data remain concordant. This might be due to the fact this mineral presents a well-crystallized structure (Shoemaker et al. 1977). All together, these observations allow us to interpret the U-Pb date of 18.4 ± 1.0 Ma obtained on pseudomalachite as its crystallization age.

On the other hand, the ages obtained on the Mn-rich chrysocolla clasts are scattered between ca. 6.1 Ma and ca. 19.7 Ma. However, the textural evidence clearly shows that chrysocolla is older than pseudomalachite. This suggests that Pb and, possibly, U were not kept within the chrysocolla structure after its initial formation. Consequently, we interpret the spread of data as the result of a complex, yet unknown, behavior of Pb and/or U in chrysocolla during late (post-crystallization) fluid event(s). For example, Pb loss may be facilitated by the mineralogical characteristics of Mn-rich chrysocolla, which has been described as a mineraloid by Schwartz (1934) and Throop and Buseck (1971) because of its poorly defined crystal structure. We can conclude, however, that Mn-rich chrysocolla has a chronometric potential, given its U and Pb concentrations and the absence of common Pb. Nevertheless, Mn-rich chrysocolla appear to be sensitive to external factors, a characteristic that has to be further examined to assess the capacity of the mineral to retain its crystallization age and/or record reopening of the isotopic system by late fluid circulation.

New constraints on Chuquicamata Mining District supergene evolution

In the CMD, several geomorphological, sedimentological, structural, and mineralogical arguments have shown the genetic relationship between the giant porphyry of Chuquicamata and the exotic mineralization of Mina Sur (Newberg 1967; Mortimer et al. 1977; Munchmeyer 1996; Fam and Rojas 1997). However, there were so far no geochronological data to prove the link between porphyry and exotic mineralization.

This study brings new light on the evolution of supergene copper mineralization in the CMD by comparing the ages

obtained on the porphyry intrusions, hydrothermal alteration, supergene alteration, and our new age on the supergene copper mineralization of Mina Sur. According to Ballard et al. (2001), the Chuquicamata porphyry complex was emplaced between 35 Ma and 33.3 ± 0.3 Ma. This was followed by hypogene hydrothermal alteration dated by $^{40}\text{Ar}/^{39}\text{Ar}$ at 33.4 ± 0.3 Ma and 31.1 ± 0.3 Ma (Reynolds et al. 1998) and by Re-Os on pyrite at 31 ± 2 Ma (Mathur et al. 2000). Supergene alunite alteration is dated between 19.0 ± 0.7 and 15.2 ± 0.5 Ma (Sillitoe and McKee 1996), in agreement with known supergene enrichment ages elsewhere in the Atacama Desert. The U-Pb dating performed on pseudomalachite bands shows a crystallization age of ca. 18.4 ± 1.0 Ma and a range of $^{238}\text{U}/^{206}\text{Pb}$ Mn-rich chrysocolla clasts ages from 19.7 ± 5.0 Ma to 6.1 ± 0.3 Ma. These data show that supergene mineralization and the formation of exotic copper deposit of Mina Sur were probably sub-contemporaneous and started as early as 19 Ma, about 11 m.y. after the Chuquicamata porphyry was exhumed (30.2 ± 4.4 Ma, Makshev and Zentilli 1999). This result is in a good agreement with those obtained by Sanchez et al. (2018) who showed that, in the mining district of Centinela (70 km south of the CMD), supergene enrichment (dated between 25 and 12 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ and K/Ar on jarosite and alunite; Riquelme et al. 2017) took place between 5 and 15 m.y. after the end of rapid exhumation of the mid-Eocene Centinela porphyries.

Furthermore, our results are consistent with the work of Mortimer et al. (1977) who showed that exotic mineralization at Mina Sur formed contemporaneously with a regional pediplain during the Paleogene-Neogene. In addition, Riquelme et al. (2017) also showed, using K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating on alunite in the Centinela mining district, that supergene enrichment and exotic mineralization formed during pediplain development until the mid-Miocene. The results of the direct dating of the exotic supergene mineralization of Mina Sur provide a strong argument and an excellent tool to demonstrate that supergene enrichment and exotic mineralization occur during relief pediplanation. Finally, at the scale of the Atacama Desert, these ages support the geochronological data obtained by K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods on K-rich minerals (Gustafson and Hunt 1975; Alpers and Brimhall 1988; Sillitoe and McKee 1996; Mote et al. 2001; Bissig and Riquelme 2010; Riquelme et al. 2017) which pointed out that supergene enrichment was active between 36 and 9 Ma and as late as 6 Ma with a principal activity between 25 and 13 Ma (Marsh et al. 1997; Mote et al. 2001; Bouzari and Clark 2002; Hartley and Rice 2005; Arancibia et al. 2006; Bissig and Riquelme 2010). In addition, Reich et al. (2009) show that in Chuquicamata, gypsum-atacamite-bearing assemblages formed around ~240 ka due to the circulation of deep waters. This ground water may account for the mobility of Pb and U, likely responsible for the disturbed U-Pb data obtained from the Mn-rich chrysocolla.

Conclusions

This study shows that exotic copper mineralization can be dated by the U-Pb method. In the Chuquicamata mining district, U-Pb LA-ICP-MS analyses carried out on pseudomalachite bands gave a robust crystallization age of ca. 18.4 ± 1.0 Ma. For the Mn-rich chrysocolla clasts, coated by pseudomalachite, the U-Pb analyses gave younger apparent $^{238}\text{U}/^{206}\text{Pb}$ ages ranging from 19.7 ± 5.0 Ma to 6.1 ± 0.3 Ma. This difference is attributed to U and/or Pb mobility during late ground water circulation. In any case, the data obtained on pseudomalachite are in agreement with geological constraints in the mining district, and bring new constraints on the in situ and exotic supergene copper deposits. They show that copper minerals precipitated in the exotic deposit at least 11 m.y. after the porphyry emplacement and the cessation of hydrothermal activity that produced the hypogene mineralization. The age of the exotic mineralization corresponds to the onset of supergene alteration process. The CMD is therefore one of the few examples in the Chilean copper belts where it is demonstrated that supergene enrichment and exotic copper deposition were probably contemporaneous. The U-Pb data on pseudomalachite provide a new tool for the understanding of the physico-chemical, climatic, and geological conditions prevailing during the formation of exotic deposits and a proxy for their exploration in Chile and elsewhere in the World.

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CHAPITRE VI :

Préservation et perturbation du signal chronométrique U-Pb
dans les minéraux cuprifères supergènes

Dans le chapitre V, les datations U-Pb réalisées sur la pseudomalachite et la chrysocolle noire ont montré que ces deux minéraux, dans le district minier de Chuquicamata, ont un potentiel chronométrique pour être daté par la méthode U-Pb. La pseudomalachite a fourni un âge de cristallisation tandis que le signal chronométrique U-Pb, dans la chrysocolle noire, présentait un comportement complexe, certainement le fait d'une mobilité de l'U et/ou du Pb.

Pour aller plus loin dans la compréhension du comportement du chronomètre U-Pb dans la pseudomalachite et la chrysocolle, nous présentons dans ce chapitre, les résultats d'une étude intégrée alliant datation *in situ* U-Pb, caractérisation isotopique de l'U (^{238}U) et du Pb (^{206}Pb , ^{207}Pb , ^{204}Pb) via LA-ICP-MS, et analyse *in situ* des isotopes de l'oxygène au SIMS. Pour avoir une idée complète de l'influence des paramètres géologiques et climatiques sur le comportement du chronomètre U-Pb, les districts miniers d'El Salvador et Potrerillos, au sud du désert d'Atacama, ont été étudiés. Les résultats obtenus montrent que le chronomètre U-Pb est fortement influencé par la chimie initiale du porphyre (i.e. sa concentration initiale en U), l'état du réseau cristallin des minéraux, la durée de l'épisode minéralisateur (i.e. la durée de l'altération supergène) et la circulation de fluides post-cristallisation pouvant lessiver l'U et/ou le Pb. Les résultats de ces travaux sont présentés dans la section VI.1 et feront l'objet d'une soumission prochaine à la revue « Chemical Geology ».

Pour comprendre dans quelle mesure les paramètres géologiques et climatiques influencent le comportement du chronomètre U-Pb, nous avons décidé d'étudier un contexte géologique et climatique différent de celui du désert d'Atacama, le district minier de Gaoua (sud-ouest du Burkina Faso). Le choix de ce site a été fait en raison de la disponibilité des échantillons. Les résultats préliminaires, présentés dans la section VI.2 de ce chapitre, montrent que, plus l'altération supergène est continue dans le temps et plus la disponibilité des eaux météoriques peut favoriser la formation récente de la minéralisation cuprifère supergène. Plausiblement, la disponibilité des eaux météoriques pourrait aussi intensifier la mobilité des éléments, perturbant de fait le signal chronométrique dans les minéraux supergènes, en l'occurrence la chrysocolle dans ce district minier.

Comme affirmé précédemment, la circulation de fluides post-cristallisation est une cause de la perturbation du signal chronométrique. Dans le désert d'Atacama, ces circulations tardives de fluides alcalins, sont responsables de la précipitation de l'atacamite et/ou de la calcite. La datation précise de

ces circulations tardives de fluides, couplé à leur étude isotopique et microthermométrie permettrait de comprendre la perturbation post-cristallisation du chronomètre U-Pb et identifier la nature des fluides perturbateurs du signal chronométrique. La section VI.3 présente la datation U-Pb de veines de calcite issus de la minéralisation exotique de Tesoro (100 Km au sud du district minier de Chuquicamata). Les âges obtenus (ca. 2 Ma) montrent que les fluides alcalins ont percolé à travers la minéralisation cuprifère durant la prévalence d'un climat hyperaride. Ces fluides alcalins pourraient engendrer une possible mobilité de l'U et/ou du Pb de la pseudomalachite et/ou de la chrysocolle.

VI.1 Understanding the preservation and disruption of U-Pb chronometer in supergene copper minerals from Atacama Desert, northern Chile: U-Pb dating coupled to U-Pb LA-ICP-MS mapping and isotopic in situ study of chrysocolla and pseudomalachite

Ce chapitre est présenté sous la forme d'un article en préparation pour une soumission prochaine à la revue *Chemical Geology*. Les annexes citées sont disponibles dans la section annexe de ce manuscrit.

Understanding the preservation and disruption of U-Pb chronometer in supergene copper minerals from Atacama Desert, northern Chile: U-Pb dating coupled to U-Pb LA-ICPMS mapping and isotopic *in situ* study of chrysocolla and pseudomalachite

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Abstract

Chrysocolla and pseudomalachite are the most common copper-bearing minerals found in the supergene copper mineralization (SCM) from the Atacama Desert in northern Chile. Supergene copper mineralization originates from a process linking supergene alteration of the primary sulfides, secondary sulfides and oxidized copper minerals *in situ* formation, and lateral migration of copper solutions to form exotic SCM. However, many uncertainties remain regarding the exact timing for the formation of these SCM since the dating of SCM formation is mainly indirect. This led us to test the potential of chrysocolla and pseudomalachite, both oxidized supergene copper minerals, as materials for U-Pb dating to place the SCM formation in a chronological context. However, variation of U content from one mineral to another, common Pb contribution and the absence of matrix-matched-standard for both minerals made U-Pb LA-ICP-MS dating of chrysocolla and pseudomalachite challenging.

This study combines texturally-controlled *in situ* LA-ICP-MS U-Pb dating and multi-elements mapping

together with SIMS oxygen isotope analyses in order to understand what controls the behavior of the U-Pb chronometer in supergene copper minerals. Chrysocolla and pseudomalachite samples were taken from Mina Sur, Damiana and El Cobre exotic copper deposits. Chrysocolla appears either as black Mn-rich clast (*a.k.a* black chrysocolla) or as massive bands, coating black chrysocolla and the sedimentary clasts. Pseudomalachite displays either millimetric turquoise to pale green bands or thin coatings filling empty spaces. Whatever their location, chrysocolla and pseudomalachite display almost homogenous chemical compositions range.

At Mina Sur, U-Pb analyses of black chrysocolla show high U content, measurable radiogenic Pb but a spreading of the data along concordia, highlighting a solid state diffusion of U as shown by the $\delta^{18}\text{O}$ analyses and isotope mapping. Chrysocolla bands show high U content but almost no radiogenic Pb. As highlighted by oxygen isotope analysis, this mineral was affected by late fluid circulation that favored radiogenic Pb leaching. U-Pb data of pseudomalachite show high U content, measurable radiogenic Pb and yield a crystallization age at ca. 19 Ma. This mineral seems to be only marginally affected by late fluid circulation and element mobility as shown by the $\delta^{18}\text{O}$ analyses and multi-element mapping.

At Damiana and El Cobre, $\delta^{18}\text{O}$ analyses show no evidence of late fluid circulation to explain the low U and radiogenic Pb/common Pb ratio. The fact that no U-Pb age can be calculated is possibly related to the recent crystallization age of chrysocolla and pseudomalachite rather than a leaching of U and/or Pb due to late fluid circulation.

Regardless their location, these results demonstrate the important role played by the local geological parameters on the control of the U-Pb chronometer in supergene copper minerals. Initial high U content of the porphyry source can promote U-rich supergene copper minerals as it is the case at Mina Sur. Additionally, a long-term supergene alteration will favor long-term water circulation in the depositional environment which can leach U from the porphyry source and allow the formation of U-low supergene copper minerals in recent times.

1. Introduction

Over the last twenty years, the constant research of absolute ages of the geological processes has motivated the development of geochronological methods, in particular with the progress of Laser Ablation Induced Coupled Plasma Mass Spectrometry (LA-ICP-MS) techniques. Dating is achieved through the use of major or accessory minerals such as mica, garnet, feldspar, zircon, monazite, titanite, rutile, apatite, baddelyite, etc., and a radioactive father-daughter isotope pair, e.g. ^{147}Sm - ^{143}Nd , ^{176}Lu - ^{176}Hf , ^{40}K - ^{40}Ar , ^{187}Re - ^{187}Os , ^{87}Rb - ^{87}Sr and the isotopic pairs of the (U-Th)-Pb system. The combination of a mineral and a radioactive isotopic system defines a geochronometer. To date, U-Th-Pb chronometry is the most widely used. Its popularity lies in the fact that many accessory minerals incorporate i) measurable U and radiogenic Pb content, ii) no or minimal common Pb during mineral formation and iii) the ability of the mineral to retain the isotopic signal after its growth, i.e. no re-opening of the system due to isotope volume diffusion or dissolution/precipitation due to late fluid circulation (Schoene, 2014). In addition, advances in analytical techniques have led to the development of standard materials, identical to the minerals to be analyzed, which are essential to overcome matrix effects and downhole U-Pb fractionation during laser ablation (Jackson et al., 2004; Wiedenbeck et al., 1995). However, if the minerals listed above are common in igneous and metasedimentary rocks, allowing the dating of crystalline rocks and metamorphic events, some are sensitive to weathering by low temperature fluids (e.g. zircon and monazite; Poitrasson et al., 2000; Seydoux-Guillaume et al., 2002; Geisler et al., 2007; Nasdala et al., 2010) and almost rare or absent in supergene systems (*i.e.* fluid temperature < 50°C-150°C). This prevents or constitutes a hindrance to the dating of supergene events, and thus to the global understanding of the functioning of these supergene environments.

In Atacama Desert of northern Chile, supergene alteration which affects hypogene sulfides from porphyry copper deposit is one of the main target for mining exploration since it represents an important economic interest. Two types of supergene copper mineralization (SCM) have been recognized. An i) *in situ* SCM, precipitated from descending meteoric water that leaches copper from the hypogene sulfides and precipitates the copper solutions downward and ii) exotic SCM, which results from the precipitation of copper minerals after lateral migration of supergene copper-rich solutions

(Münchmeyer, 1996; Sillitoe, 2005). Attempts to date this supergene alteration are based on the presence of K- and Mn-bearing weathered minerals (i.e. ^{40}K - ^{40}Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ on alunite, cryptomelane and jarosite; Sillitoe and McKee, 1996; Sillitoe, 2005; Hartley and Rice, 2005). However, the non-ubiquity of these weathering minerals, especially in the exotic SCM, and the fact that they might not be synchronous with the formation of the supergene copper minerals, result in uncertainties regarding the timing of supergene copper mineralization and hence the duration of supergene alteration and the conditions required to enable it. Therefore, trying to date the supergene copper mineralization is of prime importance.

Chrysocolla $[(\text{Cu}_{2-x}\text{Al}_x) \text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}]$, and pseudomalachite $[\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4]$ are ubiquitous supergene copper-bearing minerals in all the supergene copper deposits (Chávez, 2000). Both minerals have been characterized since decades by Electron Probe Micro-Analysis (EPMA) for major and minor elemental composition and display homogenous chemical composition (Berry, 1950; Campos et al., 2015; Menzies et al., 2015; Newberg, 1967; Pinget, 2016; Shoemaker et al., 1977). Isotopic analyses by LA-ICP-MS undertaken by Kahou et al. (2020) have shown that black chrysocolla and pseudomalachite incorporate enough radioactive U and accommodate low but detectable amount of radiogenic Pb and common Pb. Pseudomalachite U-Pb dating has shown concordant to sub-concordant data which yield a crystallization age at *ca.* 19 Ma (Kahou et al., 2020). In the other hand, U-Pb analysis of black chrysocolla, which has a poorly crystallized structure (Newberg, 1967; Sun, 1963; Van Oosterwyck-Gastuche and Grégoire, 1971), displays a spreading of the data along the concordia, indicating a complex disturbed behavior of the U-Pb chronometer (see Fig. 3 and Fig. 4 in Kahou et al., 2020). According to Kahou et al. (2020), both pseudomalachite and black chrysocolla have a chronometric potential for U-Pb dating. However, understanding the causes of the disruption of the U-Pb chronometer system in these minerals is a real challenge.

Accordingly, the aim of this study is to compare geochronological data from chrysocolla and pseudomalachite minerals from three exotic copper deposits from Atacama Desert. These minerals were selected for U-Pb *in situ* dating coupled to U-Pb mapping and *in situ* oxygen stable isotope study. The main purpose is to discuss U-Pb behavior in their crystal-lattice structure and to link it to textural information to constrain the processes that disturb the chronometric system and determine in which

cases, i) U and common Pb are incorporated during initial crystallization ii) U and Pb are remobilized and iii) post-crystallization fluid circulation has affected the U-Pb chronometric signal. In parallel, these data will allow us to discuss the local geological and climatic parameters that control the U-Pb chronometer in these supergene copper minerals.

2. Geological Setting

This section will provide a brief description of the metallogenic framework of Atacama Desert of northern Chile. Each copper deposit (Mina Sur exotic SCM within the Chuquicamata mining district; Damiana exotic SCM within the El Salvador mining district and El Cobre exotic SCM within the Potrerillos mining district) has been extensively described by previous authors (Gustafson and Hunt, 1975; Marsh et al., 1997; Cornejo et al., 1997; Mote et al., 2001; Ossandón et al., 2001; Bissig and Riquelme, 2009, 2010; Rivera et al., 2012) and only the main relevant information will be given below.

The studied supergene porphyry copper deposits are localized within the late Eocene to early Oligocene copper belt of Atacama Desert which hosts the majority of giant copper deposits of Chile (Fig. 1). This belt was formed *ca.* 42 Ma ago during the Incaic orogeny, which gave birth to the Domeyko fault system also known as the Domeyko Cordillera. The hypogene hydrothermal activity responsible for the emplacement of the porphyry copper deposits occurred between 42-31 Ma while the supergene alteration took place about 10 Ma after the end of the hypogene activity, between 34 and 14 Ma (Sanchez et al., 2018; Sillitoe and McKee, 1996). From a geomorphological point of view, it seems that supergene alteration took place during the formation of large erosion surfaces (pediplains) in the Atacama Desert (Bissig and Riquelme, 2009; Hartley and Rice, 2005; Riquelme et al., 2017; Sanchez et al., 2018). The cessation of supergene activity, which is suggested to occur with the installation of the today-known hyperarid climate, is believed to take place during middle to late Miocene according to many authors (Arancibia et al., 2006; Bissig and Riquelme, 2010; Bouzari and Clark, 2002; Hartley and Rice, 2005; Marsh et al., 1997; Mote et al., 2001; Riquelme et al., 2017; Sillitoe and McKee, 1996).

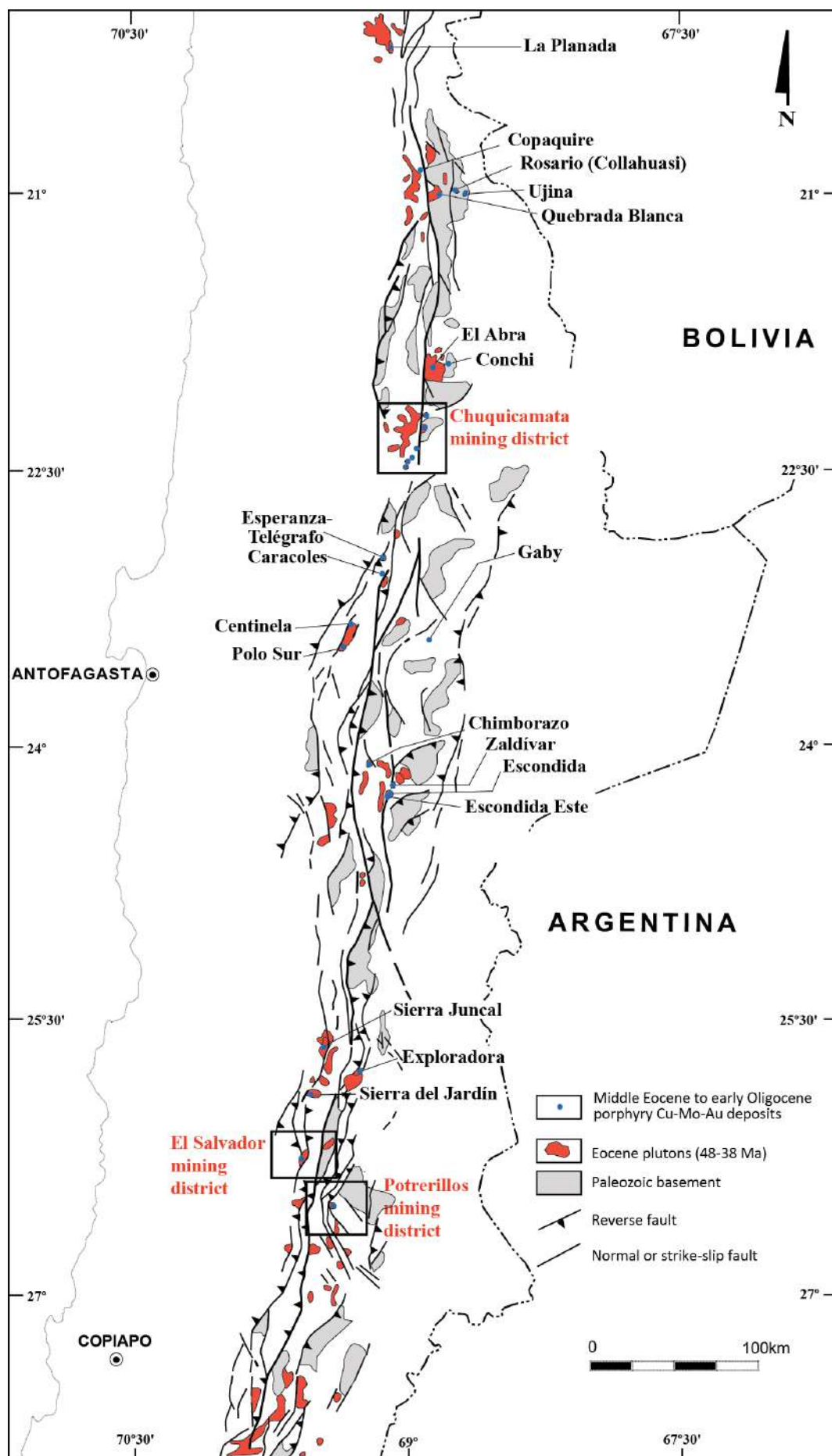
In the Chuquicamata mining district, samples were taken from the exotic SCM of Mina Sur which extends downstream 5 km away from the giant Chuquicamata porphyry copper deposit. In this area, the hypogene alteration was dated between 35 Ma and 33 Ma (Ballard et al., 2001; Campbell et al., 2006;

Rivera et al., 2012). The *in situ* supergene alteration at Chuquicamata was dated using K-Ar method on supergene alunites by Sillitoe and McKee (1996) and display results ranging from 15 Ma to 19 Ma. Until recently, the age of the exotic SCM from Mina Sur was only constrained by relative chronology of a tuff layer covering the district and giving a minimum age of $8.4 \text{ Ma} \pm 0.4 \text{ Ma}$ (Mortimer et al., 1977). Kahou et al. (2020) have recently carried out a detailed geochronological study establishing a U-Pb age on copper-rich minerals (pseudomalachite and black chrysocolla) at $18.4 \pm 1.0 \text{ Ma}$.

In the mining district of El Salvador, the hypogene hydrothermal alteration was dated between 44-45 Ma and 41 Ma (Cornejo et al., 1997; Gustafson and Hunt, 1975), while supergene alteration has been dated at 36 Ma (Gustafson and Hunt, 1975) and 23 Ma (Sillitoe and McKee, 1996). The Damiana exotic SCM, where the samples have been collected, is located approximately 6 km away from the porphyry source. This exotic deposit was dated using the $^{40}\text{Ar}/^{39}\text{Ar}$ method on alunite and copper wad (a term mainly used by miners to describe manganese, cobalt and iron-rich black copper silicate), between 35 Ma and 11 Ma, suggesting a long hydrothermal and supergene activity in this area (Mote et al., 2001).

At the Potrerillos mining district, hypogene hydrothermal alteration has been dated $\sim 35\text{-}36 \text{ Ma}$ ($^{40}\text{Ar}/^{39}\text{Ar}$ on amphibole; Marsh et al., 1997). The supergene alteration in this area is the youngest of all those recorded in the Domeyko Cordillera, i.e. between 6 and 9 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$ on alunite and jarosite; Marsh et al., 1997). The El Cobre exotic SCM is located about 4 km away from the porphyry source of Potrerillos and lies directly in the fractured and brecciated Paleocene volcanic and felsic rocks (Bissig and Riquelme, 2009). This exotic SCM has never been dated. The only age constraint, defined between 30 and 20 Ma, is given by the dating of the Sierra Checos del Cobre surface, which covers this deposit (Bissig and Riquelme, 2009).

Figure 1: Structural map of the Eocene-Oligocene copper belt (i.e. Domeyko cordillera) of northern Chile and the Domeyko Fault System showing the main tectonic features, the Paleozoic basement and the Eocene plutons and their porphyry stocks. Location of the copper mining districts studied are indicated by black squares. Simplified from Mpodozis and Cornejo (2012)



3. Analytical methods

3.1 *State of the art of U-Pb dating of unconventional minerals*

Some conventional accessory minerals such as zircon, monazite or baddeleyite are used extensively for dating geological events because, in addition to incorporate large quantities of U, they display no common Pb. Moreover, analytical advances have made possible to obtain standard reference materials for those minerals, required to overcoming analytical artefacts such as downhole U-Pb fractionation and matrix effects.

In contrast of conventional minerals (e.g. zircon, monazite, etc.), the difficulty of working with unconventional materials is that they may incorporate significant common Pb during their growth and have relatively low U and radiogenic Pb content (e.g. calcite; Roberts et al., 2017). Therefore, a correction of common Pb is necessary. This is done either by the analysis of co-genetic minerals with low U-Pb ratio or based on a choice of an initial Pb composition following the Stacey and Kramers (1975) model. Another constraint when dating unconventional minerals is the lack of known reference standards, used to correct for matrix effects and downhole U-Pb fractionation. Although reference standards are available for most of conventional minerals (e.g. GJ1 for zircon see Jackson et al., 2004; Moacir for monazite see Gasquet et al., 2010; Madagascar for apatite see Thomson et al., 2012), some conventional (e.g. allanite, titanite, etc.) and many unconventional minerals with a chronological potential, do not have a well-characterized reference standard. Hence, the correction of the U-Pb downhole fractionation and the matrix effects rely on the use of standards materials with similar optical and chemical properties, (i.e. using zircon reference material to standardize allanite mineral, two silicates-based materials; Boutin et al., 2016) and the use of a femtosecond (fs) laser ablation system that strongly reduces the inter-elemental fractionation (Poitrasson and d'Abzac, 2017).

3.2 *U-Pb in situ dating by LA-ICP-MS*

LA-ICP-MS dating technique requires the use of a “matrix-matching” standard in order to correct instruments drift and mass-bias during analyses (Schoene, 2014; Sylvester, 2008). However, U-Pb *in situ* dating of supergene copper minerals being a pioneering study, no chrysocolla and pseudomalachite

standards were available during this study. Therefore, we chose Zircon (GJ1 and Plešovice Zircons; Jackson et al., 2004; Sláma et al., 2008), a silicate-based standard, and apatite (Madagascar and Durango apatites; McDowell et al., 2005; Thomson et al., 2012), a phosphate-based standard, as analytical standards. To control the reproducibility and accuracy of the analyses, the U-Pb *in situ* dating were carried out in three different laboratories (i.e. Géosciences Rennes and GET laboratory in France and Trinity College Dublin in Ireland), with different equipment, but with the same analytical procedures: in all copper deposits, we first carried out the dating by using a ns-LA-Q-ICP-MS (at Rennes and Dublin) and to assess the potential elemental fractionation related to the use of a non-matrix-matched standards, additional analyses were carried out using a fs-LA-HR-ICP-MS (at GET laboratory, Toulouse) since the femtosecond laser has the advantage to minimize the elemental and isotopic fractionation and reduce the mass-bias (Poitrasson and d'Abzac, 2017; Russo et al., 2002). For each analytical session, the following standard bracketing control was carried out. Two analyses of the primary zircon (GJ1 zircon at Rennes and Toulouse, NIST 610 and 612 at Dublin) and apatite (Madagascar apatite in all laboratories) standard reference materials, one analysis on the secondary zircon (Plešovice zircon at Rennes and Toulouse, 91500 zircon at Dublin) and apatite (Durango and McClure apatites at Rennes, Durango apatite at Dublin and Toulouse) control standards, followed by the ablation spots of the chrysocolla, black chrysocolla and pseudomalachite materials. The analytical session ends with one analysis of the secondary control standard and two analyses of the primary standard reference materials. The analytical methods and instrumental conditions used in each laboratory are outlined in ESM 1. Data reduction was carried out with the data reduction scheme VizualAge_UcomPbine, a set of Iolite procedures that work with Igor Pro (Chew et al., 2014). Tera-Wasserburg concordia diagrams were generated using Isoplot 4 (Ludwig, 2008). Isotopic ratios and uncertainties (2σ errors) as well as apparent ages are reported in ESM 2. Uranium, Thorium and Lead content were obtained related to the primary standards. For black chrysocolla and pseudomalachite from Mina Sur, isotopic ratios and apparent ages are already reported in appendices 2 from chapter V.

3.3 U-Pb image mapping by LA-ICP-MS

Uranium and lead mapping was performed at the Trinity College of Dublin (Ireland), using an Ultra-short pulse Excimer Photon Machines 193nm ArF nanosecond laser ablation system with a two-volume ablation cell coupled to a Thermo-Fisher iCAP Qs, Q-ICP-MS (for detailed analytical procedures see ESM 1 Table 2). The analyses were performed with a short pulse duration ($< 4\text{ns}$), a short-energy of 1.2 J/cm^2 , a high repetition rate of 55 Hz and a square spot size of $12\text{ }\mu\text{m}$ and a laser scan speed of $30\text{ }\mu\text{m/s}$. Chrysocolla, black chrysocolla and pseudomalachite samples were ablated along successive linear scans (or raster) of $\sim 1.126\text{ mm}$ with no overlaps between the line scans. Chrysocolla, black chrysocolla and pseudomalachite aerosol were transported to the ICP-MS by a gas mixture of Helium (0.5 L/min) and Argon Fluoride (ArF) to reduce oxide formation. Tuning of the instrumentation and mass calibration of the Q-ICP-MS were performed on NIST SRM 612 and NIST SRM 610 reference glasses. Zircon 91500 and BCR2G glass as well as Madagascar and Durango apatites were used as secondary control standard for chrysocolla, black chrysocolla and pseudomalachite, respectively. To extract U and Pb distribution maps, data were processed using Trace_Elements data reduction scheme in Iolite (Paton et al., 2011, 2010) and the semi-quantitative standardization method. The U-Pb age maps have been extracted from the isotopic distribution maps, using the Monocle add-on for Iolite (Petrus et al., 2017). Data processing in Iolite for elemental distribution map extraction and further U-Pb 2-dimensional map extraction via Monocle is described in Drost et al. (2018).

3.4 Oxygen stable isotope analysis

Oxygen stable isotope analyses of chrysocolla, black chrysocolla and pseudomalachite were conducted on thin sections at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France) using the CAMECA IMS 1270 Ion microprobe. Two samples from Mina Sur exotic SCM as well as one sample from each other single deposit were analyzed. The primary Cs^+ was accelerated at 20 kV with a current intensity of 10 nA. Each spot consists of 30 counting cycles of 5 seconds each with a step of $40\text{ }\mu\text{m}$ for the profiles. Both ^{16}O and ^{18}O intensities were measured in a multi-collection mode using two Faraday cups. The internal standards used to correct data for instrumental fractionation are Durango Monazite (Trotter et al., 2008) for pseudomalachite and San Carlos Olivine (Wostbrock et

al., 2020) for chrysocolla and black chrysocolla. Note that due to the absence of chrysocolla and pseudomalachite standards, the absolute values are insignificant. Data are reported in ESM 3.

4. Samples description

In the following, we describe the ore deposit petrography of each sample collected, with a focus on chrysocolla, black chrysocolla and pseudomalachite, and present the chemical features of these minerals. Textural features have been obtained using optical microscopy and the JEOL JSM 6360LV scanning electron microscope (SEM) coupled to an energy dispersive spectrometry (EDS) analysis system at Géosciences Environnement Toulouse (GET, Université de Toulouse, France). The analytical conditions were 15kV for the acceleration voltage and 50 μm for the beam size. Quantitative analyses (major and minor elements) have been obtained using the CAMECA SX Five electron probe microanalyser (EPMA) at the Centre de Microcaractérisation Raimond Castaing (Université de Toulouse, France) (see Kahou et al. (2020) for details analytical condition details).

4.1 Textural characterization of chrysocollas and pseudomalachite

At Mina Sur, copper mineralization is mainly composed of black chrysocolla (*a.k.a* copper pitch or Mn-rich chrysocolla), chrysocolla, pseudomalachite (Fig. 2A). This sample has been previously described in details in Kahou et al. (2020). Black chrysocolla appears as reworked angular clasts, showing a concentric banding texture under plane polarized light (Fig. 2B). Chrysocolla and pseudomalachite appear as thick-size bands, coating black chrysocolla and the sedimentary gravels (Fig. 2B). Chrysocolla shows a pale to light-green color while pseudomalachite displays an emerald-green color and a low pleochroism (Fig. 2B). Finally, atacamite overgrowths on both chrysocolla and pseudomalachite (Fig. 2C).

At Damiana, the copper mineralization appears as a blue-color cement, coating clasts and mineralized gravels (Fig. 2D). Under plane-polarized light, this blue-like cement can be recognized as chrysocolla, which shows thin bands, light-green color, coating the sedimentary clasts (Fig. 2E). Pseudomalachite fills empty spaces within the porosity of the gravels (Fig. 2E) and shows a green color with a low pleochroism under plane-polarized light. BSE images (Fig. 2F) reveal a clear textural

relationship with i) chrysocolla, with a banded texture, coating gravels ii) pseudomalachite filling empty spaces, and finally, iii) apatite as overgrowing on chrysocolla, which indicates a late crystallization.

At El Cobre, the copper ore is hosted within the fractured and altered andesite bedrock and appear as a blue patina (Fig. 2G). Chrysocolla is the dominant supergene copper species, followed by pseudomalachite and minor copper wad. Chrysocolla appears as thin-size bands, with a banded texture, coating copper wad and filling fractures of the bedrock (Fig. 2H). Pseudomalachite appears as a green heterogeneous masses, with a core to rim texture, filling empty spaces, contemporaneously with amorphous silica (Fig. 2H). Under SEM (Fig. 2I), copper wad exhibits a banded texture, followed by chrysocolla, which shows a quite homogenous texture and is coated by pseudomalachite.

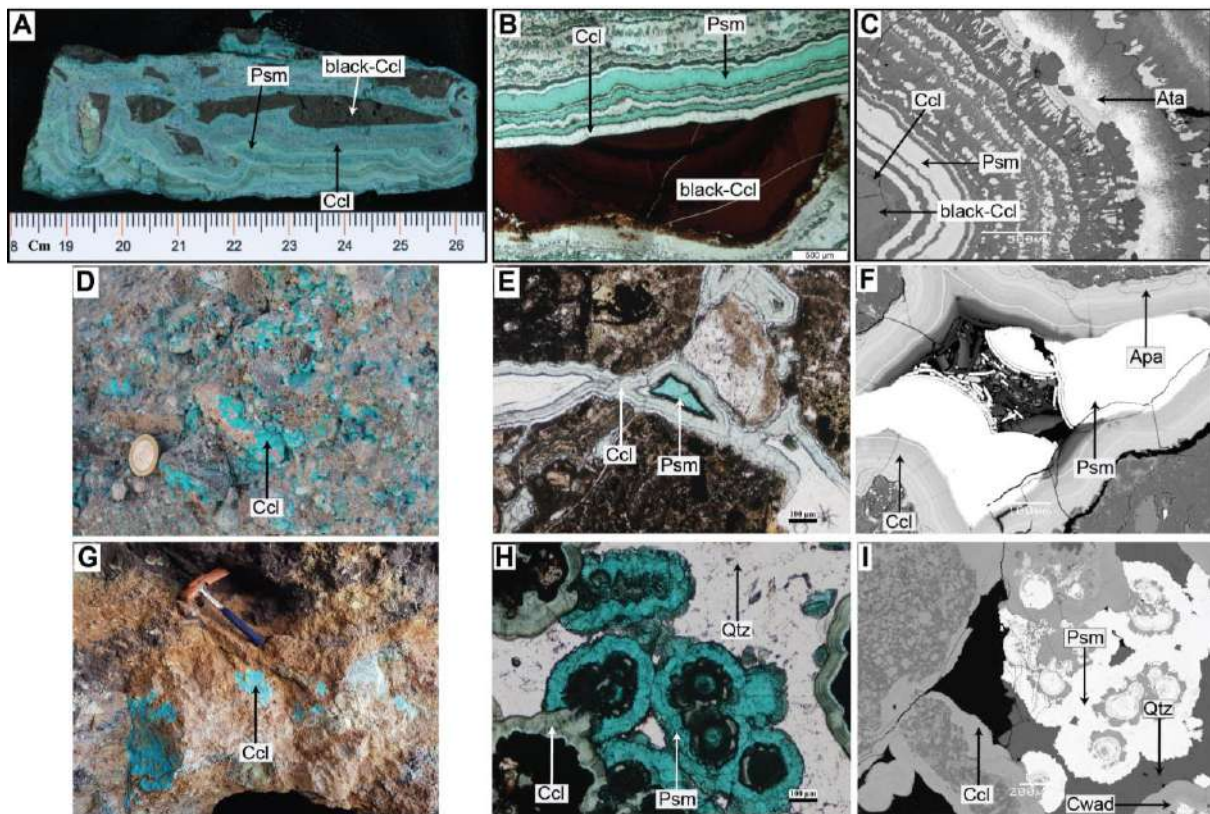


Figure 2: Sample and thin sections photographs showing the textural relationships between Mina Sur, Damiana and El Cobre copper minerals. A) Black chrysocolla (black-Ccl) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. B) Plane-polarized light photograph showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. C) SEM photomicrographs showing black chrysocolla clast (black-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite (Ata) prismatic crystals on chrysocolla and pseudomalachite. D) Chrysocolla (Ccl) filling empty spaces and porosity of the gravels. E) Plane-polarized light and F) SEM photomicrographs showing chrysocolla (Ccl) filling porosity of the gravels and pseudomalachite (Psm) crystallizing in empty spaces and an

overgrowth of apatite (Apa) on chrysocolla. **G)** Chrysocolla (Ccl) filling fractures of the altered andesite bedrock. **H)** Plane-polarized light photograph showing chrysocolla (Ccl), pseudomalachite (Psm) with an inherited core texture and amorphous quartz (Qtz) filling empty spaces filling fractures of the andesite bedrock. **I)** SEM photomicrographs showing copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl), pseudomalachite (Psm) and amorphous quartz filling empty spaces

4.2 Chemical compositions of chrysocollas and pseudomalachite

Chemical characterization of chrysocolla, black chrysocolla and pseudomalachite are summarized in ESM 4 (EPMA) and shown in Fig. 3.

Chrysocolla chemical composition is rather homogeneous between all the exotic SCM. Chrysocolla contains mainly SiO₂ (up to 50 wt. %) and CuO (up to 40 wt. %) and a variable amount of H₂O (between 0-20 wt. %; Fig. 3A). Minor elements such as CaO and Al₂O₃ can also be found. Compared to chrysocolla, black chrysocolla contains more MnO (between 2-10 wt. %, Fig. 3B), which gives the black color to chrysocolla. The CuO content within black chrysocolla is quite the same than chrysocolla with around ~ 45-50 wt. %. Black chrysocolla also contains high proportion of SiO₂ (20-40 wt. %) and H₂O (10-20 Wt. %). Pseudomalachite shows high CuO content (up to 70 wt. %), SiO₂ values between 20 wt. % and 25 wt. % and H₂O values from 5 wt. % up to 10 wt. % (Fig. 3C). Minor amounts of CaO, SiO₂ and Al₂O₃ are also included within the chemistry of pseudomalachite.

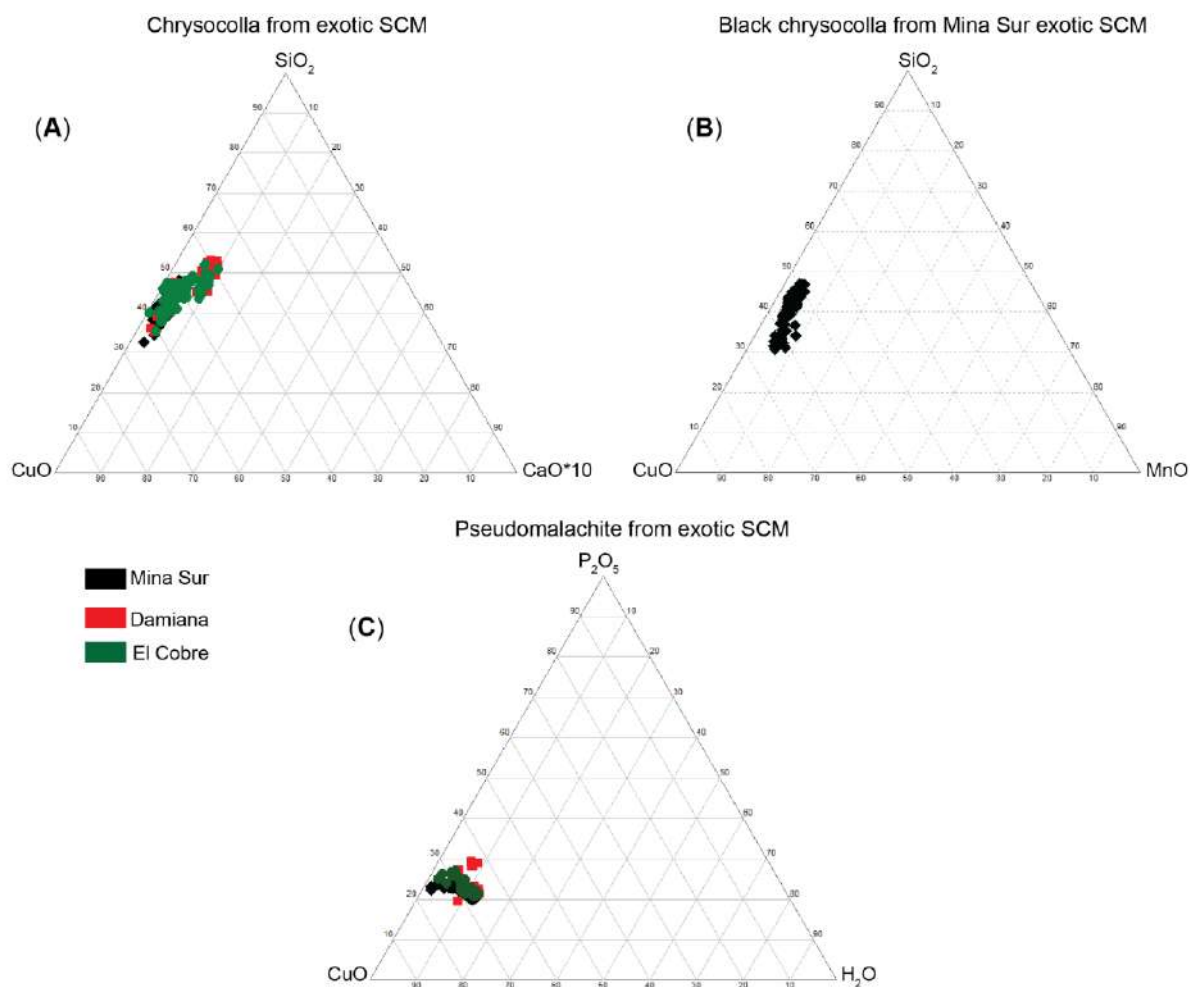


Figure 3: Representative diagrams of chrysocolla, black chrysocolla and pseudomalachite EPMA chemical composition showing in Triplot diagrams. **A)** chrysocolla chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM. **B)** Black chrysocolla chemical analyses from Mina Sur exotic SCM. **C)** Pseudomalachite chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM

5. Results

5.1 U-Pb LA-ICP-MS in situ dating of chrysocolla, black chrysocolla and pseudomalachite

At Mina Sur, U-Pb dating has been performed on chrysocolla, black chrysocolla and pseudomalachite. The analyses were performed both at Géosciences Rennes and at GET laboratory with a ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS, respectively.

In the chrysocolla bands, fifteen ns-LA-Q-ICP-MS analyses from a thin-size band show high U content (~ 500 ppm), a slight common Pb contribution but a radiogenic lead content extremely low to obtain a significant chronometric signal (see ESM 2 Table 1).

In the black chrysocolla clasts, 96 ns-LA and 133 fs-LA analyses have been carried out. In both analyses, U (~1200–1400 ppm) and Pb (~ 1 to 9 ppm) content exceed the detection limit. Plotted in a Tera-Wasserburg concordia diagram (Fig. 4A, B), the ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS data are concordant to slightly discordant. This slightly discordant position is attributed to a small common Pb contribution. Both ns-LA and fs-LA data are spreading over a range of isotopic ratios and apparent $^{206}\text{Pb}/^{238}\text{U}$ ages from 13.7 ± 0.5 Ma down to 6.1 ± 0.3 Ma and from 19.7 ± 5.0 Ma to 8.5 ± 2.0 Ma, respectively.

Thirty-six ns-LA and 90 fs-LA analyses were performed in the thin-size bands of pseudomalachite. The data display high U (~ 800-1000 ppm) and measurable Pb (~ 0.04 ppm) content. A small common Pb contribution was highlighted by a low counts of ^{208}Pb while ^{232}Th is absent (Andersen, 2002). In a Tera-Wasserburg concordia diagram, the ns-LA-Q-ICP-MS data are concordant and define a concordant age of 19.5 ± 0.2 Ma (MSWD = 2.5; Fig. 4C, D). The fs-LA-HR-ICP-MS data plot in a concordant to slightly discordant position (Fig. 4E). If the discordia is forced to a $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.837 calculated using the Stacey and Kramers Pb evolution model at 19 Ma, the lower intercept yields an age of 18.0 ± 0.1 Ma (MSWD = 2.3; Fig. 4E, F).

To understand the U-Pb distribution within chrysocolla, black chrysocolla and pseudomalachite, the ^{238}U and ^{206}Pb image mapping have been carried out at the transition between the three minerals (Fig. 5A, B), and within the black chrysocolla clasts (Fig. 5C, D). We can see a homogeneous distribution of ^{238}U within the three minerals and a zoning of ^{206}Pb within the black chrysocolla clast whilst this ^{206}Pb zoning is clearly absent inside the chrysocolla and pseudomalachite bands. If we focus on black chrysocolla, ^{238}U distribution map (Fig. 5C) is clearly homogenous while the mapping of ^{206}Pb show a perfect zoning (Fig. 5D), matching the oscillatory growth texture of black chrysocolla. This radiogenic lead zoning translates into a zoning of the apparent $^{206}\text{Pb}/^{238}\text{U}$ ages observed in the black chrysocolla from ca. 5 Ma to ca. 20 Ma (Fig. 5E).

At Damiana, the analyses have been carried out on chrysocolla and pseudomalachite at Trinity College Dublin and at GET laboratory. Within the chrysocolla bands, LA-ICP-MS data show a low but measurable U (~ 1-12 ppm) and Pb (~ 3.30-41.1 ppm) content. The ns- and fs-LA data show quite the same high common Pb contribution, i.e. $^{207}\text{Pb}/^{206}\text{Pb}$ initial values are almost identical and range between

0.750 and 1.030 for ns-LA and 0.76 and 1.50 for fs-LA. Plotted in a Tera-Wasserburg concordia diagram (Fig. 6A), the data are spreading along the discordia, highlighting a Pb loss. Therefore, since the lead signal is dominated by common lead, it was not possible to determine the crystallization age of chrysocolla.

For the pseudomalachite, both data obtained with ns-LA and fs-LA display low but measurable U content (~ 0.2 -12 ppm) and almost no radiogenic Pb (~ 0.17 -0.53 ppm) has been detected. When plotted in a Tera-Wasserburg concordia diagram (Fig. 6B), the data are scattering along the discordia curve, suggesting a Pb loss. Consequently, no U-Pb crystallization age has been obtained on pseudomalachite.

U-Pb distribution maps have been obtained on both chrysocolla and pseudomalachite (Fig. 6C). Chrysocolla texture consists of a thin-size bands, coating gravels while pseudomalachite shows a green mass, filling empty spaces (see Fig. 2E, F). ^{238}U shows a homogenous distribution within chrysocolla and pseudomalachite but with an increase of the concentration from center to rim of the pseudomalachite. ^{206}Pb and ^{204}Pb display homogenous distribution within both chrysocolla and pseudomalachite but low concentration of ^{206}Pb compared to relatively high ^{204}Pb content, especially within chrysocolla texture (see Fig. 6C).

At El Cobre, the analyses have been performed on both chrysocolla and pseudomalachite, at Trinity College Dublin and GET laboratory. For chrysocolla, ns- and fs-LA data display low but measurable U values (~ 1 -5 ppm) and high Pb concentration (average ~ 12 ppm). In a Tera-Wasserburg concordia diagram (Fig. 6D), both ns-LA and fs-LA data plot in a very discordant position, highlighting a high common lead contribution (i.e. initial $^{207}\text{Pb}/^{206}\text{Pb}$ values is 0.8 and 0.9 in average for ns-LA and fs-LA, respectively). Consequently, those data do not allow to extract a date.

For pseudomalachite, ns- and fs-LA analyses yielded low but measurable U content (average 3.1 ppm and 2.4 ppm, respectively), while Pb concentration was below detection limit. In a Tera-Wasserburg diagram, the analyses plot below the concordia curve, highlighting a preferential loss of U and/or gain of Pb (Fig. 6E).

The elemental ratio maps have been obtained on chrysocolla and pseudomalachite which present the same textural features than those from Damiana (see Fig. 2H, I). The ^{238}U , ^{206}Pb and ^{204}Pb

distribution maps (Fig. 6F) show a homogenous distribution of these isotopes within chrysocolla, with a higher amount of ^{204}Pb than ^{206}Pb . For pseudomalachite, the distribution maps of the three isotopes show a core to rim zoning as highlighted by the textural features (see Fig. 2I).

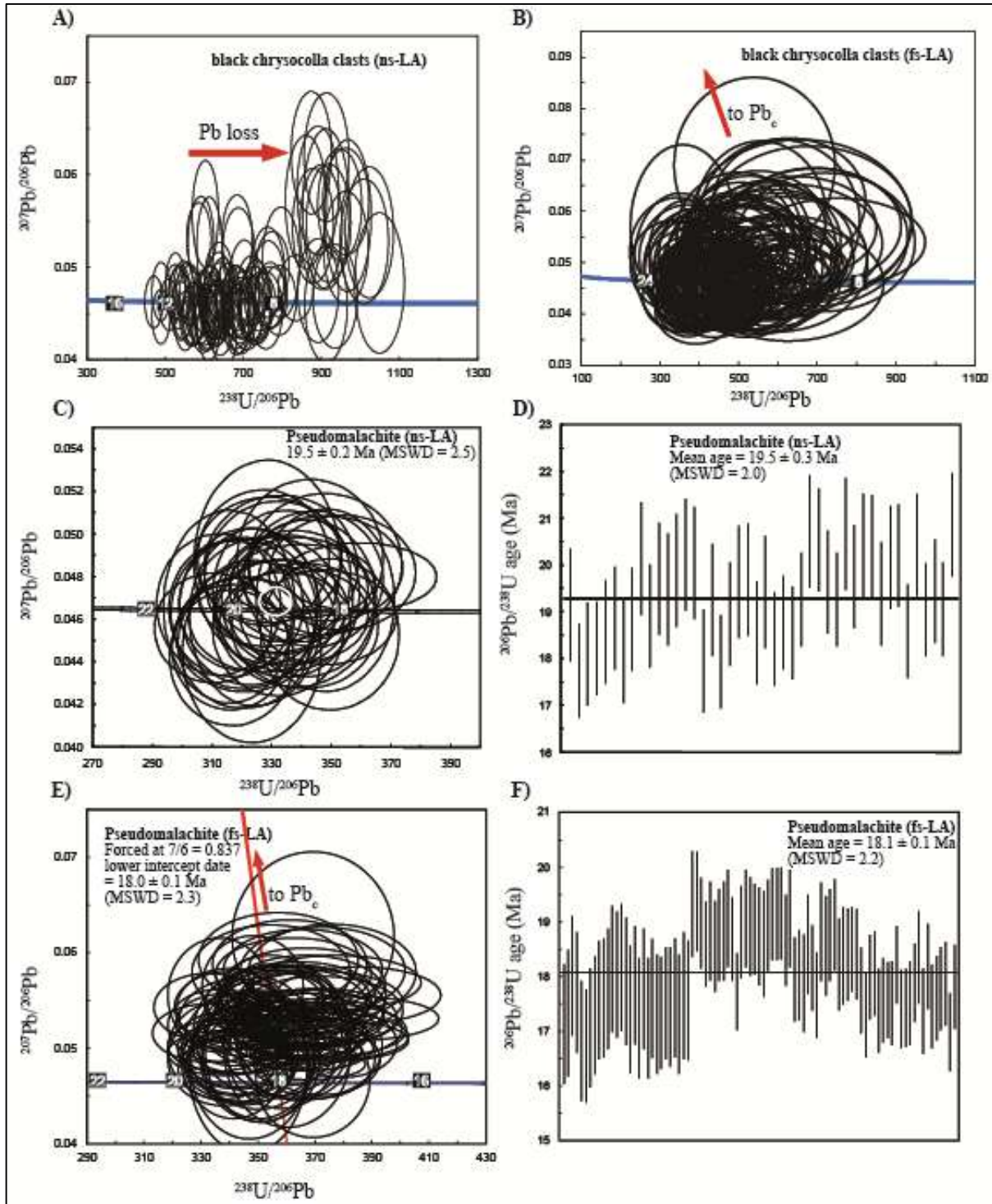


Figure 4: Tera-Wasserburg concordia diagrams and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagrams displaying the analyses made on black chrysocolla and pseudomalachite from Mina Sur exotic SCM. **A)** Tera-Wasserburg concordia diagram of black chrysocolla made by ns-LA-Q-ICP-MS. **B)** Tera-Wasserburg concordia diagram of black

chrysocolla made by fs-LA-HR-ICP-MS. C) Tera-Wasserburg concordia diagram and D) corresponding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite made on ns-LA-Q-ICP-MS. E) Tera-Wasserburg concordia diagram and F) corresponding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ diagram for pseudomalachite made on fs-LA-HR-ICP-MS

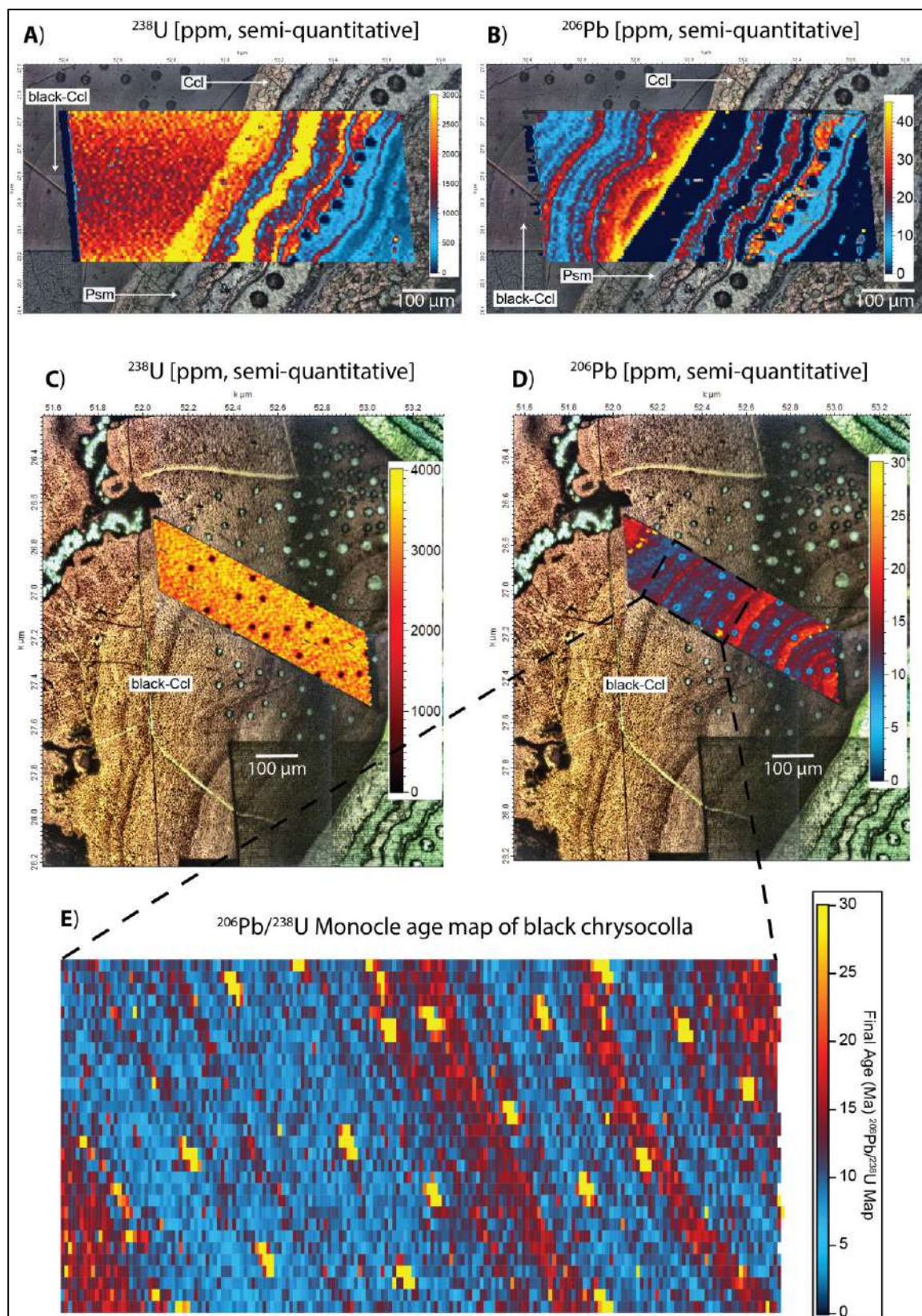


Figure 5: ^{238}U and ^{206}Pb isotopes and maps made on the transition between **A, B)** Black chrysocolla, chrysocolla and pseudomalachite and within **C, D)** Black chrysocolla from Mina Sur exotic SCM. **E)** $^{206}\text{Pb}/^{238}\text{U}$ monocle age map made within black chrysocolla from Mina Sur exotic SCM. The black square represents the area used to produce monocle map

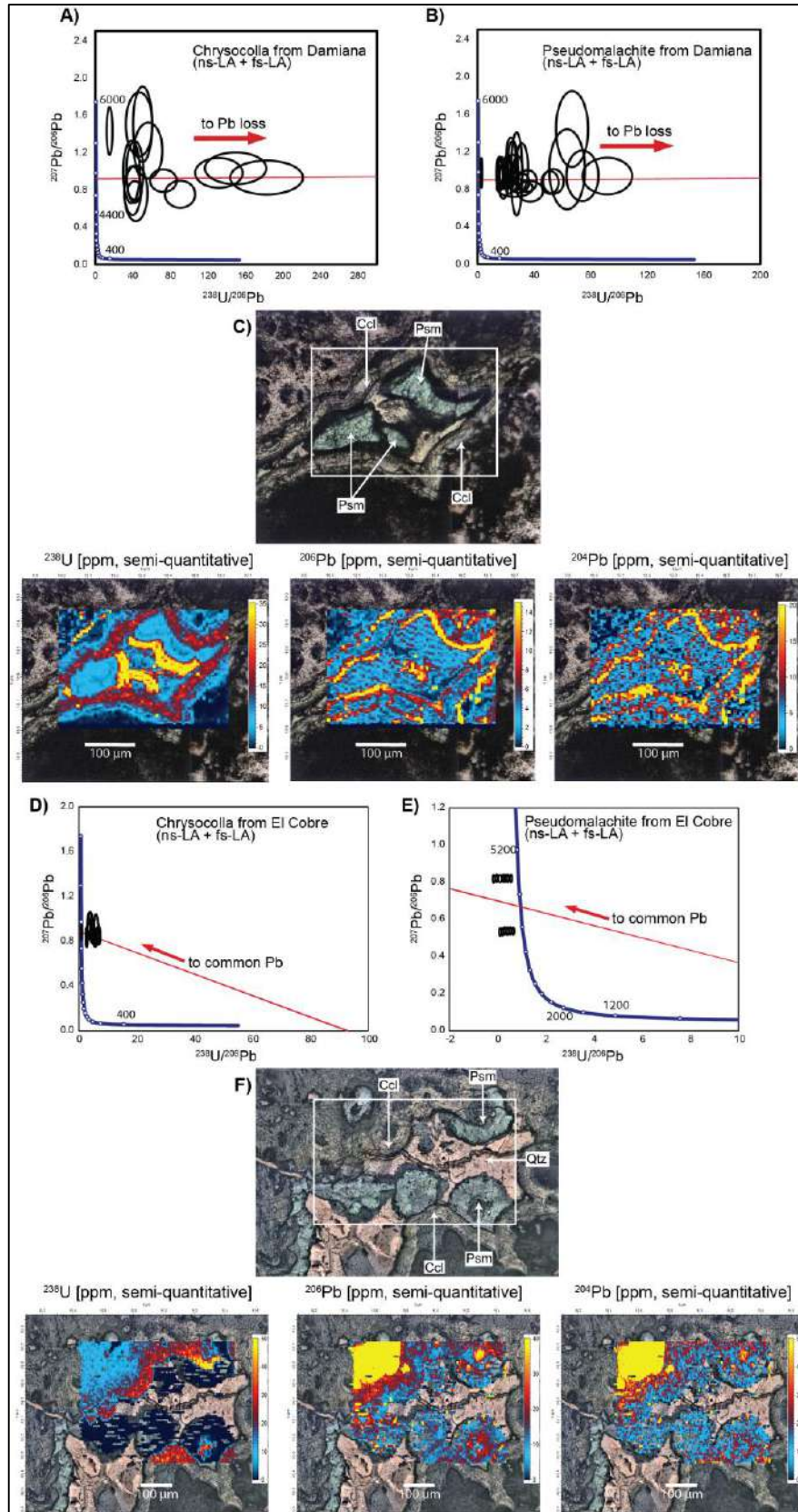


Figure 6: Tera-Wasserburg concordia diagram of **A)** chrysocolla and **B)** pseudomalachite made by ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS and **C)** ^{238}U , ^{206}Pb and ^{204}Pb isotopes and maps made on the transition between chrysocolla and pseudomalachite from Damiana exotic SCM. Tera-Wasserburg concordia diagram of **D)** chrysocolla and **E)** pseudomalachite made by ns-LA-Q-ICP-MS and fs-LA-HR-ICP-MS and **F)** ^{238}U , ^{206}Pb and ^{204}Pb elemental ratio made on the transition between chrysocolla and pseudomalachite from El Cobre exotic SCM

5.2 Oxygen isotope in situ analyses

On the sample from Mina Sur, one traverse has been performed across the oscillatory growth zoning texture of black chrysocolla, and analyses on spots have been done along chrysocolla and pseudomalachite bands, respectively (Fig. 7A). The $\delta^{18}\text{O}$ profile in black chrysocolla presents oscillatory zoning that mimics the growth zoning texture, superimposed on a global increase of the $\delta^{18}\text{O}$ value from $0.37 \pm 0.14 \text{ ‰}$ to $3.71 \pm 0.16 \text{ ‰}$ toward the rim (Fig. 7B). The $\delta^{18}\text{O}$ profile along chrysocolla bands exhibits high $\delta^{18}\text{O}$ with the average value at $15.53 \pm 0.09 \text{ ‰}$ (Fig. 7C). Within the pseudomalachite bands, the profile displays negative values with a $\delta^{18}\text{O}$ variation from $-14.41 \pm 0.06 \text{ ‰}$ to $-17.53 \pm 0.09 \text{ ‰}$ (Fig. 7D).

At Damiana, oxygen isotope composition was analyzed only on spots on chrysocolla and pseudomalachite (Fig. 7E). For chrysocolla, the $\delta^{18}\text{O}$ values show an oscillatory zoning (Fig. 7F) between $6.09 \pm 0.10 \text{ ‰}$ and $14.07 \pm 0.10 \text{ ‰}$, according to the growth zoning texture observed within the chrysocolla bands (see transect A-A' in Fig. 7E). Nine spots have been made on pseudomalachite. The $\delta^{18}\text{O}$ values are quite homogenous with the average $-11.98 \pm 0.09 \text{ ‰}$ (lowest value at $-11.72 \pm 0.11 \text{ ‰}$ and highest value at $-12.22 \pm 0.09 \text{ ‰}$, Fig. 7G).

At El Cobre, $\delta^{18}\text{O}$ values of chrysocolla and pseudomalachite have been realized on spots following straight line (Fig. 7H). Chrysocolla is characterized by $\delta^{18}\text{O}$ values scattered between $0.68 \pm 0.18 \text{ ‰}$ and $9.06 \pm 0.18 \text{ ‰}$ ($n=7$; Fig. 7I). The $\delta^{18}\text{O}$ values of pseudomalachite is characterized by an almost homogenous value around $-20.06 \pm 0.14 \text{ ‰}$ in average (from $-22.29 \pm 0.10 \text{ ‰}$ up to $-18.73 \pm 0.13 \text{ ‰}$; Fig. 7J).

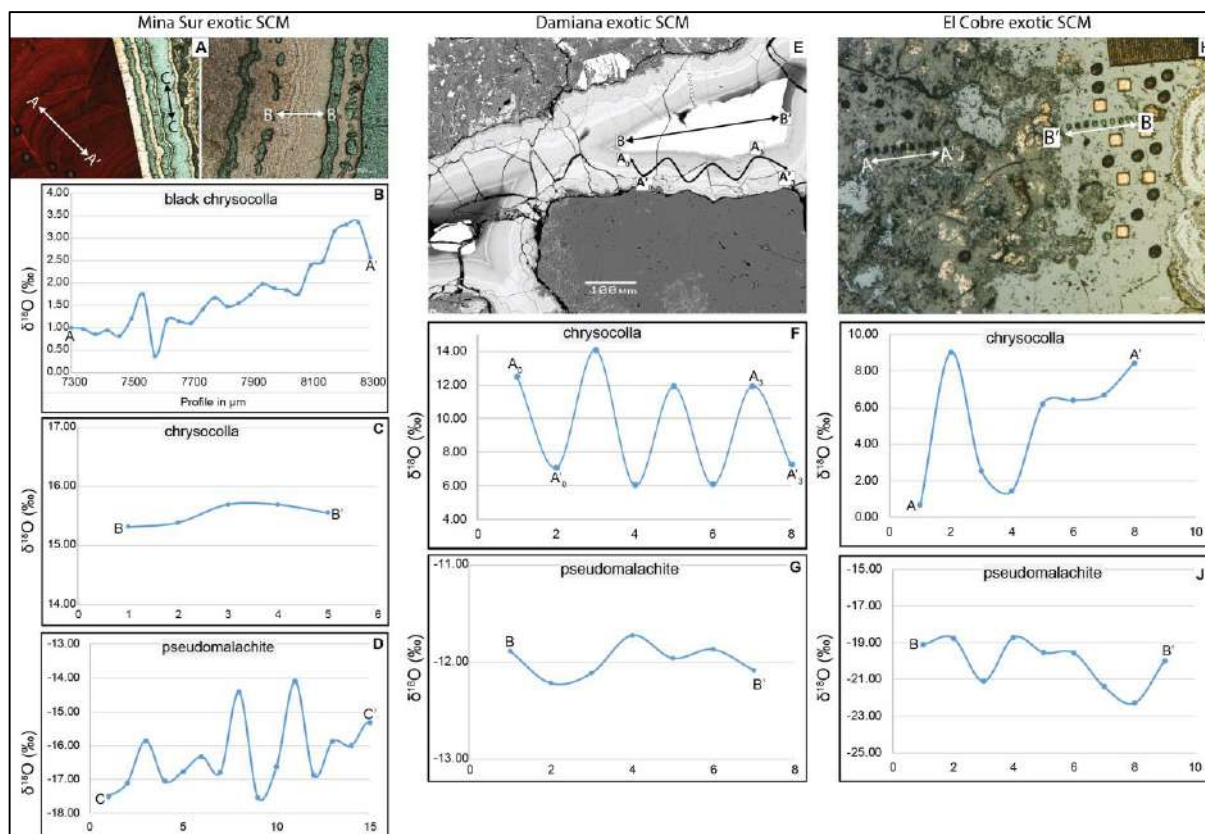


Figure 7: $\delta^{18}\text{O}$ isotope profiles in black chrysocolla, chrysocolla and pseudomalachite from Mina Sur, Damiana and El Cobre exotic SCM. Pictures A), E) and H) show the location of the $\delta^{18}\text{O}$ profile made on each single mineral. The graphs B), C) and D) represent the A-A', B-B', C-C' $\delta^{18}\text{O}$ profile made on black chrysocolla, chrysocolla and pseudomalachite from the picture A) from Mina Sur exotic SCM. The graphs F) and G) represent the A-A' and B-B' $\delta^{18}\text{O}$ profile along chrysocolla and pseudomalachite from the picture E) from Damiana exotic SCM. The graphs I) and J) represent the A-A' and B-B' $\delta^{18}\text{O}$ profile along chrysocolla and pseudomalachite from the picture H) from El Cobre exotic SCM

6. Discussion

6.1 U-Pb in pseudomalachite from Mina Sur: a chronometer for dating SCM formation

LA-ICP-MS U-Pb analysis of the exotic SCM of Mina Sur has shown the ability of pseudomalachite to preserve a chronometric signal. Within this deposit, a lower intercept date at 18.4 ± 1.0 Ma has been obtained on pseudomalachite (Kahou et al., 2020). The high U content, the measurable radiogenic Pb and the minor common Pb contribution allow us to conclude that pseudomalachite mineralization was emplaced ~ 19 m.y. ago. Hence, pseudomalachite structure has been shown to present a well-crystallized structure (Berry, 1950; Shoemaker et al., 1977) and therefore can be strongly resistant to late supergene fluid circulation. Moreover, the consistency of the analysis

on individual spots on different bands suggest that pseudomalachite crystallize in a single stage event. A good initial chemical equilibrium is attested by the homogenous distribution of the U and Pb distribution maps. Moreover, despite a slight variation of ~3‰ of the $\delta^{18}\text{O}$ value, it seems that pseudomalachite grew in an isotopic equilibrium and remained in a closed system (Talbot, 1990). These lines of evidence allow us to define pseudomalachite, at the Mina Sur exotic SCM, a strongly reliable U-Pb chronometer. Considering the U-Pb date obtained on pseudomalachite, we can infer that supergene alteration in the Chuquicamata mining district and the formation of Mina Sur exotic deposition started as early as 19 Ma, about 11 m.y. after the unroofing of the Chuquicamata porphyry (Maksaev and Zentilli, 1999) and is in agreement with the supergene alteration ages already known in this mining district (between 19 Ma and 15 Ma, K-Ar dating on supergene alunites; Sillitoe and McKee, 1996).

6.2 Initial U and common Pb content in chrysocolla and pseudomalachite

6.2.1 Uranium content in chrysocolla and pseudomalachite

Except for Mina Sur exotic SCM, chrysocolla and pseudomalachite from all the other deposits display low U content and relatively low radiogenic Pb/common Pb ratio (see ESM 2). Chrysocolla from Damiana and El Cobre exhibits U content between ~1-12 ppm and ~1-5 ppm, whilst pseudomalachite shows U content between ~0.44-12.50 ppm and ~1.44-3.71 ppm, respectively. As shown, chrysocolla and pseudomalachite are U-poor minerals. The low U content induces low radiogenic Pb content in those minerals in most cases, preventing a quantitative interpretation of the U-Pb data. As indicated earlier, chrysocolla and pseudomalachite can, in some cases, incorporate much higher U as evidenced by the U concentrations observed in chrysocolla and pseudomalachite of Mina Sur (U content is around ~ 1000 ppm and ~ 800 ppm for chrysocolla and pseudomalachite, respectively), identical to what can be found in zircon and monazite. Two hypotheses can be formulated to explain this U content variation in both chrysocolla and pseudomalachite between Mina Sur on the one hand and Damiana and El Cobre on the other hand. The first hypothesis is that the variable U content of the mineralizing fluid is directly related to different U content of the porphyry sources that host primary mineralization and/or of the rocks that host the exotic SCM. It is difficult to test this hypothesis since

whole-rock analyses that report U content are only available for Chuquicamata porphyry bodies that are the source of Mina Sur deposit (U whole-rock content is around ~ 2-3 ppm; Campbell et al., 2006) but not for porphyries that could be linked to Damiana and El Cobre deposits. The second hypothesis relates to the supergene processes and the dissolution of U-rich phases into meteoric fluids. Numerous studies have demonstrated that Damiana and El Cobre areas have experienced supergene alteration much longer than the rest of the Atacama Desert (i.e. from 34 Ma up to 5 Ma; Marsh et al., 1997; Bissig and Riquelme, 2009, 2010). Furthermore, previous studies have shown that the oxidation state of U change to hexavalent uranyl ion (UO_2^{2+}) during supergene alteration (Cathelineau, 1983; Cuney, 2009; Leroy and Turpin, 1988; Tartese et al., 2013). Once U has reached its hexavalent state, it will become more leachable by oxidized fluids and transported out from the uranium minerals (e.g. pitchblende) or U-bearing minerals (e.g. zircon, monazite, apatite, etc.). Oxidizing conditions and continuous leaching would thus progressively deplete in U the source region for late supergene mineralizing fluids and be responsible for the low U content encountered within chrysocolla and pseudomalachite at Damiana and El Cobre deposits.

6.2.2 Radiogenic Pb/common Pb ratio in chrysocolla and pseudomalachite

As illustrated by the Tera-Wasserburg concordia diagrams shown in Fig. 6, chrysocolla and pseudomalachite from Damiana and El Cobre exhibit very low radiogenic Pb/common Pb ratio. Consequently, the data spread along the discordia curve, close to the initial common Pb value. To determine a crystallization age with such data set is challenging, and requires a large common Pb correction.

Several other accessory minerals such as apatite or titanite incorporate low U and high common Pb content during crystallization. As shown by Chew et al. (2011), apatite, a common accessory mineral in igneous rocks and low temperature hydrothermal system, can display, like chrysocolla and pseudomalachite from Damiana and El Cobre, low U and high common Pb contents which is routinely corrected for U-Th-Pb dating (Chew et al., 2016, 2014). However, in the case of the copper minerals from Atacama Desert, the radiogenic Pb content is particularly low, due to the combination of i) low U content of the minerals and ii) young Oligo-Miocene age of supergene alteration (Hartley and Rice,

2005; Riquelme et al., 2017; Sillitoe, 2005; Sillitoe and McKee, 1996). As a result, uranium did not have time to produce enough radiogenic lead, and the correction of the common Pb component to the total lead results into any relevant ages. In comparison, WC-1 calcite reference standard material, which displays low U content and incorporated common Pb during its growth, is sufficiently old (i.e. 254.4 ± 6.4 Ma; Roberts et al., 2017) to allow the radiogenic Pb to dominate the total Pb isotope composition (i.e. $85\% < \text{radiogenic Pb} < 98\%$; Roberts et al., 2017) and permit a proper correction to define a U-Pb age.

6.3 Post-growth U and Pb mobility

6.3.1 Homogeneization in black chrysocolla

At Mina Sur exotic SCM, U-Pb data obtained on black chrysocolla show a large scattering along the concordia from ca. 19.7 Ma to ca. 6.1 Ma. Despite the high U and Pb contents and the negligible common Pb content (ESM 2 from chapter V), we cannot define a single crystallization event due to age dispersion along the concordia. This scattering suggests either a juxtaposition of crystal domains of different ages and/or U- and Pb- mobility due to fluid/mineral interaction. The hypothesis of mixing of different age domain can be discussed by the $^{206}\text{Pb}/^{238}\text{U}$ age map on black chrysocolla (Fig. 5E) which show different $^{206}\text{Pb}/^{238}\text{U}$ apparent ages domain following the colloform texture. This could indicate that crystallization of black chrysocolla is characterized by the gradual addition, over time, of fluids of various chemical and isotopic composition as suggested by Barrie et al. (2009) to explain crystallization of colloform texture of sphalerite from Galmoy orebody in Ireland. Likewise, numerous studies (Didier et al., 2015; Gasquet et al., 2010; Goncalves, 2005) have shown that monazite can present U-Pb discordant ages due to mixing domain of changing chemical and elemental composition. For example, Didier et al. (2015) have demonstrated, by Nano SIMS mapping, that the chemical zonation of monazite can be related to age domains mixing. However, in our case, the zoning of the $^{206}\text{Pb}/^{238}\text{U}$ ages (Fig. 5E) does not follow an evolution from the oldest at the core to the most recent at the rim. This shows that the formation of black chrysocolla is not the result of the successive crystallization of the colloform layers from ca. 19 Ma to ca. 6 Ma.

Furthermore, as shown by the isotope distribution maps (Fig. 5C, D), the ^{206}Pb clearly shows that radiogenic Pb concentration are zoned accordingly to oscillatory growth of the mineral while the ^{238}U concentration is homogenous. The radiogenic Pb zoning is not supported by U zoning. This could be explained by a late U homogenization, maybe favored by a long-term fluid circulation event that affect black chrysocolla or could correspond to post-crystallization fluid circulation. The $\delta^{18}\text{O}$ analyses of black chrysocolla (Fig. 7B) show that the oxygen isotope zoning matches the textural and chemical variation (oscillatory zoning superimposed on a global outward increase of $\delta^{18}\text{O}$). The presence of growth-related oscillatory ^{206}Pb zoning (Fig. 5D), unsupported by ^{238}U zoning (Fig. 5C) indicates post-growth homogenization of U at crystal scale, while $\delta^{18}\text{O}$ growth zoning was also preserved (Fig. 7B). In the state of our knowledge, we were not able to discuss in detail which process can homogenize U signal while preserve the Pb zoning, but the preservation of $\delta^{18}\text{O}$ growth zoning precludes massive fluid circulation and rather suggest solid state diffusion of U.

It appears that black chrysocolla can be subjected to post-crystallization U-mobility inducing U homogenization rather than Pb loss. Post-crystallization U-mobility can be enhanced by the crystal-lattice structure of black chrysocolla. Black chrysocolla presents a poorly-defined structure such as chrysocolla (Menzies et al., 2015; Pincheira et al., 2003a, 2003b). It has been shown by Bruguiere (2009) that silicate minerals have flexible crystalline structure allowing variable-angle bonding leading to poorly-crystalline states which can make easier element mobility. Moreover, Geisler et al. (2007), and references therein, have demonstrated that element mobility can be facilitated in silicates (e.g. zircon) due to open-system behavior at low temperature hydrothermal system due to self-irradiation enhanced by high-U content. Therefore, high U content encountered in black chrysocolla, coupled to its mineraloid texture, could explain U mobility within its structure.

6.3.2 Radiogenic Pb loss in chrysocolla

U-Pb data from the chrysocolla bands from the Mina Sur deposit show high U content, a significant common Pb contribution and an almost complete lack of radiogenic Pb as highlighted by the $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratios (ESM 2 Table 1). This low radiogenic Pb proportion, in spite of high U content, could be explained by a relatively recent age of chrysocolla formation and would

imply that U does not have the time to decay into radiogenic Pb or would be the result of the radiogenic Pb mobility by post-crystallization late fluid circulation. The hypothesis of a recent age of chrysocolla formation was discussed by Reich et al. (2008) and Reich et al. (2009). They have shown, in the Chuquicamata mining district, thanks to the dating of atacamite crystallization, that supergene alteration and, therefore, the circulation of mineralizing fluids were active until late Pleistocene (~ 240 ka). This argument shows that chrysocolla could have formed during the Pleistocene, thus leaving not enough time for the decay, along the time, of U into radiogenic Pb. However, this argument is swept away by the textural observations. Indeed, the textural features show that chrysocolla bands are intercalated between black chrysocolla and the pseudomalachite bands dated at ca. 19 Ma. Consequently, the hypothesis of recent crystallization of the chrysocolla bands is hardly plausible. In addition, as illustrated in Table 1 from ESM 2, if the precipitation of the chrysocolla bands is guessed to occur ca. 19 Ma (such as pseudomalachite bands), the radiogenic Pb content supposed to be obtained and those obtained after the U-Pb analyses militate for a mobility of radiogenic Pb.

The $\delta^{18}\text{O}$ analyses of chrysocolla, which display a flat profile (Fig. 7C), are not supported by its mammillary banded texture (Fig. 7A) which reflect a chemical and isotopic change of the mineralizing fluid. The $\delta^{18}\text{O}$ flat profile suggests that a late fluid circulation has homogenized the initial $\delta^{18}\text{O}$ values since the initial precipitation of the chrysocolla bands. Its therefore implies that late fluid circulation has significantly affected the chrysocolla depositional environment and leached radiogenic Pb from chrysocolla structure.

6.3.3 U and Pb behavior in chrysocolla and pseudomalachite

As highlighted in the Tera-Wasserburg diagrams (Fig. 6A, B, D and E) for Damiana and El Cobre samples, chrysocolla and pseudomalachite data are spreading along a discordia parallel to the base of the concordia curve. This suggests either U or Pb mobility by post-crystallization fluid-rock interaction or a recent age of precipitation of both minerals.

Episodic post-crystallization Pb loss at low temperature (< 200°C) due to fluid-rock interaction have been demonstrated by Geisler et al. (2007) and Xu et al. (2012) for zircon, and Poitrasson et al. (2000) for monazite, although both minerals are highly resistant to alteration. Moreover, Reddy et al.

(2006) has shown that crystal plastic deformation in zircon, caused by low temperature hydrothermal alteration, can promote Pb mobility outside zircon. Similarly, Cherniak (1997) has shown that calcite is highly susceptible to alteration or recrystallization at low temperature and can be subjected to Pb mobility by diffusion. In the case of chrysocolla, Helle and Kelm (2005) have demonstrated that it is soluble in low temperature supergene system, inducing potential U and Pb mobility. Uranium and lead mobility within chrysocolla and pseudomalachite may be favored by their crystal-lattice structure. Chrysocolla has been defined as a mineraloid (or a gel-like material) with a weakly-defined crystal structure (Frost and Xi, 2013; Newberg, 1967; Sun, 1963) which argue in favor of U and/or Pb loss through mobility within chrysocolla structure. In comparison, pseudomalachite has a well-crystallized structure (Berry, 1950; Shoemaker et al., 1977), favorable to preserve the U-Pb chronometric signal. However, at Damiana and El Cobre, pseudomalachite appears as late-filling empty spaces within gravels (see Fig. 2E, F for Damiana) and exhibits heterogenous masses with inherited core texture (see Fig. 2H, I for El Cobre). This inherited core texture is also highlighted by the isotope distribution mass within pseudomalachite, which clearly exhibits a concentric zoning of ^{238}U and ^{206}Pb (Fig. 6F). This chemical zoning could reflect fluid-mineral element transfer recording or reflects dissolution-reprecipitation processes, leading sometimes to the disturbance of the U-Pb chronometer as described by Didier et al. (2015) for monazite from a restitic xenolith from the Central Slovakia Volcanic Field.

At Damiana and El Cobre, the $\delta^{18}\text{O}$ analyses of pseudomalachite display a minor variation among minerals correlated to a slight zoning diffusion of $\delta^{18}\text{O}$ within its structure (Fig. 7D, G, J). Therefore, $\delta^{18}\text{O}$ values seems to have been preserved within pseudomalachite since its initial crystallization and was not significantly affected by later fluid circulation. For chrysocolla, $\delta^{18}\text{O}$ analyses have shown that oxygen isotope zoning matches the chemical zoning, especially at Damiana (Fig. 7E, F). This suggests that during crystallization, chemical and isotopic composition of the fluids have changed. This also means that no late fluid has resetted and homogenized the initial isotopic record. Consequently, for chrysocolla and pseudomalachite from Damiana and El Cobre, low U and radiogenic Pb/common Pb ratio coupled to the fact that no U-Pb geochronological data can be extract from the analyses is probably related to the recent crystallization age of chrysocolla and pseudomalachite and/or the composition of

the depositional environment (i.e. few U content in the porphyry source) rather than U and Pb mobility due to late fluid circulation.

6.4 Geological and climatic controls on U-Pb chronometer in supergene copper minerals from Atacama Desert

In Atacama Desert of northern Chile, the geological and climatic parameters controlling the formation of supergene copper minerals are well-known and result from a subtle balance between tectonic uplift to exhume the primary copper mineralization, adequate precipitation to leach copper and precipitate the supergene copper minerals (i.e. secondary sulfides and oxidized copper minerals) and moderate erosion to preserve the supergene column formed. In addition to these regional geological parameters, local parameters such as the initial U content of the porphyry, age and duration of supergene alteration and the presence or absence of post-crystallization fluids are the main factors that control the U-Pb chronometer in these supergene copper minerals.

In the Chuquicamata mining district, whole-rock analyses from the parental porphyry copper of the Mina Sur exotic SCM showed high U values that are reflected in the supergene copper minerals from this exotic deposition, i.e. pseudomalachite, black chrysocolla and chrysocolla have average U content $> \sim 500$ ppm. Within this mining district, supergene alteration has been documented by Sillitoe and McKee (1996) to have occurred between ca. 19 Ma and ca. 15 Ma. This supergene alteration, although recent at the geological time scale, allowed the decay of U to radiogenic Pb into measurable proportions. Thereafter, the installation of a hyperarid climate between middle and late Miocene inhibited the circulation of post-crystallization fluids and allowed the preservation of the U-Pb signal in the pseudomalachite bands in which a formation age of ca. 19 Ma was reported by Kahou et al. (2020) and this study. However, as illustrated by Reich et al. (2009), late fluid circulations occurred in the Chuquicamata mining district at ~ 240 ka to promote atacamite formation. These post-hyperarid saline fluid circulations could therefore explain the leaching of radiogenic Pb from the chrysocolla bands, enhanced by its weak crystalline structure.

In the southern part of the Atacama Desert, tectonic and climatic conditions were different from those in the north, suggesting an asynchronous duration of supergene alteration of porphyry copper and

a different formation age of the supergene copper mineralization. If in the northern part of the Atacama Desert, the tectonic event responsible for the supergene alteration took place only during the Incaic phase (42-33 Ma; Maksaev and Zentilli, 1999), in Damiana and El Cobre areas, the Quechua tectonic event, between middle and late Miocene (Kay et al., 1999; McKee and Noble, 1989), followed the Incaic orogeny. In Salvador region, the Quechua event favored the incision of erosion surfaces and the formation of large canyons (Salado and Asiento canyons; Bissig and Riquelme, 2010). This incision has favored the descent of the phreatic level and promoted recent episodes of supergene alteration in Salvador area (Bissig and Riquelme, 2010). At El Cobre, the Quechua phase allowed the elevation of the area to about 4000 m a.s.l., favoring capture of moisture and thus the availability of meteoric waters to favor a continuous episode of supergene alteration during middle to late Miocene period (Bissig and Riquelme, 2010, 2009). These tectonic episodes could therefore suggest a recent age of formation of chrysocolla and pseudomalachite and could explain the low U obtained for both minerals. On the other hand, these low U content and common Pb/radiogenic Pb ratios could be the result of a permanent fluid circulation since the beginning of the supergene alteration which will either i) leach, along time, U from the parent porphyry and thus explain the absence of high U content in chrysocolla and pseudomalachite from the exotic deposits of Damiana and El Cobre or ii) favor the behavior of the minerals in open system and thus allow the mobility of U and/or Pb due to post-crystallization fluid circulation.

7. Summary and conclusions

The combination of U-Pb dating and mapping with oxygen isotope, textural and geochemical analyses provide a unique set of data to understand what control the preservation and disturbance of the U-Pb chronometer in supergene copper minerals.

- 1- Pseudomalachite from Mina Sur deposit is a reliable U-Pb chronometer to date supergene copper deposits. This mineral is weakly affected by late weathering/fluid circulation and keep U and Pb within his structure after its initial crystallization. However, as shown in Damiana and El Cobre deposits, only first-stage crystallization minerals in contrast to late-filling empty spaces have the capacity to keep U, accumulated radiogenic Pb and incorporated minor common Pb.

- 2- Black chrysocolla presents a chronometric potential given the U and radiogenic Pb content. However, the poorly crystallized structure and the high U content makes this mineral eligible to post-growth U homogenization by solid state diffusion.
- 3- Attempts to date chrysocolla have been unsuccessful. The high common Pb content, more abundant than radiogenic Pb, found in all the deposits, lead us to say that chrysocolla is a mineral, like apatite or titanite, which incorporates common Pb during its initial crystallization. Common Pb comes possibly from destruction of Pb-rich minerals (e.g. apatite) during supergene alteration of the porphyry copper. At Mina Sur, in spite of high U encountered, almost no radiogenic Pb has been detected, suggesting a leaching by post-crystallization fluid circulation that oxygen isotope analyses have confirmed. At Damiana and El Cobre, low U content and radiogenic Pb/common Pb ratio in chrysocolla and pseudomalachite suggest low U incorporation during minerals precipitation due to the few U content in the porphyry source. $\delta^{18}\text{O}$ seems to have been preserved in chrysocolla and pseudomalachite and allow us to argue that low U content are mainly caused by low U grades in the mineralizing fluids rather than leaching by post-crystallization fluid circulation.

Finally, to be able to properly explain the isotopic preservation and disturbance of U-Pb chronometer of supergene copper minerals, further investigation should be carry out, in particular to link nanoscale textural characterization to geochronological results by identifying the emplacement sites of U and Pb atoms in the lattice structure and understand the mechanisms behind U and Pb mobility at the nanoscale. Quantitative isotope analyses as well as fluid inclusion studies could also be appropriate to better understand U and Pb mobility process and know what kind of fluid (e.g. alkali, acidic, saline basinal brines, etc.) can disturb the U-Pb chronometer. Furthermore, as it has been shown that exotic copper mineralization is a microbial-involved process (Nelson et al., 2007; Sillitoe et al., 1996), further investigations should take into account bacterial activity as possible factors of U content variation within chrysocolla and pseudomalachite from the mining districts studied.

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VI.2 Insights of the timing of supergene copper mineralization in the Gaoua porphyry Cu-Au district, southwestern of Burkina Faso

Introduction & geological background

The Gaoua porphyry Cu-Au district, located in the southeastern area of Burkina Faso, is part of the West African craton (WAC) which consists of an Archean core, juxtaposed against Paleoproterozoic greenstone belts *a.k.a* Boromo-Goren greenstone belt in Burkina Faso (Fig. VI.2.A; Baratoux et al., 2011). Paleoproterozoic greenstone belt of WAC took place during the Eburnean orogeny, about 2.25 Ga to 2.15 Ga (Baratoux et al., 2011). These Boromo-Goren greenstone belt consists of volcanic to plutonic rocks affected by a regional metamorphism, mainly greenschist facies. These volcano-plutonic rocks were intruded by granitoids and deformed successively by three deformation stages (Baratoux et al., 2015, 2011; Béziat et al., 2008). At a local scale, the Gaoua district is located at the southwestern margin of the Boromo Belt (Fig. VI.2.B). The basement comprises a thick-sequence of mafic rocks (i.e. gabbro, basalt, andesite), followed by calc-alkaline intrusive bodies (diorite, granodiorite, dolerite, granite, rhyolite). All the series have undergone a regional greenschist-facies metamorphism (Baratoux et al., 2015). Hypogene copper mineralization is hosted by the greenschist facies volcanic flows and quartz-diorite intrusions (Le Mignot et al., 2017). These hypogene copper ore are present as veins, hydrothermal breccia filling and dissemination within quartz-diorite porphyry stocks (Le Mignot et al., 2017).

Supergene copper mineralization (SCM) of Gaoua district is linked to the Tertiary history of the West African craton linked to the opening of the Atlantic sea. During Cenozoic times, the installation of a hot and wet tropical climate, alternating with dry seasons, in this tectonically stable craton and the low denudation rates (2-20 m/Ma; see Beauvais and Chardon, 2013), allowed the formation of large and flat erosion surfaces *a.k.a* pediplains. These pediplains, which result from chemical and mechanical alteration of the bedrock (i.e. Birimian greenstone belts; Gunnell, 2003), sometimes overlie supergene mineralization of various economic importance, i.e. manganese at Tambao, and copper at Gaoua (Chardon et al., 2018). However, to the best of our knowledge, no studies have been published about the recognition and/or the characterization of SCM of Gaoua porphyry copper district. Here we present

new mineralogical (see chapter III), geochronological and oxygen isotope studies in order to discuss the timing of formation of supergene copper mineralization within the mining district and linked it to the Cenozoic evolution of the West African craton.

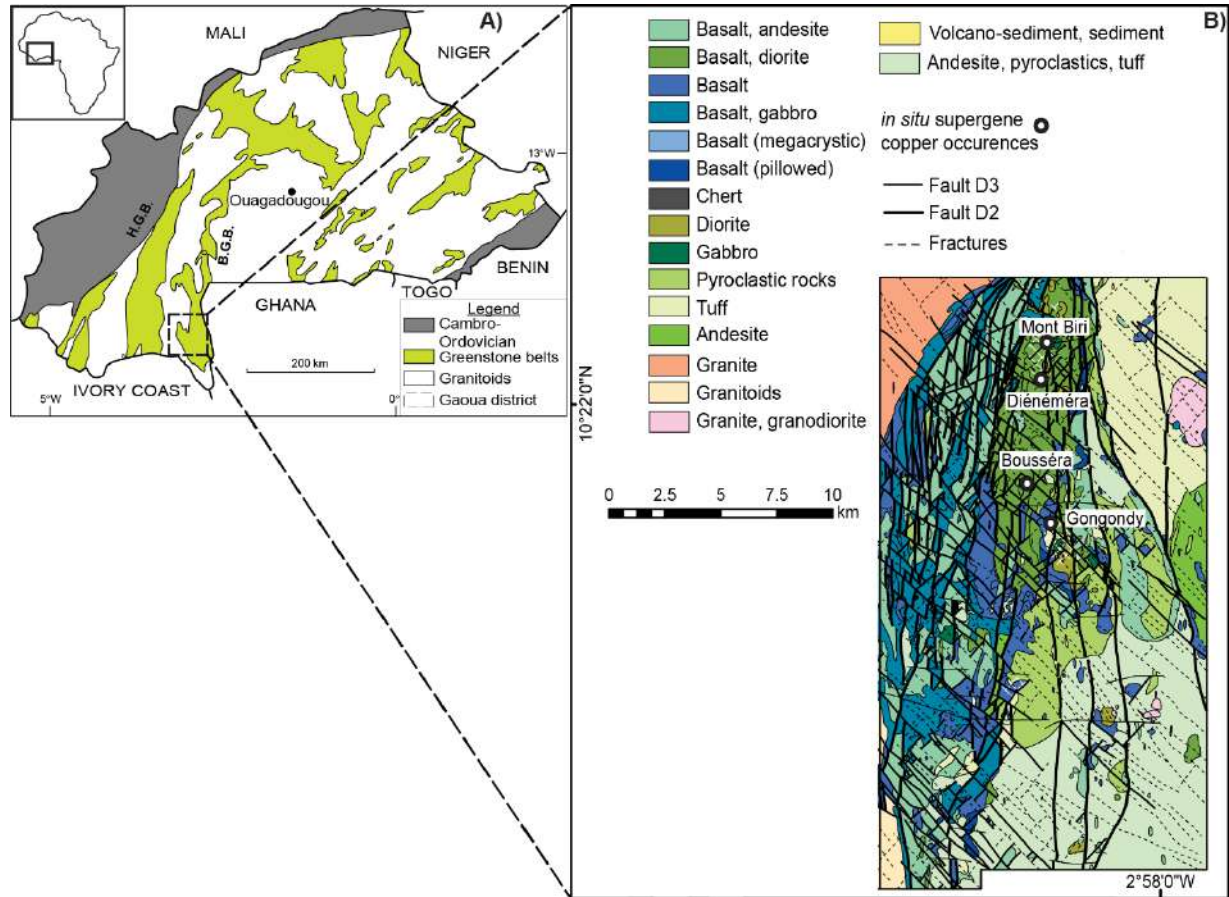


Figure VI.2.1: Location and geological map of the Gaoua porphyry Cu-Au district. A) Black square represents the location of the Gaoua district within the geological map of Burkina Faso (after Béziat et al., 2008). B) Detailed geological map of the Gaoua Cu-Au district showing the location of the Mont Biri, Diénémara, Gongondy and Bousséra in situ supergene copper occurrences (Baratoux et al., 2015; Le Mignot et al., 2017)

Textural characterization of supergene copper ore

Except the unpublished report of Sillitoe (2007) within the Dienemera and Gongondy Cu-Au prospects, no other studies have been found in the available literature. The copper mineralization (i.e. primary sulfides) are within andesite and quartz-diorite porphyry stocks as disseminations, veins and hydrothermal breccia filling (Le Mignot et al., 2017). Oxidized SCM are hosted, as well as the primary sulfides, within the veins of the porphyries disseminated inside or filling it. The description of the

textural features as well as the chemical characterization have been done in the chapter III of the manuscript.

Results

U-Pb LA-ICP-MS *in situ* dating of chrysocolla

In this section, we present the U-Pb *in situ* dating results of chrysocolla. We first carried out the dating by using a ns-LA-Q-ICP-MS (i.e. at Trinity college Dublin) and to assess the potential elemental fractionation related to the use of a non-matrix-matched standards, additional analyses were carried out using a fs-LA-HR-ICP-MS (i.e. at GET laboratory, Toulouse) since the femtosecond laser has the advantage to minimize the isotopic fractionation and reduce the mass-bias (Poitrasson and d'Abzac, 2017). The results are shown in Fig. VI.2.2 and Table VI.2.1.

Six analyses were performed out on each ns- and fs-LA equipments. The U and Pb content were enough to obtain a chronometric signal with average ~ 39 ppm of U and 8 ppm of Pb on ns-LA and 18 ppm of U and 4 ppm of Pb on fs-LA, respectively. In a Tera-Wasserburg concordia diagram, both ns- and fs-LA data plot in a discordant position with a common Pb contribution (Fig. VI.2.2A, B). The unforced lower intercept date is 31 ± 22 Ma (MSWD = 0.85) and 0 ± 44 (MSWD = 0.36) for the ns- and fs-LA analyses, respectively. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios being almost identical, it becomes difficult to obtain a well constrained date in a Tera-Wasserburg concordia diagram. The U and Pb distribution maps (Fig. VI.2.2C) carried out on chrysocolla show a fairly homogenous distribution of ^{204}Pb and ^{206}Pb and slightly heterogenous distribution of ^{238}U , highlighting the heterogenous texture of chrysocolla with a lot of crystal inclusions or impurities.

Oxygen isotope *in situ* analyses

Oxygen isotope composition was carried out along one traverse in chrysocolla (Fig. VI.2.2D and Table 3). Fourteen spots were made in chrysocolla large area, close to U-Pb *in situ* dating spots ablation. The $\delta^{18}\text{O}$ values show a variation from 5.23 ± 0.19 ‰ to 13.19 ± 0.11 ‰ (average at 8.93 ‰). This isotopic variation could reflect the diffusive zoning of oxygen, enhanced by the textural heterogeneity/impurities of chrysocolla.

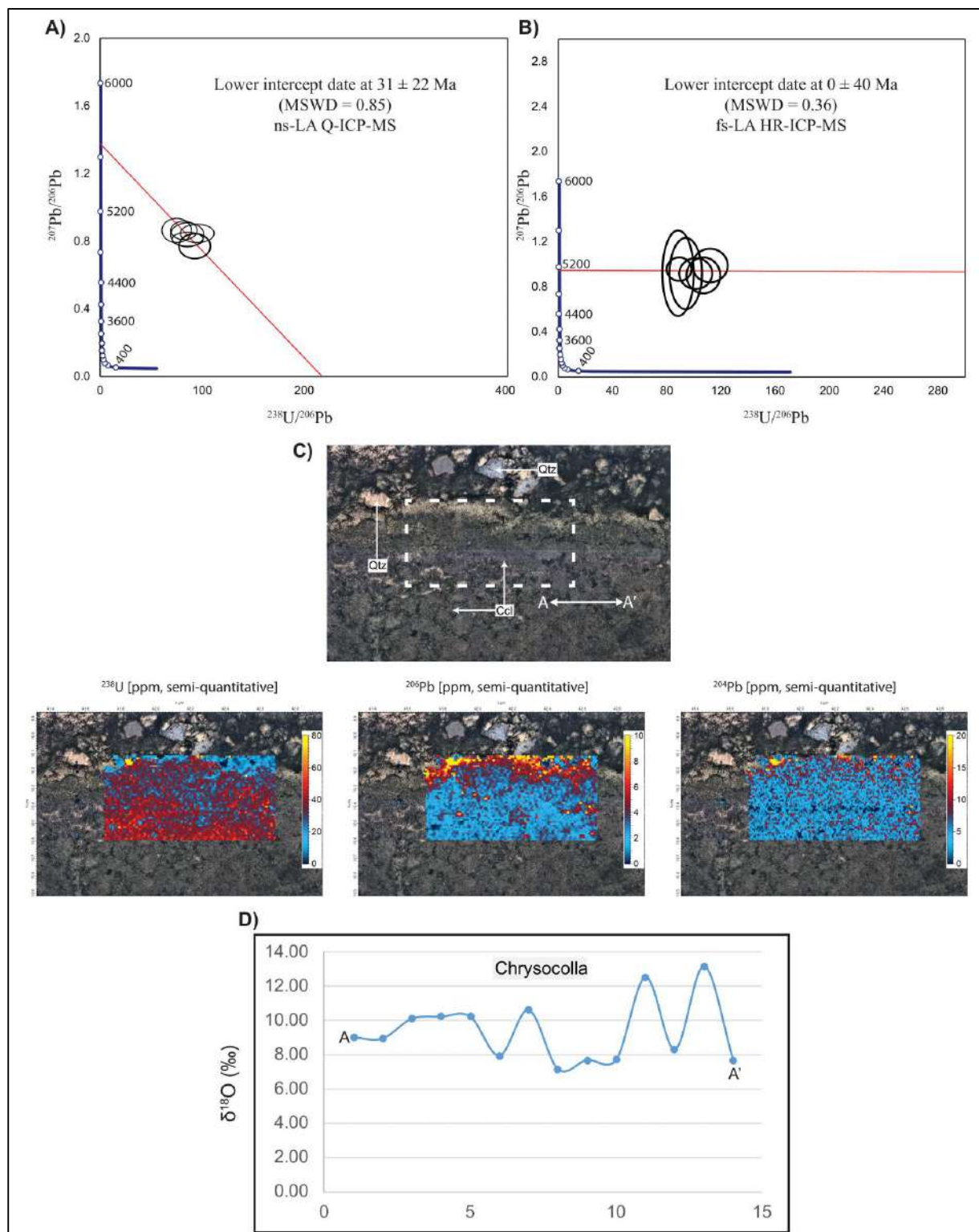


Figure VI.2.2: Tera-Wasserburg concordia diagrams of chrysocolla made by A) ns-LA-Q-ICP-MS and B) fs-LA-HR-ICP-MS. C) ^{238}U , ^{206}Pb and ^{204}Pb elemental ratio made on chrysocolla. D) $\delta^{18}\text{O}$ isotope A-A' profile made on chrysocolla. The distance between each spot is $40\ \mu\text{m}$

Table VI.2.1: U-Th-Pb data carried out on chrysocolla from ns-LA-Q-ICP-MS (Table 1) and fs-LA-HR-ICP-MS (Table 2) and Oxygen isotope analyses of chrysocolla (Table 3) from the Gaoua supergene copper ore

Table 1 U-Th-Pb ns-LA-Q-ICP-MS (Dublin) data carried out on chrysocolla							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
GM1_01	7.80	35.10	0.02	75.19	15.79	0.87	6.70
GM1_02	8.90	42.60	0.00	85.47	15.38	0.84	7.02
GM1_03	7.10	40.60	0.01	95.24	14.29	0.85	5.18
GM1_04	8.40	41.30	0.00	81.97	13.11	0.86	5.09
GM1_05	7.60	40.20	0.00	85.47	14.53	0.81	4.31
GM1_06	7.20	37.20	0.00	92.59	13.89	0.77	7.90

Table 2 U-Th-Pb fs-LA-HR-ICP-MS (Toulouse) data carried out on chrysocolla							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
GM-1.FIN2	3.24	16.64	0.01	94.34	10.38	0.92	28.26
GM-2.FIN2	2.51	15.84	0.01	106.95	9.52	0.90	14.44
GM-3.FIN2	2.94	18.09	0.01	111.86	9.51	0.99	12.12
GM-4.FIN2	3.58	16.38	0.02	88.50	10.62	0.92	33.70
GM-5.FIN2	4.28	19.58	0.03	89.45	8.32	0.96	8.85
GM-6.FIN2	3.68	20.10	0.02	101.32	9.83	0.92	11.96

Table 3 Oxygen isotope analyses for chrysocolla				
Spots	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
GM1-L1_01	1049189106	2176793	9.03	0.12
GM1-L1_02	1120699903	2320816	8.96	0.11
GM1-L1_03	1069681565	2220103	10.12	0.13
GM1-L1_04	1056530536	2193910	10.25	0.08
GM1-L1_05	1037024004	2154569	10.25	0.09
GM1-L1_06	794460432	1661254	7.96	0.15
GM1-L1_07	978764487	2037124	10.64	0.09
GM1-L1_08	1018843091	2111784	7.18	0.09
GM1-L1_09	992063135	2058490	7.71	0.13
GM1-L1_10	1008615794	2091847	7.74	0.12
GM1-L1_11	855056860	1790591	12.56	0.13
GM1-L1_12	985100032	2044681	8.34	0.18
GM1-L1_13	1024844272	2135535	13.19	0.11
GM1-L1_14	1005590411	2085995	7.68	0.29

Discussion

Chrysocolla from Gaoua: feasibility of U-Pb dating

Coupled ns- and fs-LA, both analyses show significant amount of U (~ 15-42 ppm), similar to those that could be detected in zircon (Hoskin and Schaltegger, 2003), offset however by a significant contribution of common Pb and a low proportion of radiogenic Pb. Furthermore, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are almost identical for both ns- and fs-LA analyses. The absence of a common Pb-rich cogenetic mineral as well as the high $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratios prevent an adequate common Pb correction. In this case, an accurate measurement of ^{204}Pb using a multi-collector (MC)-ICP-MS could allow to anchor a common Pb value, required to obtain a possible precipitation age of chrysocolla. Tera-Wasserburg concordia diagram, which display the data on the discordia curve could suggest a recent formation of chrysocolla with the U-Pb chronometer behaves in an open system. This open system behavior is corroborated by the amorphous crystalline structure of chrysocolla, which makes it an ideal candidate for U and/or Pb mobility that can lead to discordant ages. However, $\delta^{18}\text{O}$ analyses of chrysocolla which show a preservation of the heterogenous texture of chrysocolla, highlighting by the oscillatory profile (see Fig. 2D) would seem to indicate that this mineral has not undergone any post-crystallization fluid disturbance which could have reset the isotopic signal of oxygen and consequently favor U and/or Pb mobility.

Evidence of SCM formation during Cenozoic time

In the Cu-Au mining district of Gaoua, magmatic-hydrothermal activity has been dated from the Paleo-Proterozoic, i.e. between 2.2 and 2.1 Ga (Baratoux et al., 2011; Le Mignot et al., 2017). Such as the mining districts of the southern Atacama Desert (i.e. Salvador and Potrerillos), no data in the literature have published U whole-rock content, preventing any correlation between those U whole-rock content and the U concentrations obtained in chrysocolla. In Gaoua, supergene alteration took place throughout Cenozoic, contemporaneously with the formation of erosion surfaces and bauxitic crusts (Chardon et al., 2018). K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating carried out on the supergene manganese deposit of Tambao and on the pediplains have made possible to constrain the timing of supergene alteration in

the Gaoua district from late Paleocene to early Quaternary (Beauvais et al., 2008). Supergene alteration is credited to the wet/dry seasonal changes that have begun since the opening of the Atlantic Ocean (Séranne, 1999). Atlantic sea opening has favored the onset of a wet/dry climate in western Africa, which in turn favor slow denudation rates, and consequently a slow unroofing of the porphyry copper. The U-Pb dating of chrysocolla, which show very low radiogenic Pb content, compared to high common Pb contribution, could therefore reflect a recent crystallization age of chrysocolla enhanced by favorable geological and climatic conditions to permit SCM formation throughout the Cenozoic, i.e. low erosion rates and a relatively humid climate. Moreover, permanent supergene alteration throughout Cenozoic times corroborates the hypothesis of an uninterrupted fluid circulation that could facilitate the mobility of U from the depositional environment by oxidized fluids since it has been shown that U is easily leached in supergene fluids (Cuney, 2009; Tartese et al., 2013). Finally, the perennial settlement of an arid climate (i.e. Sahelian) contemporaneously with the Antarctic ice cap formation and the low erosion rates have undoubtedly allowed the preservation of the supergene copper mineralization of Gaoua without preventing the circulation of fluids that could precipitate chrysocolla and/or favor the mobility of the U and/or Pb from the existing chrysocolla.

Conclusion

Preliminary U-Pb dating results, combined to published geomorphological data militates for a recent age of chrysocolla formation, contemporaneously with the formation of West African pediments throughout Cenozoic. The depositional environment seems to be affected by the long-lived supergene alteration which favor chrysocolla formation from Paleocene to recent times. Nonetheless, these promising results need to be more investigated to precise the age of the SCM formation (i.e. more U-Pb dating spots and count ^{204}Pb on MC-ICP-MS) and understand what control the disturbance of the U-Pb ages (i.e. nature of the fluids via stable isotope oxygen on rock powder).

VI.3 U-Pb dating of calcite from Tesoro Central exotic copper mineralization: a window into post-crystallization fluid circulation?

As explained in the section VI.1 of this chapter, the discordance of U-Pb ages can be caused by multiple factors including i) mixing of different age domains ii) important common Pb contribution, and iii) U and/or Pb mobility by post-crystallisation fluid circulation. The latter is particularly enhanced by the poorly-crystallized structure of some minerals (e.g. chrysocolla in our study) or the behavior of some minerals in the presence of low temperature fluids (e.g. apatite; Chew et al., 2011).

In Atacama Desert, the circulation of meteoric fluids is linked to the supergene alteration that affect porphyry copper deposits in a semi-arid to arid climatic context. The latter occurred between ~ 15-19 Ma in the Chuquicamata mining district and from ~ 35 Ma up to ~ 6 Ma in the mining districts of El Salvador and Potrerillos. Subsequently, the onset of a hyper-arid climate inhibited the circulation of meteoric waters and thus, of fluids that could potentially disrupt the U-Pb chronometric signal.

In the Centinela mining district, 100 km south of the Chuquicamata mining district, the Tesoro Central mine exposes exotic copper mineralization hosted in Miocene-age sediments (Riquelme et al., 2017). The sedimentary context as well as the exotic copper mineralization have been described by Riquelme et al. (2017) and Fernández-Mort et al. (2018). This copper mineralization were dated between 10-14 Ma by Sanchez (2017) via cosmogenic nuclides. Crystallizing after the exotic mineralization, Fernández-Mort et al. (2018) highlighted the precipitation of mosaic calcite veins via diagenetic processes.

The U-Pb dating of the calcite veins (Fig. VI.3.1, Table VI.3.1 and ESM VI.3.1) was carried out in this thesis by ns-LA Q-ICP-MS at Geosciences Rennes. The results showed similar "free" and "forced" apparent ages between ca. 2 Ma and ca. 1 Ma (MSWD = 1.8). This absolute age shows that alkaline fluids, responsible for the precipitation of calcite, have circulated in the region long after the onset of the hyperarid climate. These alkaline fluids could be responsible for the precipitation of atacamite observed in the exotic copper mineralization of Mina Sur (see Chapter III), 100 km north of Tesoro Central mine, and could also explain the mobility of radiogenic Pb encountered in the chrysocolla bands of the copper mineralization of Mina Sur as explained in section VI.1 of this chapter.

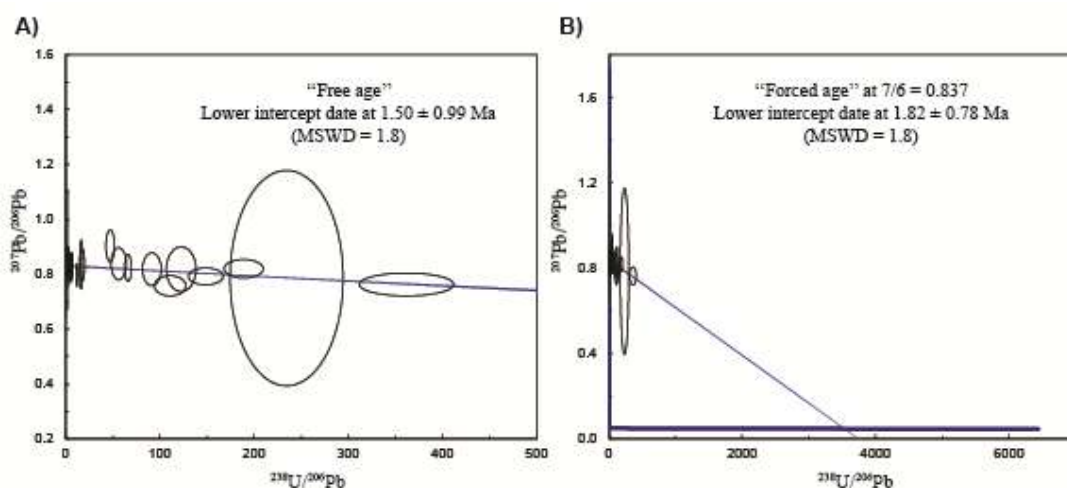
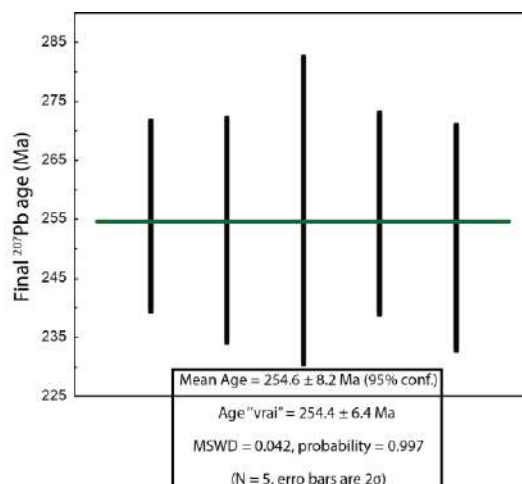


Figure VI.3.1: Tera-Wasserburg diagrams displaying the analyses made on calcite veins. A) T-W concordia diagram representing the unforced discordia B) T-W concordia diagram showing the lower intercept if the initial common Pb value forced to $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.837

Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (Abs)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (Abs)
calcS2_1	0.17	3.20	-	123.00	13.00	0.818	0.068
calcS2_2	0.13	7.29	-	362.00	41.00	0.762	0.035
calcS2_3	0.62	5.86	-	66.00	2.90	0.823	0.040
calcS2_4	0.17	5.39	-	235.00	49.00	0.785	0.320
calcS2_5	0.09	0.15	-	12.19	0.60	0.795	0.034
calcS2_6	0.15	0.13	-	6.15	0.81	0.811	0.034
calcS2_7	0.23	3.78	-	111.00	14.00	0.757	0.031
calcS2_8	0.30	6.39	-	149.00	15.00	0.791	0.025
calcS2_9	0.14	0.11	-	5.97	0.48	0.837	0.035
calcS2_10	0.15	0.12	-	5.94	0.43	0.820	0.034
calcS2_11	0.08	0.18	-	17.00	1.40	0.835	0.073
calcS2_12	0.27	3.05	-	91.50	7.90	0.819	0.049
calcS2_13	0.11	0.04	-	2.53	0.46	0.826	0.058
calcS2_14	0.14	0.02	-	1.22	0.07	0.842	0.053
calcS2_15	0.15	0.06	-	3.18	0.64	0.848	0.041
calcS2_16	0.12	0.03	-	1.97	0.11	0.890	0.180
calcS2_17	0.17	0.01	-	0.59	0.05	1.020	0.310
calcS2_18	0.25	1.30	-	47.30	3.50	0.903	0.047
calcS2_19	0.21	0.47	-	18.30	1.80	0.833	0.046
calcS2_20	0.16	0.97	-	56.50	6.70	0.838	0.049
calcS2_21	0.20	0.15	-	6.68	0.95	0.835	0.036
calcS2_22	0.20	0.05	-	2.32	0.10	0.824	0.032
calcS2_23	0.72	15.00	-	189.00	17.00	0.819	0.027

Table VI.3.1: LA-ICP-MS U-Th-Pb data for the studied calcite veins

Spot	Pb (ppm)	U (ppm)	Th (ppm)	Final ^{207}Pb age	$\pm 2\sigma$ (Abs)
WC1_1	-	-	-	255.6	16
WC1_2	-	-	-	253.2	19
WC1_3	-	-	-	256.5	26
WC1_4	-	-	-	256	17
WC1_5	-	-	-	251.9	19



ESM VI.3.1: Representative ^{207}Pb -corrected final age and average ages for the WC1 calcite standard used to monitor the analyses

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CHAPITRE VII

Synthèse et discussion

Ce chapitre se veut une synthèse des résultats présentés dans les chapitres III, IV, V et VI. En premier lieu, je discute de la genèse des minéralisations cuprifères supergènes *in situ* et exotiques au regard de la caractérisation minéralogique et chimique effectuée, présentée au chapitre III. Dans un second temps, je discute du comportement du chronomètre U-Pb dans les minéraux cuprifères supergènes étudiés, i.e. chrysocolle, chrysocolle noire et pseudomalachite. J'aborde la faisabilité de la datation *in situ* U-Pb de ces minéraux au regard des techniques analytiques utilisées, des concentrations en U, Pb radiogénique et en Pb commun. Par la suite, je porte une analyse sur ce qui préserve et perturbe le chronomètre U-Pb dans ces minéraux comme exposé dans les chapitres V et VI.

La deuxième partie de la discussion met l'accent sur des aspects purement métallogénique. A la lumière de la caractérisation minéralogique, géochimique, géochronologique et isotopique, je discuterai de l'âge des minéralisations cuprifères supergènes et des conditions géologiques locales et régionales qui favorisent la formation de ces minéralisations cuprifères supergènes autant dans le désert d'Atacama chilien, qu'au SW du Burkina Faso, dans la région de Gaoua. Enfin, nous discuterons de l'implication de ces résultats sur l'amélioration des stratégies de prospection des minéralisations cuprifères supergènes.

VII.1 Genèse des minéralisations cuprifères supergènes

La formation et la préservation d'un profil d'altération supergène nécessitent un équilibre entre la tectonique, le climat et les taux d'érosion/exhumation. Le profil supergène ainsi créé se compose généralement du sommet vers la base d'un i) chapeau lessivé ii) d'un horizon oxydé iii) d'un horizon enrichi en sulfures secondaires et iv) du protore.

La caractérisation effectuée pendant cette thèse a porté sur l'horizon oxydé. Dans tous les dépôts étudiés, la minéralisation cuprifère supergène était presque identique avec la chrysocolle comme minéral prépondérant suivi par des proportions mineures de pseudomalachite, de copper wad et d'atacamite. A la lumière des études minéralogiques, chimiques, géochimiques et isotopiques, le processus de formation de ces minéralisations cuprifères supergènes est discuté ci-après.

Les carbonates, oxydes, phosphates, chlorures et silicates de cuivre de l'horizon oxydé résultent de la migration verticale des solutions cuprifères provenant de l'altération supergène des sulfures primaires. Au-dessus de la nappe phréatique, ces solutions cuprifères forment des minéralisations cuprifères supergènes *in situ*. Transportés sur des centaines de mètres voire des kilomètres de distance et déposés dans des bassins en aval des porphyres, ils forment des minéralisations cuprifères supergènes exotiques. Dans les districts miniers de l'Atacama et de Gaoua, dans les minéralisations *in situ* et exotiques, la chrysocolle est le minéral le plus abondant. Durant l'altération supergène du porphyre cuprifère, les solutions acides chargées en ions H^+ vont altérer les sulfures primaires (pyrite et chalcoppyrite) et mettre la silice en solution. Combinée au cuivre déjà en solution, la chrysocolle va précipiter dans les fractures et en remplissage de cavités. Suivant la pente, ces solutions acides riches en Cu et en Si vont être transportées en aval et précipiter la chrysocolle en interstice, dans les fractures des roches encaissantes et enrobant les graviers du bassin. La chrysocolle, qui présente parfois une texture collomorphe, témoigne de l'enregistrement des variations du fluide minéralisateur mais aussi d'une activité microbiologique.

D'un point de vue chimique, Newberg (1967) a montré que la précipitation de la chrysocolle est optimale à $pH \sim 7$. La précipitation de la pseudomalachite est liée à la présence de phosphates. Dans les environnements porphyriques, le phosphate en solution est produit par la déstabilisation de l'apatite.

Dès lors, les solutions cuprifères vont s'enrichir en H_2PO_4 et précipiter la pseudomalachite. L'alternance de bandes de pseudomalachite et de chrysocolle, observée dans la minéralisation exotique de Mina Sur, implique, en plus d'autres paramètres thermodynamiques (Eh, Ph, etc.), un changement de la chimie des fluides minéralisateurs en fonction de la prédominance temporaire de l'un ou l'autre des ions H_4SiO_4 ou H_2PO_4 . L'atacamite, un chlorure de cuivre très soluble en présence d'eaux météoriques, n'a été observée que dans le district minier de Chuquicamata. La cristallisation de l'atacamite requiert des solutions riches en sel (e.g. saumures de bassins, eaux souterraines salines) et un climat hyperaride pour être préservé. Le fait que l'atacamite n'ait été observée qu'à Mina Sur, au nord du désert d'Atacama, dénote du fait que cette région du désert d'Atacama ait été soumise à un climat hyperaride indispensable pour préserver l'atacamite. Ceci implique aussi que dans les districts miniers du sud du désert (i.e. Salvador et Potrerillos) et celui de la région de Gaoua, aucune solutions salines n'étaient disponibles pour favoriser la formation de l'atacamite ou encore que ces districts aient subi des circulations de fluides post-cristallisation capable de dissoudre l'atacamite et/ou une prévalence de conditions arides où la circulation pérenne de fluides empêcherait la formation de l'atacamite. Ce dernier argument est corroboré par le fait que les districts miniers de Salvador et de Potrerillos, en plus d'être situés à des altitudes élevées favorisant la capture de l'humidité, soient passés sous un climat hyperaride qu'à la fin du Miocène-début du Pliocène et que la région de Gaoua n'ait jamais expérimenté un climat hyperaride, essentiel à la préservation de l'atacamite.

Les fluides impliqués dans la formation des minéralisations cuprifères supergènes ont longtemps été sujet à débat, i.e. mélange de fluides hydrothermaux et météoriques, température des fluides météoriques, etc. Les caractérisations isotopiques ($\delta^{18}\text{O}$, δD) ont montré que les fluides minéralisateurs sont uniquement d'origine météorique (Fernández-Mort et al., 2018; Torres-Ruiz et al., 2020). Les analyses géochimiques effectuées sur la chrysocolle et la pseudomalachite s'inscrivent dans cette même tendance avec une anomalie négative en Ce dans les minéralisations exotiques dénotant d'une ininteruption des conditions oxydantes. Dans les minéralisations supergènes *in situ*, les analyses géochimiques ont montré à la fois une anomalie négative et positive en Ce qui reflèteraient des changements des conditions redox entre le sommet et la base de l'horizon oxydé. La caractérisation des isotopes du Cu a mis en lumière la relation paragénétique existante entre les minéraux sulfurés et la

minéralisation oxydée. Dans tous les dépôts supergènes étudiés, la chrysocolle et la pseudomalachite montrent une signature isotopique élevée en $\delta^{65}\text{Cu}$ comparativement aux valeurs des sulfures primaires reportées dans la littérature (i.e. autour de 0 ‰). Cet important fractionnement serait dû à la dissolution des sulfures primaires par des fluides oxydants. Ces fluides oxydants vont remobiliser le cuivre, s'enrichir en ^{65}Cu et précipiter des minéraux supergènes enrichis en ^{65}Cu .

Pour résumer, la prédominance de la chrysocolle serait sans doute le signal d'un système supergène mature, développé sous des conditions neutres à légèrement alcalines lors de la précipitation de ce minéral. Cette prédominance implique aussi que toutes les phases minérales pouvant acidifier le pH (i.e. pyrite, chalcoppyrite) aient été consommées et que le système a été sous des conditions d'altération très oxydantes, favorables à la formation d'un épais horizon oxydé.

VII.2 Comportement du chronomètre U-Pb dans la pseudomalachite et la chrysocolle

VII.2.1 La pseudomalachite de Mina Sur : un minéral approprié pour dater l'âge des minéralisations cuprifères supergènes

Tel que mis en évidence dans le chapitre V, publié dans la revue *Mineralium Deposita*, les datations U-Pb effectuées sur les bandes de pseudomalachite ont montré des teneurs importantes en U, des concentrations mesurables en Pb radiogénique et une contribution mineure du Pb commun. Dans le diagramme concordia Tera-Wasserburg (voir chapitre V, section Résultats), l'intercept inférieur à 18.4 ± 1.0 Ma obtenu, permet de conclure que la pseudomalachite de la minéralisation exotique de Mina Sur s'est formée il y a ~ 19 Ma. Par ailleurs, les cartes de distributions isotopiques de l' ^{238}U et du ^{206}Pb montrent une répartition homogène de ces isotopes à l'intérieur des bandes de pseudomalachite et les valeurs qualitatives du $\delta^{18}\text{O}$ sont globalement homogènes (i.e. variations $< 3\text{‰}$). Ceci suggère que les bandes de pseudomalachite ont cristallisé à l'équilibre isotopique et sont restées en système fermé, que ce soit pour les isotopes de l'U, du Pb ou de l'O. De plus, la structure cristalline de la pseudomalachite étant robuste (Berry, 1950; Shoemaker et al., 1977), elle serait potentiellement résistante à des circulations de fluides post-cristallisation pouvant lessiver l'U et/ou le Pb. Ces arguments permettent

de définir la pseudomalachite de la minéralisation exotique de Mina Sur, comme un chronomètre approprié pour des datations U-Pb. En prenant en compte la date de 18.4 ± 1.0 Ma obtenue, nous pouvons affirmer que la formation du dépôt exotique de Mina Sur a commencé dès 19 Ma, en accord avec les âges connus du fonctionnement de l'altération supergène dans le district minier de Chuquicamata, i.e. entre 15 Ma et 19 Ma (Sillitoe and McKee, 1996). A l'échelle du désert d'Atacama, plusieurs études ont montré que l'installation de l'hyperaridité a été asynchrone entre le nord et le sud du désert d'Atacama. Dans la région de Chuquicamata, l'initiation de l'hyperaridité a été datée entre la moitié du Miocène et jusqu'au Pliocène via des datations K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ sur des minéraux d'altération (Sillitoe and McKee, 1996), des datations des surfaces d'altération (Jordan et al., 2014) et des études sédimentologiques (Hartley and Chong, 2002). Par ailleurs, même si des évidences de circulations tardives de fluides ont été documentées par Reich et al. (2008) et Reich et al. (2009) comme s'étant déroulées à la fin du Pléistocène, la structure cristalline robuste de la pseudomalachite a sans doute limité la mobilité de l'U et du Pb pouvant être causée par des réactions fluide-minéral.

VII.2.2 Les causes de la perturbation du chronomètre U-Pb dans la pseudomalachite et la chrysocolle

Comme discuté et montré par de nombreux auteurs, un minéral est adapté à la datation U-Pb s'il emmagasine de l'uranium lors de sa cristallisation, que cet uranium ait le temps de se désintégrer en Pb radiogénique, qu'il incorpore de faibles quantités de Pb commun ou encore que ce minéral ait évolué en système fermé après sa cristallisation.

A la lumière du chapitre VI, les causes majeures de la discordance des âges U-Pb enregistrés dans la chrysocolle et la pseudomalachite sont la mobilité post-cristallisation de l'U, la mobilité du Pb radiogénique favorisée par la circulation de fluides post-cristallisation et les concentrations initiales de l'U, du Pb radiogénique mais aussi de Pb commun.

VII.2.2.1 La mobilité de l'U et du Pb dans la chrysocolle noire et la chrysocolle de Mina Sur

Les analyses ns- et fs-LA effectuées sur les clastes de chrysocolle noire de la minéralisation exotique de Mina Sur, dans le district minier de Chuquicamata, ont révélé des teneurs importantes en U (~ 1200 – 1600 ppm), en Pb radiogénique (~ 1 à 9 ppm) et des quantités négligeables de Pb commun comme l'atteste l'étalement des points en position concordante à sub-concordante sur la courbe concordia (voir chapitre V). Cette richesse en U et la faible proportion de Pb commun confèrent à la chrysocolle noire un potentiel chronologique indéniable pour des datations U-Pb. Cependant, à cause de l'étalement des âges apparents le long de la courbe concordia, de ca. 19.7 Ma à ca. 6.1 Ma, un âge de cristallisation unique n'a pu être déterminé. Cet étalement des âges apparents serait dès lors la conséquence d'un mélange de domaines d'âges différents et/ou le résultat de la mobilité de l'U et/ou du Pb par le biais de réactions fluides-minéraux ou des phénomènes de mobilité intra-cristalline.

L'hypothèse d'un mélange d'âges de domaines différents est mise en lumière par la microscopie optique et la carte de distribution des âges $^{206}\text{Pb}/^{238}\text{U}$ (voir chapitre VI). La texture collomorphe qui résulte de l'addition de fluides de différentes compositions chimiques et isotopiques (Barrie et al., 2009) impliquerait donc différents âges de formation pour chacune des bandes. Nombre d'études (Goncalves, 2005; Gasquet et al., 2010; Didier et al., 2015) ont montré que les zonations de croissances minérales, si elles n'étaient pas clairement identifiées en microscopie optique (cathodoluminescence, SEM-BSE, etc.) et en cartographie chimique (nano-SIMS, LA-ICP-MS), pourraient présenter des âges U-Pb discordants ou faussement concordants dû à des mélanges de domaines de différentes compositions chimiques. La carte de distribution des âges $^{206}\text{Pb}/^{238}\text{U}$ (voir chapitre VI), qui présente une variation des âges $^{206}\text{Pb}/^{238}\text{U}$ suivant la texture collomorphe des clastes de chrysocolle noire, montre que l'étalement des âges apparents est vraisemblablement le fait d'un mélange d'âges de domaines différents. Ces derniers correspondent généralement à des séquences de croissance du minéral depuis le centre du minéral jusqu'à sa périphérie. Cependant, il serait difficile d'interpréter l'étalement des âges entre ca. 19 Ma et ca. 6 Ma, c'est-à-dire 13 millions d'années, comme correspondant à la durée du processus de formation des bandes de croissance de la chrysocolle noire.

Par ailleurs, comme illustré par les cartes de distribution isotopiques du ^{206}Pb et de l' ^{238}U réalisées dans la chrysocolle noire, le ^{206}Pb montre une zonation isotopique qui épouse les zonations de croissances de la chrysocolle noire. Par contre, l' ^{238}U ne montre pas de zonation. Une explication plausible serait une ré-homogénéisation tardive du signal isotopique de l' U causée par des circulations tardives de fluides post-cristallisation qui aurait pu remobiliser l' U et non le Pb . L'argument d'une mobilité de l' U est renforcé par la structure faiblement cristalline de la chrysocolle noire (Throop and Buseck, 1971; Pincheira et al., 2003; Menzies et al., 2015). De plus, Bruguier (2009) et Geisler et al. (2007) ont respectivement montré que les silicates ont des structures cristallines flexibles pouvant engendrer des états faiblement cristallins et que les éléments chimiques (e.g. U et Pb) seraient mobiles dû à l'auto-irradiation des silicates dans les systèmes hydrothermaux de basse température, renforcé par les teneurs importantes en U . Reporté à la chrysocolle noire qui est un silicate à structure cristalline amorphe et riche en U , on pourrait supposer que l' U soit très mobile en présence de fluides supergènes. De plus, Mathieu et al. (2001) ont montré que l' U a une solubilité importante dans les saumures diagénétiques oxydées, favorisant sa mobilité. Cependant, comme l'ont montré les diagrammes des rapports isotopiques du $\delta^{18}\text{O}$ (voir chapitre VI, Figure 7), les valeurs du $\delta^{18}\text{O}$ montrent des variations qui épousent les zonations de croissance de la chrysocolle noire, suggérant que l'oxygène est resté stable sans diffusion ni mobilité post-cristallisation. Cet argument montre de fait que des circulations de fluides post-cristallisation n'ont pu induire la mobilité de l' U . Nous proposons donc que cette ré-homogénéisation du signal de l' U serait plutôt le fait d'une diffusion à l'état solide de l' U à l'intérieur du réseau cristallin de la chrysocolle noire. En outre, la structure faiblement cristalline de la chrysocolle noire pourrait très bien accentuée cette mobilité intra-cristalline.

Pour résumer, les arguments texturaux et isotopiques sus-cités montrent que la chrysocolle noire, par sa texture, enregistre les variations chimiques du fluide pendant sa précipitation, précipitation qui se fait en équilibre avec le fluide minéralisateur, sans diffusion ni mobilité comme le montrent les analyses du $\delta^{18}\text{O}$ effectuées. Les arguments isotopiques montrent que la chrysocolle noire peut être sujette à des phénomènes de mobilité post-cristallisation (i.e. diffusion à l'état solide) pouvant induire la mobilité de l' U au dépend du Pb à l'intérieur de la structure cristalline. Malgré ce talon d'Achille, la chrysocolle noire possède bel et bien un potentiel chronologique et pourrait servir à dater l'âge de

formation des minéralisations cuprifères supergènes, pour peu que l'U préserve sa signature isotopique initiale.

Dans les bandes de chrysocolle de la minéralisation exotique de Mina Sur, les analyses ns-LA ont montré des teneurs élevées en U, une contribution du Pb commun, et surtout une quasi absence de Pb radiogénique comme le montrent les rapports isotopiques $^{238}\text{U}/^{206}\text{Pb}$ et $^{207}\text{Pb}/^{206}\text{Pb}$ (Chapitre VI, ESM 2 Table 1). Cette faible proportion de Pb radiogénique, en dépit de concentrations élevées en U, pourrait s'expliquer par un âge de formation relativement jeune de la chrysocolle et impliquerait que l'uranium n'eut pas le temps de se désintégrer en Pb radiogénique ou encore pourrait être le résultat de la mobilité du Pb radiogénique par des circulations tardives de fluides post-cristallisation. La prévalence des conditions favorables à l'altération supergène au Néogène a été discutée par Reich et al. (2008) et Reich et al. (2009). Ils ont montré, dans le district minier de Chuquicamata, grâce à la datation du gypse associé à l'atacamite, que l'altération supergène a été active jusqu'à la fin du Pléistocène (~ 240 ka). Cet argument montre que la chrysocolle aurait pu se former durant le Pléistocène, limitant fortement la désintégration, avec le temps, de l'uranium en Pb radiogénique. Cependant, cet argument est balayé par les observations texturales. En effet, les informations texturales montrent que les bandes de chrysocolle sont intercalées entre les clastes de chrysocolle noire ayant subi une ré-homogénéisation de l'U et les bandes de pseudomalachite datées à ca. 19 Ma. Par conséquent, l'hypothèse d'une cristallisation récente des bandes de chrysocolle est difficilement plausible. Ceci milite donc pour une mobilité du Pb radiogénique causée par des circulations de fluides post-cristallisation qui vont uniquement lessiver le Pb radiogénique des bandes de chrysocolle tout en préservant le signal isotopique des clastes de chrysocolle noire et des bandes de pseudomalachite. De plus, comme présenté dans le tableau 1 (voir chapitre VI, ESM 2 Table 1), si on subodore un âge de précipitation de la chrysocolle à ~ 19 Ma (comme la pseudomalachite), les teneurs en Pb radiogénique censées être obtenues et celles obtenues après analyse plaident pour une mobilité du Pb radiogénique. Par ailleurs, au contraire des minéraux conventionnels utilisés dans la datation U-Pb, la chrysocolle a une structure cristalline amorphe et est définie comme un minéraloïde (Van Oosterwyck-Gastuche and Grégoire, 1971; McKeown, 1994; Hariu et al., 2013; Campos et al., 2015). Cette structure peu cristallisée pourrait dès lors sous-entendre que la chrysocolle soit sujette à des phénomènes de mobilité du Pb par des événements perturbateurs

(circulation tardive de fluides, diagenèse, etc.) qui vont lessiver le Pb après la formation du minéral. Ces circulations de fluides post-cristallisation sont corroborées par les analyses des isotopes de l'oxygène. En effet, les analyses du $\delta^{18}\text{O}$ des bandes de chrysocolle montrent un profil plat (Chapitre VI, Figure 7), en contradiction avec la texture à bandes mamillaires qui suggère une variation de la chimie et de l'isotopie du fluide minéralisateur. Ceci tendrait à confirmer une ré-homogénéisation du signal isotopique de l'oxygène et serait marqueur d'une circulation tardive de fluides post-cristallisation.

VII.2.2.2 La chrysocolle et la pseudomalachite de Damiana et El Cobre : des minéraux pauvres en U et riches en Pb commun

A Damiana et El Cobre, à la limite méridionale du désert d'Atacama, seules la chrysocolle et la pseudomalachite ont été sujettes à des datations U-Pb. Les teneurs en U ont montré des valeurs basses, i.e. entre $\sim 1\text{-}12$ ppm et $\sim 1\text{-}5$ ppm pour la chrysocolle et $\sim 0.44\text{-}12.5$ ppm et $\sim 1.44\text{-}3.71$ ppm pour la pseudomalachite, respectivement à Damiana et El Cobre. De plus, les concentrations en Pb radiogénique étaient trop faibles, empêchant toute interprétation quantitative des données U-Pb. Comme démontrée dans la section précédente, la chrysocolle peut incorporer des quantités importantes d'uranium. Dès lors, cette faible concentration d'uranium observée dans la chrysocolle et la pseudomalachite, pourrait avoir une explication à l'échelle du district minier. Un premier argument pourrait provenir des concentrations en U du porphyre parent. En effet, de faibles concentrations en U dans les porphyres parents des minéralisations exotiques de Damiana et El Cobre pourraient se refléter par des concentrations moindres en U comme reportées dans la chrysocolle et la pseudomalachite, au contraire de celles observées à Mina Sur. Cependant, aucune donnée d'analyse d'uranium sur roche totale n'existant sur les porphyres sources de ces deux minéralisations exotiques, cet argument est à prendre avec précaution.

Par ailleurs, l'altération supergène, et donc des conditions climatiques semi-arides à arides, étaient actives jusqu'à environ 6 Ma dans le sud du désert d'Atacama (i.e. de 34 Ma à 6 Ma ; Marsh et al., 1997) impliquant de fait une circulation pérenne de fluides et donc une possible précipitation de la

chrysocolle et de la pseudomalachite à une période relativement récente ou une mobilité de l'U et/ou du Pb par des circulations de fluides post-cristallisation.

De nombreux auteurs ont montré que l'état d'oxydation de l'uranium, passe d'un état tétravalent (U^{4+}) à un état hexavalent (U^{6+}) dans les fluides supergènes. Dans cet état, l'U est plus facilement sujet à un lessivage par des fluides supergènes post-cristallisation. Par conséquent, les faibles concentrations en U et en Pb radiogénique seraient le reflet d'une circulation latente de fluides oxydants qui ont favorisé une mobilité permanente de l'U dans la chrysocolle et la pseudomalachite dans les porphyres sources. Concernant la chrysocolle, la mobilité des éléments pourrait être favorisée par sa structure cristalline amorphe. Pour la pseudomalachite, qui possède une structure cristalline robuste au contraire de la chrysocolle, la mobilité de l'U et du Pb pourraient être dus à des circulations de fluides oxydants post-cristallisation de basse température. Comme démontré par Poitrasson et al. (2000) pour la monazite et Geisler et al. (2007) pour le zircon, ces minéraux très résistants à l'altération peuvent être sujets à des pertes épisodiques de Pb, dues à des interactions fluides-roches à des températures basses ($< 200^{\circ}C$). Cependant, les analyses du $\delta^{18}O$ de la chrysocolle montrent que les variations chimiques et isotopiques liées à la texture en bandes mamillaires de ce minéral ont été préservées (spécialement à Damiana, voir Chapitre VI). Les analyses du $\delta^{18}O$ de la pseudomalachite montrent une très légère variation du $\delta^{18}O$ à l'intérieur de ce minéral. Ceci tend à suggérer qu'aucun fluide n'a réinitialisé et ré-homogénéisé l'enregistrement isotopique initial et montrerait que la chrysocolle et la pseudomalachite n'aient pu subir une mobilité de l'U et/ou du Pb via des circulations de fluides post-cristallisation. Les faibles teneurs en U seraient donc le fait de faibles teneurs en U dans le porphyre source et favorisé par un âge de formation récent de ces deux minéraux due à la perdurance de l'altération supergène jusqu'à une époque relativement récente (i.e. jusqu'à 4 Ma). Dans le sud du désert d'Atacama, ces faibles teneurs dans le porphyre source seraient potentiellement liées à un lessivage intense de l'U par des fluides supergènes depuis l'initiation de l'altération supergène à ca. 35 Ma (Mote et al., 2001) jusqu'à la récente installation pérenne de l'hyperaridité (Bissig and Riquelme, 2009; Bissig and Riquelme, 2010).

En addition des faibles teneurs en U, les analyses U-Pb montrent une importante contribution du plomb commun. Comme discuté par Chew et al. (2011) pour l'apatite et Roberts et al. (2017) pour la calcite, les minéraux relativement pauvres en U et riches en Pb commun, comme le sont la chrysocolle

et la pseudomalachite, peuvent être appropriés pour des datations U-Pb si une bonne correction du Pb commun est faite via les méthodes connues à ce jour, i.e. la méthode des isochrones, la mesure du Pb d'une phase minérale co-génétique et le modèle d'évolution crustale du Pb (Stacey and Kramers, 1975; Schoene and Bowring, 2006). Cependant, comme illustrée par la Figure 6 du chapitre VI, la très grande proportion de Pb commun par rapport au Pb radiogénique et l'absence d'une phase co-génétique riche en Pb empêchent toute correction du Pb commun.

II.2.2.3 La chrysocolle de la minéralisation supergène in situ de Gaoua : un minéral modérément riche en U et en Pb commun

A Gaoua, seule la chrysocolle a fait l'objet de datation U-Pb via ns- et fs-LA. Couplées, ces analyses montrent des teneurs importantes en U (~ 15-42 ppm), semblables à celles qu'on pourrait déceler sur un zircon (Hoskin and Schaltegger, 2003), contrebalancées cependant par une contribution importante du Pb commun (Chapitre VI, section VI.2) et une proportion faible de Pb radiogénique. De plus, les rapports $^{207}\text{Pb}/^{206}\text{Pb}$ sont quasiment identiques, autant pour les analyses ns- que fs-LA. L'absence de phase co-génétique riche en Pb commun ainsi que les rapports $^{207}\text{Pb}/^{206}\text{Pb}$ très élevés empêchent une correction adéquate du Pb commun. Dans ce cas, une mesure précise du ^{204}Pb à l'aide d'un multi-collecteur ICP-MS pourrait permettre une correction précise du Pb commun, indispensable pour obtenir un âge de précipitation de la chrysocolle.

Le diagramme concordia Tera-Wasserburg qui affiche les données sur la courbe discordia, parallèle à la concordia semble indiquer que la formation de la chrysocolle est récente, avec un comportement du chronomètre U-Pb en système ouvert. Ce comportement en système ouvert est corroboré par la structure faiblement cristalline de la chrysocolle, décrite dans les sections précédentes, qui en fait un candidat idéal à une mobilité de l'U et/ou du Pb menant à des âges discordants. Cependant, les analyses du $\delta^{18}\text{O}$ de la chrysocolle semblerait indiquer que ce minéral n'ait subi aucune perturbation post-cristallisation par des fluides qui aurait pu réinitialiser le signal isotopique de l'oxygène. D'autre part, l'hypothèse d'une formation récente de la chrysocolle est renforcée par les travaux de Beauvais and Chardon (2013) et Chardon et al. (2018) qui ont montré, à l'échelle du Burkina Faso et du craton ouest Africain, que l'altération supergène s'est mis en place simultanément avec la formation du

régolithe latéritique et la formation des pédiments depuis la limite Crétacé-Cénozoïque jusqu'à l'actuel, dans un climat semi-aride à sahélien. Dès lors, la formation récente de la chrysocolle induirait la proportion infime de Pb radiogénique détectée et le fait qu'aucun âge apparent n'ait été extrait de ces données U-Pb.

VII.2.2.4 Faisabilité de la datation in situ U-Pb par LA-ICP-MS des minéraux cuprifères supergènes : les méthodes analytiques

Les datations *in situ* U-Pb via LA-ICP-MS requièrent l'utilisation d'un matériau standard de référence, possédant, autant que faire se peut, les mêmes propriétés chimiques, minéralogiques et optiques que le minéral à analyser. Ce « matrix-matched-standard » permet dès lors de pouvoir corriger du fractionnement inter-élémentaire se produisant lors de l'ionisation des atomes et surveiller la dérive instrumentale qui intervient, au fil du temps, lors des analyses. Durant cette thèse, l'impossibilité d'obtenir des standards de chrysocolle et de pseudomalachite a constitué dès lors un challenge pour la datation U-Pb de ces derniers. Le choix a donc été fait d'utiliser un standard de zircon, un minéral à matrice silicatée tout comme la chrysocolle, et un standard d'apatite, un minéral à matrice phosphatée tout comme la pseudomalachite.

Ces deux choix de standards primaires ont été triviaux. En effet, tout comme la chrysocolle, le zircon est modérément à très enrichi en U. Cependant, contrairement à la chrysocolle qui est un minéraloïde, le zircon a une structure cristalline robuste. Ce qui en fait deux minéraux aux propriétés optiques différentes. Concernant la pseudomalachite, elle possède les mêmes propriétés optiques que le standard d'apatite, i.e. une structure cristalline robuste. De plus, tout comme la pseudomalachite, le standard d'apatite incorpore de faibles quantités d'U (< 100 ppm) et des concentrations faibles à modérées de Pb commun.

Lors des sessions analytiques, le choix a été fait d'utiliser à la fois un laser nanoseconde (ns-LA), largement répandu dans les laboratoires de géochronologie, et, pour s'affranchir de possibles effets de matrice dû à l'utilisation d'un « non-matrix-matched-standard », un laser femtoseconde (fs-LA). En effet, Poitrasson and d'Abzac (2017) ont montré que le fs-LA a l'avantage de minimiser le fractionnement élémentaire dû à l'utilisation d'un « non-matrix-matched-standard ». De plus, la courte

longueur d'onde des fs-LA permet une meilleure ablation et réduit ainsi la nécessité d'une standardisation des matériaux à analyser avec des standards de matrice identique, permettant dès lors l'analyse de minéraux non-conventionnels dont la mise au point de standards n'est pas aussi avancée que celle des minéraux conventionnels.

Les analyses effectuées sur la chrysocolle et la pseudomalachite (des mines de Mina Sur, Damiana, El Cobre et Gaoua) et sur la chrysocolle noire (uniquement dans la mine de Mina Sur), entre le ns-LA et fs-LA, ont montré des rapports isotopiques et des âges apparents presque tous similaires (voir ESM 2 du Chapitre VI). De plus, les standards secondaires (i.e. les zircons Fish Canyon Tuff et Plešovice et l'apatite Durango) utilisés pour contrôler la reproductibilité et la précision des analyses inter-laboratoires ont fourni des âges similaires dans l'erreur (ESM 2 du chapitre V). De fait, l'hypothèse d'un biais inter-laboratoire a pu être écartée vu que les standards secondaires ont donné des âges similaires dans l'erreur. Dès lors, la légère différence de rapports isotopiques et d'âges apparents observée entre les minéraux analysés pourrait être due à un léger effet de matrice, soulignée par l'utilisation de lasers de longueur d'onde différente et de spectromètres différents. Le fs-LA HR-ICP-MS étant plus sensible que le ns-LA Q-ICP-MS, il en résulte de fait une meilleure ablation et une meilleure ionisation des particules dans la torche plasma. En conséquence, une légère différence est observée dans les âges apparents et les rapports isotopiques. Nonobstant cette légère différence, le fait que les analyses effectuées entre différents laboratoires (i.e. Rennes, Toulouse et Dublin), possédant différents équipements (i.e. ns-LA Q-ICP-MS à Rennes et Dublin, fs-LA HR-ICP-MS à Toulouse), mais avec le même protocole analytique, donnent des résultats similaires, est rassurante. Ceci permet de conclure que l'effet de matrice dû à l'utilisation d'un « non-matrix-matched-standard » est négligeable et permet donc la standardisation de la chrysocolle et de la pseudomalachite avec les standards de zircon et d'apatite utilisés, en dépit des caractères optiques différents observés entre la chrysocolle et le zircon. Ceci nous conforte quant à la solidité, autant qualitative que quantitative, des résultats géochronologiques obtenus dans cette étude.

VII.3 Age de l'altération supergène dans les districts miniers de l'Atacama et du sud-ouest du Burkina Faso

L'essor de la géochronologie ces trente dernières années et les avancées technologiques et techniques ont permis d'utiliser le chronomètre U-Pb pour dater aussi bien l'âge et la durée des processus magmatiques, métamorphiques que la formation des dépôts métalliques. L'âge des minéralisations était parfois le chaînon manquant à la compréhension globale de la métallogénie des dépôts métalliques. Dans le cas des minéralisations cuprifères, l'absence de minéraux conventionnels (i.e. le zircon, la monazite, la colombo-tantalite, etc.) dans ces environnements d'altération constituait un frein à la datation. La caractérisation des minéraux d'altération (i.e. alunite, cryptomélane, jarosite, natroalunite) et l'essor des techniques de datation K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ ont permis d'apporter une contrainte temporelle quant à l'âge et à la durée du processus d'altération supergène des porphyres cuprifères. Cependant, ces minéraux d'altération ne sont pas ubiquistes dans tous les dépôts cuprifères supergènes (i.e. *in situ* et exotique) et parfois cristallisent postérieurement. Tous ces facteurs, nous ont poussé à explorer le chronomètre U-Pb pour dater les minéraux cuprifères supergènes et ainsi obtenir un âge absolu de fonctionnement de l'altération supergène. De fait, les travaux de datation réalisés pendant cette thèse constituent une étude pionnière en ce sens que la datation de la minéralisation cuprifère supergène n'avait jamais été documentée.

Dans le désert d'Atacama, les datations K-Ar et $^{40}\text{Ar}/^{39}\text{Ar}$ des minéraux d'altération ont permis de contraindre la durée de fonctionnement de l'altération supergène entre 45 et 6 Ma (Hartley and Rice, 2005; Arancibia et al., 2006) avec un âge de fonctionnement différent entre les différentes zones morphotectoniques et à différentes latitudes. Dans la zone morphotectonique d'étude, i.e. la ceinture de cuivre Eocene-Oligocene (*a.k.a* la cordillère Domeyko), l'altération supergène s'est mis en place entre 36 Ma et 6 Ma (Hartley and Rice, 2005) avec un fonctionnement différent entre le nord et le sud du désert d'Atacama.

Au nord du désert d'Atacama, dans le district minier de Chuquicamata, à environ ~ 2300 m d'altitude, la durée du processus d'altération supergène a été contrainte par Sillitoe and McKee (1996) entre ca. 15 Ma et ca. 20 Ma sur des alunites supergènes du chapeau de fer des porphyres cuprifères de

Chuquicamata et Ministro Hales. Nos données U-Pb sur la minéralisation exotique de Mina Sur (confère chapitre V), combinées aux données déjà publiées, corroborent l'hypothèse d'un début de fonctionnement de l'altération supergène à environ ~ 19 Ma comme l'ont montré les datations U-Pb sur les bandes de pseudomalachite. A l'échelle du district minier, ces premières datations effectuées sur la minéralisation cuprifère supergène montrent que l'altération supergène *in situ* des porphyres cuprifères et la formation des minéralisations exotiques de Cu sont forts probablement contemporains. Dans le complexe porphyrique de Chuquicamata, l'activité magmatique et hydrothermale s'est mis en place entre 35 et 31 Ma (Ballard et al., 2001; Campbell et al., 2006). Les données obtenues sur la pseudomalachite montrent que l'altération supergène et la formation de l'horizon oxydé du profil supergène se sont faites environ 11 million d'années après la fin de l'activité hydrothermale. Ceci corrobore les études respectives de Sillitoe and McKee (1996) et Sanchez et al. (2018), qui ont montré qu'à l'échelle du désert d'Atacama et du district minier de Centinela, la formation de la minéralisation cuprifère supergène s'est déroulée entre 5 et 15 millions d'années après l'exhumation des porphyres cuprifères. D'un point de vue géomorphologique, l'âge de la minéralisation cuprifère supergène coïncide avec la formation d'une surface d'érosion régionale (i.e. la pédiplaine d'Atacama) à la limite Oligocène-Miocène, confirmant les hypothèses de Sillitoe (2005) et Riquelme et al. (2017) qui ont montré que la formation des minéralisations cuprifères supergènes *in situ* et exotique sont contemporaines de la phase de pénéplanation des reliefs. Dans le district minier de Chuquicamata, la rareté des âges plus récents que 15 Ma, combinée à la fin de l'érosion et de la formation des surfaces d'érosion, militent pour une dessiccation du climat à ~ 15 Ma qui aurait stoppé le processus d'altération supergène en limitant les apports d'eaux (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996; Mote et al., 2001; Arancibia et al., 2006). Cependant, Reich et al. (2008) et Reich et al. (2009) ont montré, par la datation de l'atacamite en intercroissance avec le gypse, que la circulation des eaux météoriques a été effective même durant la prévalence de l'hyperaridité, par le biais de fenêtres climatiques plus ou moins humides (e.g. phénomènes El Niño et La Niña) favorisant la formation et la préservation de l'atacamite à 240 ka.

Au sud du désert, les conditions tectoniques et climatiques étaient différentes de celles du nord, suggérant une durée asynchrone de l'altération supergène des porphyres cuprifères et de la formation

des minéralisations cuprifères supergènes entre le nord et le sud du désert d'Atacama. Dans le district minier de Salvador-Potrerillos, l'altération supergène s'est déroulée entre ca. 36 Ma et ca. 11 Ma (à Salvador ; Mote et al., 2001) et ca. 6 Ma (à Potrerillos ; Marsh et al., 1997; Bissig and Riquelme, 2010). Ces datations obtenues sur les minéraux d'altération des porphyres cuprifères de Salvador et de Potrerillos et ceux de la minéralisation exotique de Damiana sont en accord avec les données déjà publiées à l'échelle du désert d'Atacama. Ces dernières ont montré que la minéralisation cuprifère supergène se met en place entre 5 et 15 millions d'années après la fin du processus magmatique-hydrothermal, estimé à 41 Ma à Salvador et 35 Ma à Potrerillos (Marsh et al., 1997; Mote et al., 2001). Dans ces deux districts miniers, les datations U-Pb effectuées sur la chrysocolle et la pseudomalachite ont montré des concentrations faibles en U et presque inexistantes en Pb radiogénique, suggérant un âge de formation relativement récent de la minéralisation cuprifère supergène. Si, dans le district minier de Salvador, aucun âge de formation récent de la minéralisation cuprifère supergène n'a été documenté dans la littérature, des évidences d'un fonctionnement récent de l'altération supergène dans le district minier de Potrerillos ont été évoquées par Bissig and Riquelme (2010). Ces deux auteurs ont montré, via des datations $^{40}\text{Ar}/^{39}\text{Ar}$ sur des minéraux d'altération (à interpréter avec précaution car souffrant d'un excès d'argon), que l'altération supergène s'est déroulée sur différentes périodes depuis le Miocène jusqu'à l'actuel, corroborant de fait l'âge de formation récent évoqué pour ces deux minéraux et plausiblement les faibles concentrations en U et en Pb radiogénique obtenues sur la chrysocolle et la pseudomalachite.

Comme affirmé précédemment, le nord et le sud du désert d'Atacama ont subi une histoire tectonique et géomorphologique différente. Si dans le nord de l'Atacama, l'évènement tectonique responsable de l'exhumation des porphyres s'est déroulé uniquement entre la fin de l'Eocène et le début de l'Oligocène, au sud, dans les districts miniers de Salvador et de Potrerillos et dans le district minier de Maricunga, des épisodes tectoniques se sont succédés à l'évènement Inca (Sillitoe and McKee, 1996; Bissig and Riquelme, 2009). A la suite de l'orogénèse Inca, s'est superposé l'évènement tectonique Quechua, au milieu (18-14 Ma) et à la fin du Miocène (~ 6 Ma) (Bissig and Riquelme, 2009; Bissig and Riquelme, 2010). Ces soulèvements tectoniques ont engendré d'une part, la baisse de nappe phréatique, primordiale à la formation de la minéralisation cuprifère supergène, et d'autre part, ont permis

l'élévation de la région à des altitudes importantes (e.g. 4000 m d'altitude à El Cobre) favorisant la capture de l'humidité et donc la disponibilité des eaux météoriques pour favoriser l'altération supergène et la formation des minéralisations cuprifères supergènes. Cependant, même si le district minier de Salvador, 30 km au nord de celui de Potrerillos, n'a pas atteint des altitudes aussi élevées, l'incision des surfaces d'érosion et la formation des canyons d'El Salado et Asientos à la fin du Miocène (Bissig and Riquelme, 2010) ont favorisé une baisse régionale du niveau des nappes phréatiques susceptible d'entraîner la formation des minéralisations cuprifères supergènes depuis la fin du Miocène jusqu'à l'actuel. L'installation d'un climat hyperaride, à la fois dans les districts miniers de Salvador et de Potrerillos, semble s'être initié à la fin du dernier épisode tectonique tardi-Miocène, ou l'altitude a sans doute empêché la migration de l'humidité amazonienne et intensifiée l'évaporation des eaux météoriques captées aux hautes altitudes. Ce processus d'évaporation à haute altitude a été documenté par Godfrey et al. (2003) pour expliquer la formation et l'évolution du salar de Humber Muerto (4100 m d'altitude).

Dans le district minier de Gaoua, au SW du Burkina Faso, la formation de la minéralisation cuprifère supergène est liée à l'histoire Mésocénozoïque du craton ouest Africain. Les travaux récents de Gunnell (2003), Beauvais and Chardon (2013) et Chardon et al. (2018) ont montré le lien entre la formation des surfaces d'érosion et celle des minéralisations supergènes de manganèse et de bauxite. En particulier, Beauvais and Chardon (2013) et Chardon et al. (2018) ont montré que les surfaces d'érosion, au Burkina Faso, se sont formées entre ~ 45-24, ~ 24-11 et ~ 11-0 Ma via des datations $^{40}\text{Ar}/^{39}\text{Ar}$ sur des oxydes de potassium et de manganèse provenant de ces surfaces. Nos données U-Pb obtenues sur la chrysocolle corroborent ces hypothèses en montrant des rapports isotopiques $^{207}\text{Pb}/^{206}\text{Pb}$ et des valeurs de Pb radiogénique semblant indiquer une formation récente (à l'échelle des temps géologiques) de la chrysocolle. La formation de la chrysocolle pourrait donc être corrélée au dernier épisode de « pédimentation » connu au Burkina Faso, entre 11 Ma et l'actuel. Par ailleurs, la persistance d'un climat tropical, couplée à une exhumation lente et un taux d'érosion lent et homogène depuis le Cénozoïque, favoriserait la formation continue de la minéralisation cuprifère supergène depuis le début du Cénozoïque jusqu'à l'actuel. Au contraire du désert d'Atacama qui a évolué vers un climat

hyperaride à la fin du Miocène, stoppant l'altération supergène et préservant la minéralisation supergène formée.

VII.4 Les paramètres géologiques et climatiques contrôlant le chronomètre U-Pb dans les minéralisations cuprifères supergènes

L'utilisation du chronomètre U-Pb pour dater la minéralisation cuprifère supergène dépend de paramètres géologiques et climatiques autant globaux que principalement locaux/régionaux. Ces facteurs globaux sont maintenant bien connus et résultent d'une balance subtile entre le soulèvement tectonique, le climat via les apports d'eau météorique et une érosion modérée pour préserver le profil supergène créé. En plus de ces paramètres globaux, le succès de la datation U-Pb dépend de facteurs locaux tels que la chimie du porphyre, i.e. sa concentration initiale en U et en Pb commun, l'âge et la durée du fonctionnement de l'altération supergène, et le climat local, i.e. l'absence ou la présence de fluides post-cristallisation pouvant perturber le signal chronométrique U-Pb.

i) la tectonique et le climat. Ces deux paramètres sont indissociables dans le processus d'altération supergène. La formation des porphyres cuprifères est généralement voire exclusivement associée aux marges actives actuelles (e.g. la côte pacifique chilienne) et aux zones l'ayant été au cours de leur histoire (e.g. le bouclier ouest-africain). La subduction entraîne un raccourcissement crustal qui engendre un soulèvement tectonique et donc une érosion importante, portant à la sub-surface la minéralisation cuprifère hypogène née de l'activité magmatique-hydrothermale. Parallèlement, la nappe phréatique et les apports d'eau entraînent le lessivage du cuivre et la formation d'une colonne supergène. En somme, la chimie du porphyre cuprifère exhumée, les circulations ou apports d'eau et la durée de l'altération supergène influenceront sur la préservation ou la perturbation du signal chronométrique dans la chrysocolle et la pseudomalachite.

Dans le complexe porphyrique de Chuquicamata, l'activité magmatique et la minéralisation hypogène ont eu lieu lors de l'orogénèse incaïque (42-33 Ma ; Maksaev and Zentilli, 1999). Le complexe porphyrique de Chuquicamata s'est mis en place entre 35 et 33 Ma (Fig. VII.1A), résultant de la superposition de deux événements magmatiques-hydrothermaux (Ballard et al., 2001; Ossandón et al., 2001). Les analyses roche totale en U ont donné des valeurs élevées (environ 2-3 ppm ; Campbell

et al., 2006). Dans les minéraux cuprifères étudiées (i.e. les chrysocolles et la pseudomalachite), les concentrations en U sont très importantes (des centaines à un millier de ppm) dénotant, de fait, un lien entre les concentrations initiales en U du porphyre et celles de la minéralisation cuprifère supergène. A Chuquicamata, le processus d'altération supergène *in situ* a été documenté par Sillitoe and McKee (1996) comme s'étant déroulé entre ca. 15 Ma et ca. 19 Ma (K-Ar sur alunites ; Sillitoe and McKee, 1996), environ ~ 12 Ma après le dernier épisode hydrothermal, dans un contexte climatique aride. Cette altération supergène, quoique récente à l'échelle des temps géologiques, a permis la désintégration de l'U en Pb radiogénique en des proportions mesurables (Fig. VII.1.B). Par la suite, l'installation d'un climat hyperaride, entre la moitié du Miocène et le Pliocène, a inhibé la circulation de fluides post-cristallisation et permis de préserver le signal U-Pb dans les bandes de pseudomalachite ou un âge de formation à ca. 19 Ma a été reporté par Kahou et al. (2020). Cependant, comme reporté par Reich et al. (2009), des circulations tardives de fluides ont eu lieu dans le district minier de Chuquicamata à environ ~ 240 ka, en lien avec des épisodes climatiques humides. Ces circulations de fluides post-hyperaridité pourraient donc expliquer le lessivage du Pb radiogénique des bandes de chrysocolle, intensifié par la structure cristalline peu robuste de la chrysocolle (Fig. VII.1.D).

Au sud du désert d'Atacama (26°-27°S), dans les districts miniers de Salvador et Potrerillos, aucune étude n'a reporté, en l'état actuel des connaissances, les concentrations d'U sur roche totale des porphyres cuprifères de Salvador et de Potrerillos. Cette absence de données ne permet que des suppositions sur le rôle joué par la chimie initiale du porphyre sur les concentrations en U des minéralisations cuprifères supergènes (i.e. la chrysocolle et la pseudomalachite). Les faibles concentrations en U pourraient donc être le crédit d'autres facteurs. Dans le district minier de Salvador, l'altération supergène s'est mis en place entre 35 et 11 Ma (Mote et al., 2001), tandis qu'à Potrerillos, Marsh et al. (1997) ont reporté des âges $^{40}\text{Ar}/^{39}\text{Ar}$ sur alunite entre ca. 6 Ma et ca. 13 Ma. D'un point de vue tectonique, le sud du désert d'Atacama a subi deux épisodes tectoniques. La première phase est liée à l'orogénèse Inca (42-33 Ma ; Makshev and Zentilli, 1999), responsable de la mise en place des porphyres cuprifères de Salvador (Gustafson et al., 2001) et de Potrerillos (Marsh et al., 1997) et d'un premier épisode d'altération supergène. Ce premier épisode a été documenté par Mote et al. (2001) comme ayant permis la formation de la minéralisation exotique de Damiana entre 35 et 11 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$

sur copper wad). Par la suite, un second évènement tectonique, la phase Quechua, au début du Miocène (~ 18 Ma, la phase Quechua I ; Kay et al., 1999) et à la fin du Miocène (~ 6 Ma, la phase Quechua II ; McKee and Noble, 1989), a engendré un soulèvement tectonique et plausiblement, un second épisode d'altération supergène. Dans le district minier d'El Salvador, la phase Quechua est responsable de l'incision des surfaces d'érosion et de la formation des canyons d'El Salado et Asientos (Bissig and Riquelme, 2010 et références y figurant). L'incision et la formation de ces canyons ont entraîné une descente du niveau de la nappe phréatique et sans doute un nouvel épisode d'altération supergène. Dans le district minier de Potrerillos, ce second évènement tectonique a été décrit dans les secteur de la Coya et El Hueso par Bissig and Riquelme (2010). Ces derniers ont montré, via des datations $^{40}\text{Ar}/^{39}\text{Ar}$, que des natroalunites supergènes se sont formées à l'actuel en lien avec la phase Quechua. Cette altération supergène récente, liée à l'évènement tectonique Quechua, pourrait expliquer, d'une part, l'absence de Pb radiogénique dans la chrysocolle et la pseudomalachite due à la formation récente de ces minéraux. D'autre part, les faibles concentrations en U observées dans la chrysocolle et la pseudomalachite pourraient être le résultat d'une circulation pérenne de fluides liée aux évènements tectoniques Inca et Quechua, qui vont lessiver l'U des porphyres sources vu qu'il a été démontré que l'U est très mobile dans les fluides oxydants et supergènes (Cathelineau, 1983; Tartese et al., 2013; Kraemer et al., 2015). Ceci pourrait expliquer, de facto, les faibles concentrations d'U observées dans les minéraux cuprifères des minéralisations exotiques de Damiana et El Cobre (Fig. VII.2.C). Par ailleurs, l'initiation de l'hyperaridité qui fût asynchrone entre le nord et le sud du désert d'Atacama, et le fait que les districts miniers de Salvador et de Potrerillos aient été à des altitudes élevées (~ 3000 m a.s.l) dès l'Oligocène, et présentement à 4000 m a.s.l pour le district minier de Potrerillos (Bissig and Riquelme, 2010), militent pour une capture de l'humidité et donc une disponibilité de fluides météoriques pouvant potentiellement former la chrysocolle et la pseudomalachite jusqu'à une époque relativement récente ou entrainer la mobilité de l'U des porphyres sources. Les épisodes tectoniques tardi-Miocène et l'installation tardive de l'hyperaridité, combinée aux hautes altitudes, ont donc favorisé le comportement du milieu de dépôt (i.e. le porphyre cuprifère en amont et la minéralisation exotique en aval) en système ouvert, empêchant toute préservation du signal chronométrique U-Pb dans la chrysocolle et la pseudomalachite (Fig. VII.2.D).

Dans le district minier de Gaoua (sud-ouest du Burkina Faso), l'activité magmatique et hydrothermale est datée du Paléoprotérozoïque, i.e. entre 2.2 et 2.1 Ga (Baratoux et al., 2011; Le Mignot et al., 2017). De même que les districts miniers de Salvador et Potrerillos, aucune donnée dans la littérature n'a publié de valeurs d'U sur roche totale, empêchant toute corrélation entre ces dernières et les concentrations en U obtenues dans la chrysocolle (quelques dizaines de ppm). A Gaoua, l'altération supergène s'est mise en place depuis le début du Paléogène jusqu'à l'actuel, contemporanément à la formation des surfaces bauxitiques et des surfaces d'érosion. Des datations effectuées sur le gisement manganésifère de Tambao ont permis de contraindre le fonctionnement de l'altération supergène au Burkina Faso sur une période de temps allant de la fin du Paléocène au début du Quaternaire (Beauvais et al., 2008). Cette altération supergène est à mettre au crédit des alternances saisonnières humides/sèches débutée depuis l'ouverture de l'Atlantique (Séranne, 1999). La chrysocolle, qui montre de faibles teneurs en Pb radiogénique (comparativement à des teneurs importantes en Pb commun) pourrait donc refléter une cristallisation récente de la chrysocolle intensifiée par des conditions géologiques et climatiques favorables tout au long du Cénozoïque, i.e. faible taux d'érosion et un climat relativement humide. En outre, cette altération supergène pérenne depuis le Cénozoïque jusqu'à l'actuel corrobore l'hypothèse d'une circulation ininterrompue de fluides pouvant faciliter la mobilité du Pb par des fluides météoriques post-cristallisation. Enfin, l'apparition d'un climat aride (i.e. sahélien) contemporanément à la formation de la calotte antarctique a sans doute permis la préservation de la minéralisation cuprifère supergène de Gaoua sans pour autant empêcher des circulations de fluides pouvant précipiter la chrysocolle et/ou favoriser la mobilité de l'U et/ou du Pb de la chrysocolle existante (Fig. VII.3).

ii) l'érosion et le facteur temps. Les taux d'érosion sont fortement dépendants du climat et de la tectonique. Des apports d'eau conséquents (i.e. climats tropicaux humides), non contrebalancés par des taux d'exhumation adéquats, vont lessiver le cuivre supergène et entraîner de fait la mobilité de l'U et du Pb dans l'environnement de dépôt (i.e. autant dans le porphyre source que la minéralisation exotique), empêchant toute extraction d'informations à partir des données géochronologiques. En conditions climatiques arides, les précipitations modérées et les faibles taux d'érosion sont favorables à une préservation du signal chronométrique au sein des minéraux. Cependant, intervient le facteur

temps. Dans le complexe porphyrique de Chuquicamata, les quatre millions d'années de fonctionnement de l'altération supergène ont sans doute été propices à la préservation du signal U-Pb dans la pseudomalachite. Cependant, au sud du désert d'Atacama et dans la région de Gaoua, l'altération supergène qui s'est déroulée sur un laps de temps beaucoup plus important (e.g. 23 millions d'années pour la formation de la minéralisation exotique de Damiana obtenus par des datations $^{40}\text{Ar}/^{39}\text{Ar}$ sur minéraux d'altération ; Mote et al., 2001; Bissig and Riquelme, 2010) a sans doute favorisé la mobilité constante de l'U par un apport permanent de fluides supergènes et donc un fonctionnement en système ouvert, empêchant sa désintégration en Pb radiogénique. De plus, cette altération supergène de longue durée a sans doute permis d'incorporer des quantités importantes de Pb commun qui au regard des faibles proportions de Pb radiogénique, empêchent d'extraire des données U-Pb correctes via une correction du Pb commun.

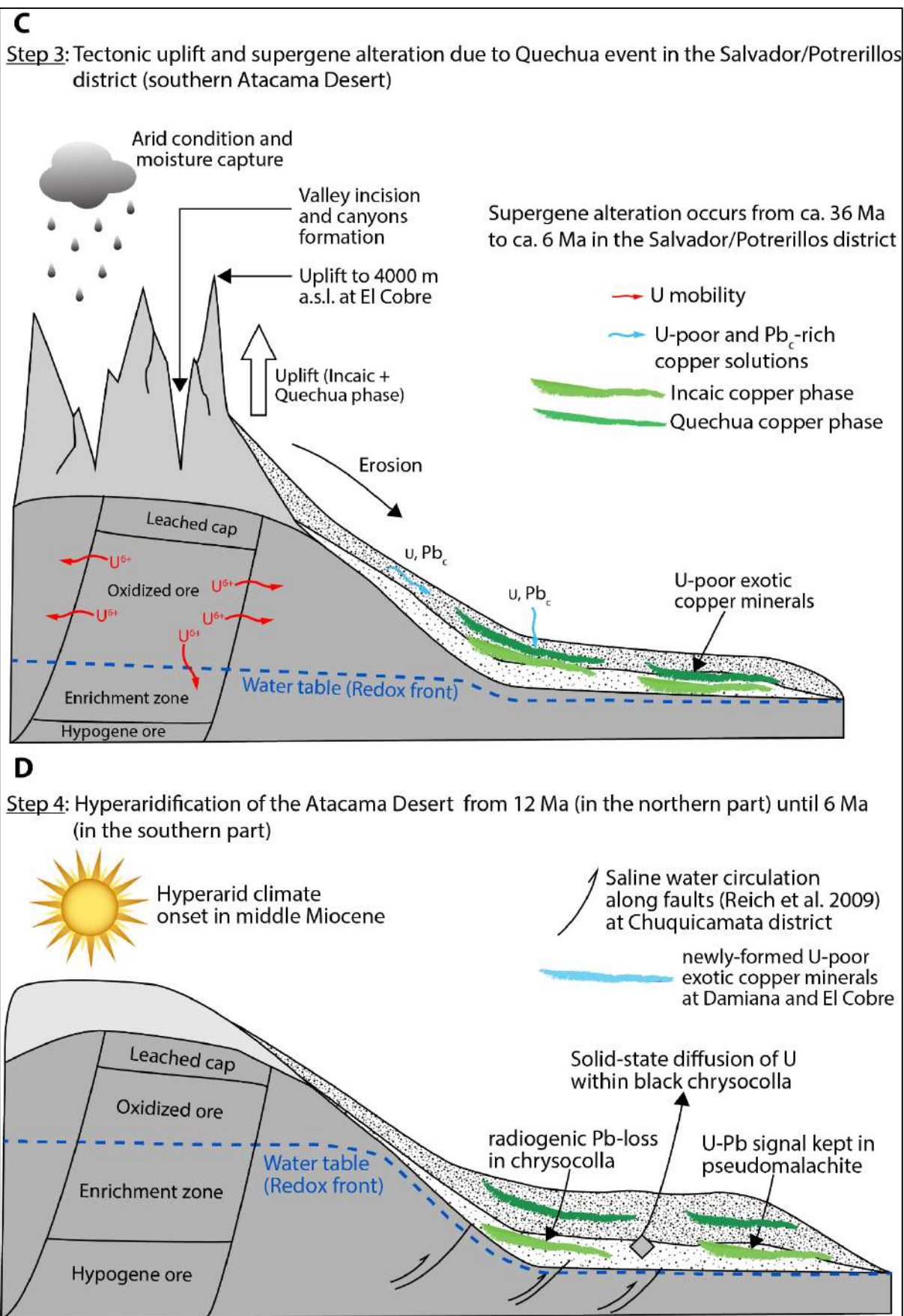


Figure VII.2 : Synthèse de l'évolution géologique du district minier de Salvador/Potrerillos depuis l'altération supergène (C) jusqu'à l'hyperaridification du désert d'Atacama (D)

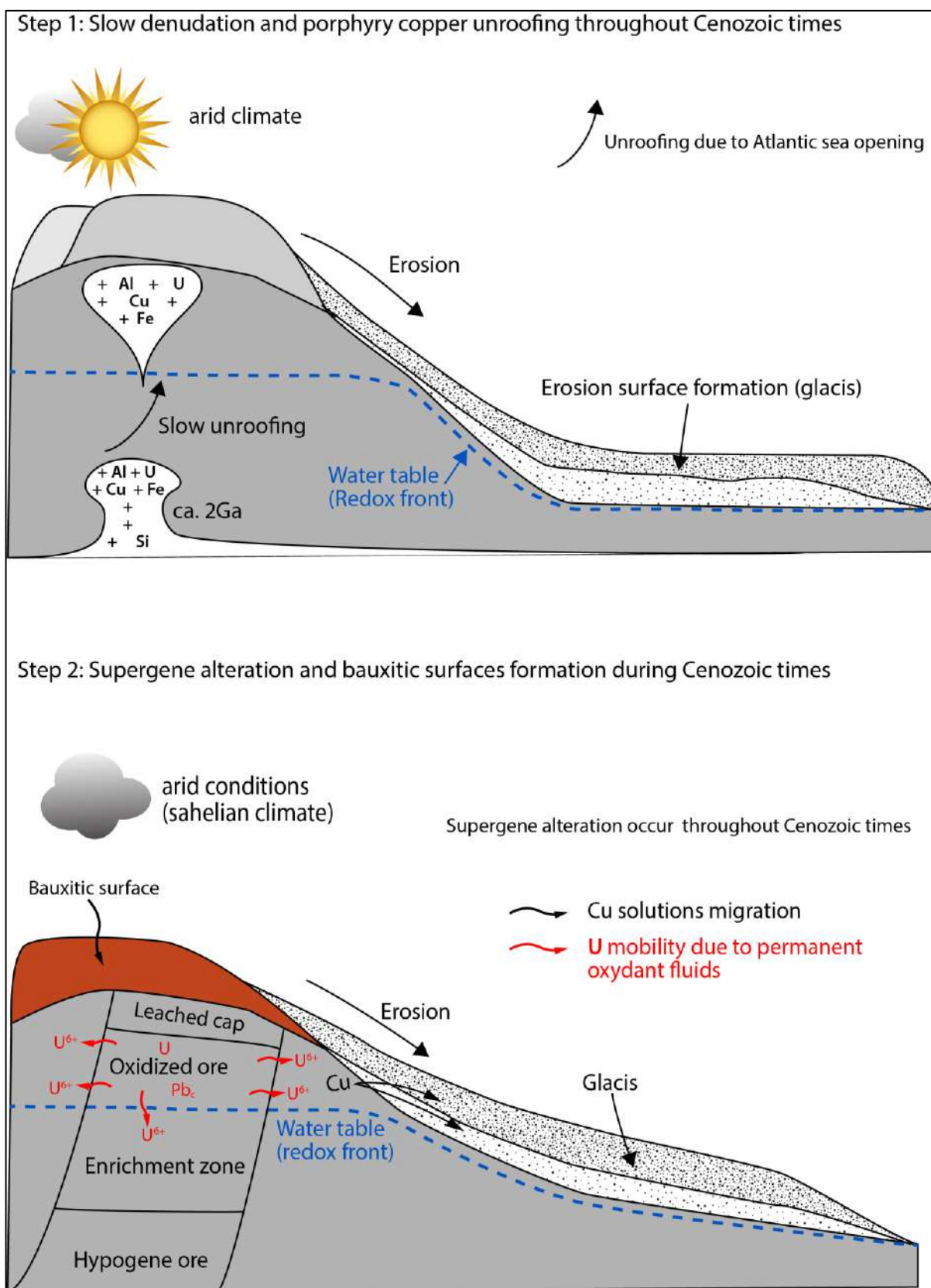


Figure VII.3 : Synthèse de l'évolution géologique du district minier de Gaoua depuis l'exhumation du porphyre lors de l'ouverture de l'océan Atlantique (step 1) et durant le fonctionnement de l'altération supergène dans le district minier tout au long du Tertiaire

VII.5 Guides d'exploration

Avant les travaux présentés dans cette thèse, de nombreuses incertitudes persistaient quant à la simultanéité ou non des dépôts supergènes *in situ* et des minéralisations exotiques de Cu. De plus, en l'absence de minéraux d'altération, aucune contrainte temporelle absolue ne pouvait définir le laps de temps entre la fin de l'activité magmatique-hydrothermal et le début du processus d'altération supergène. A l'inverse des minéralisations cuprifères supergènes *in situ*, qui ont été énormément étudiés, l'absence d'une base de données sur la caractérisation géochimique, isotopique et géochronologique des minéralisations exotiques de cuivre, empêchait une compréhension globale du fonctionnement de l'altération supergène des porphyres cuprifères depuis la formation de la minéralisation *in situ* jusqu'au transport latéral des solutions cuprifères pour engendrer la formation des minéralisations exotiques.

Les minéralisations cuprifères supergènes, *in situ* et exotique, résultent de la migration verticale et latérale des solutions cuprifères supergènes. La distribution minéralogique au sein de ces minéralisations renseigne sur la maturité ou non du profil supergène. Ainsi, la prédominance de la chrysocolle est interprétée comme étant le signe d'une colonne supergène mature, où tous les minéraux pouvant acidifier le pH (pyrite, chalcoppyrite) ont été consommés pour former une zone d'enrichissement supergène et un horizon oxydé suffisamment épais. De même, la prédominance de la chrysocolle au sein des dépôts exotiques renseigne sur la distance entre le porphyre source et la minéralisation exotique (Münchmeyer, 1996). Entre 2 et 6 km de distance, les solutions acides passent à un pH modérément acide à neutre et sont saturés en silice dû à l'altération progressive des feldspaths potassiques. Elles peuvent donc abondamment précipiter la chrysocolle. L'anomalie en Ce définit par les analyses géochimiques montre que la minéralisation exotique a été formée sous des conditions oxydantes ininterrompues. Ce qui dénote de la maturité géochimique du porphyre, en amont, ayant engendré cette minéralisation exotique.

Les isotopes du Cu peuvent aussi constituer un excellent métallotecte dans la recherche de minéralisation cuprifère supergène. En effet, les travaux entrepris, depuis une vingtaine d'années, sur le fractionnement isotopique dans la colonne supergène ont mis en évidence une zone lessivée appauvrie

en ^{65}Cu , une zone oxydée et une zone d'enrichissement supergène enrichis en ^{65}Cu et un protore avec des valeurs de $\delta^{65}\text{Cu}$ proches de zéro. En effet, plus le fractionnement isotopique est important dans les horizons oxydés et enrichis et plus les minéraux acides (i.e. pyrite et chalcopryrite) auront été consommés, dénotant d'une maturité du profil supergène. Les analyses sur les minéraux supergènes des minéralisations exotiques de Mina Sur, Damiana et El Cobre ont montré des valeurs de $\delta^{65}\text{Cu}$ supérieures à zéro. Ceci révèle que le transport depuis le porphyre en amont vers la source en aval n'entraîne pas un fractionnement particulier. Par conséquent, des valeurs isotopiques élevées seraient le signe qu'en amont, un profil supergène est enfoui sous des sédiments.

Par la datation de la minéralisation cuprifère supergène et plus précisément de la minéralisation exotique de Cu, ce travail apporte des outils supplémentaires à la compréhension de la géologie des gisements supergènes. Premièrement, nous avons montré que l'altération supergène *in situ* et la formation des minéralisations exotiques sont contemporaines. Ce qui sous-entend que chaque porphyre cuprifère ayant une colonne supergène peut avoir, dans ses alentours, une minéralisation exotique, si les conditions géomorphologiques (i.e. la pente) et sédimentologiques (i.e. les sédiments peuvent servir de tampon aux fluides) le permettent. Par ailleurs, les datations obtenues à Damiana, El Cobre et Gaoua mettent en lumière un âge de formation relativement récent de la minéralisation cuprifère supergène *in situ* et exotique. Prenant en compte les paramètres géologiques locaux propres à chaque district minier, ces datations signifieraient que l'altération supergène et la formation de la minéralisation exotique se sont faites bien après l'initiation de l'hyperaridité dans le désert d'Atacama, où les eaux météoriques étaient rares, et de manière continue dans la région de Gaoua, depuis le Paléocène jusqu'à l'actuel. Par conséquent, les stratégies de prospection, plus spécifiquement dans le sud du désert d'Atacama, devraient inclure une étude géomorphologique et sédimentologique détaillée afin de cartographier les surfaces d'érosion plus jeunes que 6 Ma (i.e. âge d'initiation de l'hyperaridité selon Hartley and Rice (2005)), susceptibles de recouvrir des colonnes supergènes d'un porphyre ou contenir des minéralisations exotiques de cuivre.

Dans le désert d'Atacama chilien, et plus récemment à l'échelle du craton ouest-africain, le lien entre la formation des minéralisations cuprifères supergènes et la géomorphologie a été depuis très longtemps reconnu. Dans le district minier de l'Atacama, la formation des surfaces d'érosion (i.e.

pédiments ou glacis) constitue un métallotecte très important dans la prospection des horizons supergènes enfouis sous des sédiments (Sillitoe et al., 1968; Mortimer, 1973; Mortimer and Sarič, 1975; Riquelme et al., 2017). Les pédiments sont des surfaces d'érosion formés en contexte climatique aride à semi-aride, lors de l'aplanissement du relief (Dohrenwend and Parsons, 2009). Elles enregistrent l'évolution physiographique d'une zone en lien avec la tectonique, le climat et l'érosion. Dans le désert d'Atacama, certains auteurs comme Sillitoe (2005) les considèrent comme n'étant pas un prérequis indispensable à la formation des minéralisations cuprifères supergènes. A l'inverse, Bissig and Riquelme (2009), Bissig and Riquelme (2010) et Riquelme et al. (2017) ont montré que l'altération supergènes des porphyres cuprifères est contemporaine de la formation des surfaces d'érosion. La datation de ces surfaces d'érosion, jumelée à la datation de la minéralisation supergène pourrait permettre de mieux contraindre la relation et l'impact de la formation de ces surfaces d'érosion sur celles des minéralisations cuprifères supergènes. En Afrique de l'Ouest, l'étude récente de Chardon et al. (2018) a montré que ces surfaces d'érosion sont étroitement liées à la formation des minéralisations supergènes métalliques (e.g. les bauxites latéritiques, le gisement de manganèse supergène de Tambao, etc.). Les travaux de Beauvais and Chardon (2013), Grimaud (2014) et Chardon et al. (2018) ont montré que la cartographie de ces surfaces d'érosion et leur caractérisation géochimique sont très importantes pour la prospection des régolithes latéritiques et d'autres gisements supergènes enfouis sous des épaisseurs de sédiments.

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CONCLUSIONS GENERALES ET PERSPECTIVES

Ce travail de thèse est le fruit d'une approche multidisciplinaire alliant échantillonnage dans des sites miniers, étude minéralogique et pétrologique, géochronologique et isotopique. Ces méthodes ont été appliquées principalement sur les minéralisations exotiques de cuivre de Mina Sur, Damiana et El Cobre puis dans un second temps sur les minéralisations supergènes *in situ* de Zaldivar, Gaby et Gaoua.

L'objectif premier de ce travail de thèse était d'obtenir une base de données géochronologiques afin de préciser et contraindre, de manière directe, l'âge de formation des minéralisations cuprifères supergènes dans le désert d'Atacama. Plus largement, les minéralisations exotiques ayant été peu étudiées, un travail métallogénique complet s'imposait de sorte à obtenir une compréhension claire de la genèse des minéralisations exotiques, en lien avec l'altération supergène des porphyres cuprifères.

Ce travail de thèse constitue de fait une étude pionnière car il apporte la première contrainte temporelle absolue quant à l'âge de formation des minéralisations cuprifères supergènes et fournit, pour la première fois, des arguments isotopiques (isotope du Cu) et géochimiques (REE et éléments mineurs) directs quant à la nature des fluides donnant naissance à ces minéralisations cuprifères supergènes et précisément les minéralisations exotiques de cuivre.

Les aspects purement métallogéniques ont été décrits dans les chapitres III et IV. Les minéralisations cuprifères supergènes naissent de l'équilibre entre soulèvement tectonique, apport d'eau et érosion. La chimie du porphyre (i.e. ratio pyrite/chalcopyrite) influe sur l'épaisseur de la colonne supergène *in situ* et sur la prédominance d'une phase minérale par rapport à une autre (e.g. chalcocite versus covellite, chrysocolle versus brochantite). La formation des minéralisations supergènes exotiques est quant à elle très dépendante du pH, de la nature des fluides minéralisateurs et du tampon chimique (nature des sédiments, évapoconcentration, etc.) qui favorisera la précipitation de cette dernière. La caractérisation de l'isotopie du cuivre a démontré que les fluides météoriques oxydants étaient les seuls impliqués dans la formation des minéralisations exotiques supergènes *in situ* et exotiques.

L'étude géochronologique a montré que le chronomètre U-Pb est adéquat pour dater la chrysocolle et la pseudomalachite vu les teneurs en U. Dans le désert d'Atacama, un âge de ca. 19 Ma a été obtenu sur la pseudomalachite de la minéralisation exotique de Mina Sur, apportant la première contrainte absolue sur l'âge de la minéralisation cuprifère supergène. Dans les autres districts miniers

de l'Atacama, la somme des analyses géochronologiques et isotopiques a montré que la teneur en U des minéraux supergènes est étroitement liée à la durée de fonctionnement de l'altération supergène et donc à la présence de fluides syn- et post-cristallisation dans l'environnement de dépôt. L'uranium peut être mobile via de la diffusion à l'état solide favorisé par la texture cristalline amorphe de la chrysocolle. Le Pb radiogénique quant à lui est facilement lessivé par des circulations tardives de fluides post-cristallisation intensifié par la structure faiblement cristalline de la chrysocolle.

A Gaoua, en contexte tectonique stable, les faibles taux d'exhumation, entraînant une faible érosion et un climat aride depuis le Paléocène, ont permis le fonctionnement continu de l'altération supergène, en système ouvert, ce qui a constitué un frein à l'accumulation de quantités importantes d'U et leur désintégration en Pb radiogénique.

Ces nouvelles données acquises, comparées à la bibliographie, montrent que le fonctionnement de l'altération supergène et la formation des minéralisations cuprifères supergènes sont liés intrinsèquement à des facteurs locaux tels que la chimie du porphyre, le ratio pyrite-chalcoppyrite et la disponibilité de fluides. Elles montrent aussi que l'incorporation et la préservation du signal U-Pb dans la chrysocolle et la pseudomalachite sont liées à la robustesse du réseau cristallin du minéral, à la quantité initiale d'U dans le porphyre cuprifère lors de sa formation, à la durée de fonctionnement de l'altération supergène et à l'absence ou non des fluides post-cristallisation pouvant favoriser la mobilité de l'U et/ou du Pb.

Pour conclure, la pseudomalachite, de la minéralisation exotique de Mina Sur, est un bon géochronomètre pour dater l'âge de formation des minéralisations cuprifères supergènes car en plus d'incorporer de l'U et posséder une structure cristalline robuste, elle est capable d'incorporer peu de Pb commun. La chrysocolle (i.e. la chrysocolle noire et la chrysocolle) incorpore des quantités importantes d'U mais des quantités non-négligeables de Pb commun ce qui pourrait être un frein à la datation de ce minéral. De par sa structure faiblement cristalline, la chrysocolle est sensible à la mobilité de l'U et/ou du Pb due aux réactions fluide-roche ou encore à la mobilité intracristalline via la diffusion à l'état solide. Ces deux minéraux sont très sensibles aux paramètres géologiques liés à leur environnement de dépôt qui peuvent influencer la préservation ou la perturbation du signal chronométrique au sein du réseau cristallin, i.e. la concentration initiale en U et en Pb commun du porphyre cuprifère, la durée du

processus d'altération supergène, la prévalence d'un climat pouvant inhiber la circulation de fluides post-cristallisation.

Les résultats acquis durant cette thèse ouvrent de nombreuses perspectives qui pourraient être explorées pour aller plus loin dans la compréhension de la genèse des minéralisations cuprifères supergènes et au-delà, dans la compréhension du comportement de l'U et du Pb vis-à-vis de l'évolution physico-chimique de leur milieu de dépôt.

- i) Les résultats obtenus apportent une contrainte sur la nature et la température relative des fluides impliqués dans la genèse des minéralisations cuprifères supergènes. Nous proposons d'aller plus dans la caractérisation des fluides en réalisant une étude microthermométrie détaillée sur les minéraux formés autant dans la colonne supergène *in situ* que dans les minéralisations exotiques (e.g. calcite, gypse, atacamite). Les inclusions fluides piéger dans ces minéraux qui cristallisent à la fin ou à posteriori du processus d'altération supergène, pourraient apporter une contrainte absolue sur la température des fluides responsables de ce processus.
- ii) Une autre voie serait celle des analyses des isotopes de l'oxygène de la chrysocolle et de la pseudomalachite sur roche totale. Des contacts ont déjà été noués avec Christophe Drouet de l'université Claude-Bernard de Lyon et Marc de Rafélis de l'université Paul Sabatier de Toulouse. Elles nous fourniraient des données quantitatives sur la température des fluides minéralisateurs et les conditions paléoclimatiques de formation (i.e. aridité, hyperaridité, évapoconcentration).
- iii) Des informations texturales à l'échelle nanométrique seront aussi indispensables pour comprendre comment l'U et le Pb sont distribués dans le réseau cristallin de la chrysocolle et de la pseudomalachite afin de pouvoir relier les informations texturales aux résultats géochronologiques et comprendre comment l'état du réseau cristallin (i.e. cristallin, amorphe) perturbe le signal chronométrique U-Pb. Les premiers résultats de cette étude sont présentés dans la section annexe de ce manuscrit.

ANNEXES

Chapitre III

Electronic Supplementary Materials (ESM) 1: Summary of supergene copper minerals EPMA analyses from exotic and *in situ* SCM deposits

Table 1 Chemical compositions of supergene copper minerals from Mina Sur exotic copper deposition				Table 2 Chemical compositions of supergene copper minerals from Damiana exotic copper deposition			
	Black chrysocolla	Chrysocolla	Pseudomalachite		Chrysocolla	Pseudomalachite	Apatite
N	105	79	123	N	21	23	10
wt %				wt %			
Al ₂ O ₃	0.057	2.159	0.090	Al ₂ O ₃	2.463	0.212	0.014
SiO ₂	32.177	36.780	0.221	SiO ₂	47.617	1.521	0.093
K ₂ O	0.000	0.050	0.000	K ₂ O	0.036	0.012	0.015
CaO	0.420	0.442	0.124	CaO	0.960	0.278	48.880
Cl	0.153	0.119	0.016	Cl	0.033	0.015	0.002
MnO	6.385	0.038	0.014	MnO	0.022	0.006	0.034
FeO	0.066	0.049	0.011	FeO	0.111	0.040	0.077
Na ₂ O	0.000	0.063	0.000	Na ₂ O	0.036	0.004	0.746
MgO	0.152	0.121	0.005	MgO	0.203	0.037	0.081
BaO	0.179	0.077	0.032	BaO	0.015	0.017	0.005
P ₂ O ₅	0.080	0.030	24.189	P ₂ O ₅	0.206	22.673	31.303
SO ₃	0.341	0.099	1.327	SO ₃	0.064	0.428	3.015
CuO	49.047	50.782	68.441	CuO	41.070	65.806	1.424
Total	89.057	90.809	94.470	Total	92.836	91.048	85.690

Table 3 Chemical compositions of supergene copper minerals from Damiana (bedrock)			Table 4 Chemical compositions of supergene copper minerals from El Cobre exotic copper deposition			
	Chrysocolla	Pseudomalachite		Chrysocolla	Pseudomalachite	Copper wad
N	21	23	N	135	68	7
wt %			wt %			
Al ₂ O ₃	0.025	0.525	Al ₂ O ₃	0.693	0.117	1.670
SiO ₂	43.247	0.222	SiO ₂	43.456	0.790	28.680
K ₂ O	0.015	0.025	K ₂ O	0.032	0.011	0.047
CaO	0.276	0.228	CaO	0.414	0.175	0.800
Cl	0.052	0.010	Cl	0.073	0.005	0.029
MnO	0.014	0.044	MnO	0.052	0.016	13.529
FeO	0.013	0.022	FeO	0.086	0.036	1.510
Na ₂ O	0.005	0.003	Na ₂ O	0.023	0.000	0.098
MgO	0.106	0.008	MgO	0.089	0.021	0.084
BaO	0.013	0.006	BaO	0.015	0.026	0.032
P ₂ O ₅	0.034	28.506	P ₂ O ₅	0.038	22.401	0.057
SO ₃	0.056	0.065	SO ₃	0.098	0.067	0.106
CuO	52.629	62.814	CuO	49.229	67.156	41.713
Total	96.486	92.475	Total	94.299	90.820	88.354

Table 5 Chemical compositions of supergene copper minerals from Gaby <i>in situ</i> copper deposition					Table 6 Chemical compositions of supergene copper minerals from Zaldivar <i>in situ</i> copper deposition			
	Chrysocolla	Sulfide relicts/Brochantite	Copper wad	Atacamite		Chrysocolla	Pseudomalachite	sulfides relicts/brochantite
N	21	18	3	6	N	33	54	58
wt %					wt %			
Al ₂ O ₃	0.477	0.036	5.235	0.048	Al ₂ O ₃	0.271	0.028	0.028
SiO ₂	32.753	0.789	25.541	5.449	SiO ₂	43.760	0.670	2.478
K ₂ O	0.018	0.019	0.911	0.015	K ₂ O	0.113	0.012	0.014
CaO	0.770	1.192	1.290	0.219	CaO	0.218	0.083	0.027
Cl	0.173	0.009	0.029	12.861	Cl	0.050	0.005	0.010
MnO	0.031	0.016	14.489	0.010	MnO	0.032	0.130	0.034
FeO	0.075	0.022	0.817	0.055	FeO	0.232	0.082	0.278
Na ₂ O	0.002	0.008	0.124	0.003	Na ₂ O	0.140	0.001	0.003
MgO	0.131	0.019	0.201	0.090	MgO	0.046	0.031	0.018
BaO	0.026	0.030	0.159	0.018	BaO	0.014	0.025	0.025
P ₂ O ₅	0.039	0.058	0.054	0.074	P ₂ O ₅	0.031	22.117	0.164
SO ₃	0.042	29.435	0.062	0.128	SO ₃	0.442	0.766	18.436
CuO	55.197	89.018	36.138	76.305	CuO	51.252	68.122	78.613
Total	89.733	120.651	85.050	95.276	Total	96.602	92.070	100.128

Table 7 Chemical compositions of supergene copper minerals from Gaoua <i>in situ</i> copper deposition		
	Chrysocolla	Pseudomalachite
N	160	5
wt %		
Al ₂ O ₃	1.363	0.028
SiO ₂	40.885	1.957
K ₂ O	0.039	0.018
CaO	0.380	0.040
Cl	0.047	0.002
MnO	0.018	0.044
FeO	0.072	0.006
Na ₂ O	0.017	0.000
MgO	0.276	0.030
BaO	0.018	0.008
P ₂ O ₅	0.047	20.721
SO ₃	0.087	0.049
CuO	50.558	66.979
Total	93.806	89.882

ESM 2: Summary of LA-ICP-MS REE and trace elements analyses carried out on supergene copper minerals from exotic and *in situ* SCM deposits. Operating conditions and data obtained on standards materials are also listed

Mina Sur exotic copper deposition

Table 1 REE analyses of black chrysocolla

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Black chrysocolla_1	2.730	1.040	0.740	2.470	0.590	0.252	1.720	0.235	1.500	0.430	0.910	0.145	0.890	0.134
Black chrysocolla_2	2.740	0.920	0.734	2.640	0.660	0.181	1.860	0.297	1.760	0.496	0.920	0.112	0.820	0.127
Black chrysocolla_3	2.480	0.950	0.570	2.230	0.570	0.179	1.400	0.216	1.580	0.366	0.770	0.113	0.840	0.084
Black chrysocolla_4	2.370	0.940	0.600	2.030	0.600	0.160	1.546	0.280	1.450	0.346	0.760	0.100	0.650	0.091
Black chrysocolla_5	2.650	1.040	0.613	2.200	0.550	0.161	1.500	0.270	1.940	0.397	0.880	0.110	0.810	0.130
Black chrysocolla_6	2.800	1.030	0.658	2.440	0.570	0.189	1.680	0.250	1.650	0.420	1.050	0.127	0.710	0.114
Black chrysocolla_7	2.900	0.930	0.790	3.000	0.530	0.295	1.930	0.320	2.260	0.450	1.160	0.166	1.020	0.158
Black chrysocolla_8	2.560	0.860	0.584	2.630	0.590	0.208	1.620	0.290	1.850	0.340	0.830	0.115	0.840	0.086
Black chrysocolla_9	2.400	0.890	0.559	2.390	0.470	0.178	1.660	0.270	1.550	0.362	0.950	0.138	0.790	0.101
Black chrysocolla_10	2.800	1.400	0.750	2.580	0.840	0.273	2.030	0.279	1.760	0.358	0.980	0.125	0.720	0.100

Table 2 REE analyses of chrysocolla

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_1	0.410	0.390	0.052	0.260	NA	NA	NA	NA	0.160	0.037	NA	NA	NA	NA
Chrysocolla_2	0.340	0.224	0.032	NA	NA	NA	NA	0.021	0.195	0.025	NA	NA	NA	NA
Chrysocolla_3	0.780	1.000	0.140	0.660	NA	0.048	0.290	0.048	0.160	0.030	0.130	0.012	NA	NA
Chrysocolla_4	0.580	0.500	0.069	0.330	0.130	NA	0.200	0.024	0.153	0.022	0.031	NA	NA	0.011
Chrysocolla_5	0.570	0.520	0.071	0.470	0.070	NA	0.250	0.018	0.151	0.030	NA	NA	NA	NA
Chrysocolla_6	0.630	0.650	0.104	0.550	0.048	0.039	NA	0.022	0.139	NA	NA	0.017	NA	NA
Chrysocolla_7	0.650	0.720	0.079	0.300	NA	NA	NA	0.032	0.180	0.028	NA	0.020	0.030	NA
Chrysocolla_8	0.680	0.800	0.115	0.380	NA	0.023	0.140	0.033	0.202	0.031	0.135	0.021	NA	0.005
Chrysocolla_9	0.520	0.520	0.064	0.260	NA	NA	NA	0.036	0.150	0.037	0.088	0.016	0.044	NA
Chrysocolla_10	1.070	1.300	0.140	0.780	0.110	NA	0.240	0.060	0.220	0.056	0.090	0.018	NA	NA

Table 3 REE analyses of pseudomalachite

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Pseudomalachite_1	3.970	1.670	0.700	3.960	0.920	0.470	4.060	0.688	4.300	1.110	2.730	0.290	1.700	0.214
Pseudomalachite_2	4.070	1.980	0.880	4.510	1.450	0.580	5.100	0.747	5.300	1.240	3.160	0.360	1.870	0.289
Pseudomalachite_3	6.260	5.000	1.610	9.560	3.040	1.080	9.800	1.650	11.500	2.540	6.310	0.726	4.270	0.630
Pseudomalachite_4	4.040	1.890	0.774	4.170	1.180	0.510	4.850	0.793	5.400	1.170	3.140	0.350	1.770	0.261
Pseudomalachite_5	4.270	2.110	0.820	4.620	1.530	0.440	5.500	0.753	5.900	1.350	3.360	0.440	2.160	0.312
Pseudomalachite_6	4.250	2.370	0.990	4.860	1.520	0.630	5.320	1.021	6.610	1.540	4.070	0.463	2.320	0.348
Pseudomalachite_7	6.710	5.810	1.890	10.800	3.550	1.440	11.700	2.110	14.300	3.080	7.500	0.937	5.080	0.670
Pseudomalachite_8	6.890	6.120	1.930	11.000	4.050	1.530	12.400	2.140	13.900	3.290	8.120	1.052	5.640	0.810
Pseudomalachite_9	7.460	6.970	2.180	13.300	4.230	1.650	13.400	2.300	15.700	3.520	9.100	1.070	5.600	1.000
Pseudomalachite_10	6.350	5.950	2.000	12.700	4.270	1.470	12.700	2.240	14.600	3.310	8.660	1.140	5.230	0.843

Mina Sur exotic copper deposition

Table 4 Trace elements analyses (ppm) of black chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Fe	Co	Ni	Zn	Rb
Black chrysocolla_1	Below LOD	1150.0	430.0	103.0	3400.0	2.3	Below LOD	8.4	Below LOD	34.7	9.8	2450.0	0.9
Black chrysocolla_2	Below LOD	910.0	400.0	58.0	2820.0	2.2	1.5	4.9	Below LOD	33.7	7.6	2430.0	1.2
Black chrysocolla_3	Below LOD	1110.0	420.0	49.0	3200.0	2.3	0.8	7.7	7.1	33.3	7.7	2620.0	1.2
Black chrysocolla_4	Below LOD	1040.0	450.0	58.6	3200.0	2.1	0.6	7.3	Below LOD	35.0	9.3	2510.0	1.2
Black chrysocolla_5	Below LOD	1060.0	450.0	65.0	3450.0	2.3	0.8	7.4	Below LOD	39.0	8.3	2510.0	1.3
Black chrysocolla_6	Below LOD	930.0	380.0	56.9	2700.0	1.7	0.9	5.2	Below LOD	36.0	7.7	2410.0	1.1
Black chrysocolla_7	10.0	900.0	470.0	57.0	3090.0	2.0	Below LOD	Below LOD	Below LOD	28.3	6.9	2260.0	1.0
Black chrysocolla_8	Below LOD	1050.0	400.0	61.0	2920.0	2.0	Below LOD	8.6	8.4	33.1	7.3	2530.0	1.3
Black chrysocolla_9	Below LOD	1020.0	410.0	58.0	3070.0	1.9	Below LOD	Below LOD	Below LOD	37.4	7.1	2440.0	1.4
Black chrysocolla_10	Below LOD	1030.0	460.0	57.0	3300.0	2.0	Below LOD	10.8	Below LOD	64.0	6.8	2580.0	1.2
Sample	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U	
Black chrysocolla_1	75.0	17.5	Below LOD	Below LOD	Below LOD	Below LOD	284.0	0.0	0.0	Below LOD	Below LOD	770.0	
Black chrysocolla_2	74.0	17.3	1.4	0.0	Below LOD	Below LOD	274.0	0.0	0.0	0.0	Below LOD	800.0	
Black chrysocolla_3	71.0	13.9	Below LOD	0.0	Below LOD	0.1	266.0	0.0	Below LOD	Below LOD	Below LOD	810.0	
Black chrysocolla_4	74.0	13.4	Below LOD	Below LOD	Below LOD	Below LOD	301.0	0.0	Below LOD	Below LOD	Below LOD	780.0	
Black chrysocolla_5	74.0	14.1	Below LOD	Below LOD	Below LOD	0.1	272.0	0.0	Below LOD	Below LOD	0.0	780.0	
Black chrysocolla_6	44.0	14.6	Below LOD	0.0	Below LOD	Below LOD	241.0	0.0	Below LOD	Below LOD	0.0	620.0	
Black chrysocolla_7	43.0	16.6	Below LOD	0.0	Below LOD	0.1	238.0	0.0	Below LOD	0.1	0.0	730.0	
Black chrysocolla_8	59.0	13.2	Below LOD	Below LOD	Below LOD	Below LOD	306.0	0.0	0.0	Below LOD	0.0	800.0	
Black chrysocolla_9	54.0	13.0	Below LOD	Below LOD	Below LOD	0.1	256.0	0.0	Below LOD	Below LOD	Below LOD	780.0	
Black chrysocolla_10	73.0	14.4	Below LOD	Below LOD	Below LOD	Below LOD	262.0	0.0	Below LOD	Below LOD	Below LOD	820.0	

Table 5 Trace elements analyses (ppm) of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Fe	Co	Ni	Zn	Rb
Chrysocolla_1	Below LOD	2100.0	860.0	133.0	3800.0	1.4	11.0	9.4	180.0	1.7	3.0	2500.0	1.4
Chrysocolla_2	Below LOD	670.0	584.0	44.0	2990.0	1.4	Below LOD	11.1	Below LOD	0.5	Below LOD	2480.0	1.5
Chrysocolla_3	Below LOD	80000.0	2000.0	39.0	5300.0	1.5	25.0	14.5	260.0	1.0	Below LOD	2370.0	2.1
Chrysocolla_4	Below LOD	4400.0	1200.0	76.0	3600.0	1.2	44.0	9.2	150.0	1.0	2.3	2260.0	1.8
Chrysocolla_5	Below LOD	3700.0	1230.0	72.0	3800.0	1.5	5.0	10.8	95.0	1.0	Below LOD	2570.0	2.2
Chrysocolla_6	Below LOD	4500.0	1250.0	97.0	4600.0	1.4	15.0	8.6	280.0	1.2	2.5	2570.0	2.7
Chrysocolla_7	2.6	4900.0	1300.0	76.0	4100.0	1.1	10.0	Below LOD	150.0	1.3	Below LOD	2800.0	2.6
Chrysocolla_8	Below LOD	4900.0	1400.0	74.0	3800.0	1.2	11.0	12.5	130.0	1.5	Below LOD	2910.0	2.5
Chrysocolla_9	Below LOD	4100.0	1200.0	81.0	3100.0	1.1	7.0	11.3	160.0	1.0	3.6	2700.0	1.9
Chrysocolla_10	Below LOD	80000.0	2000.0	470.0	5300.0	1.4	19.0	18.2	310.0	2.1	Below LOD	2990.0	3.4
Sample	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U	Mn
Chrysocolla_1	42.8	1.4	Below LOD	Below LOD	Below LOD	Below LOD	13.2	Below LOD	Below LOD	0.7	0.1	1310.0	1270.0
Chrysocolla_2	54.0	1.2	Below LOD	Below LOD	Below LOD	Below LOD	6.7	0.0	0.0	0.2	0.0	1310.0	374.0
Chrysocolla_3	45.0	1.8	5.1	0.1	2.6	Below LOD	12.5	0.2	0.0	0.8	0.2	1270.0	920.0
Chrysocolla_4	Below LOD	1.2	2.4	0.0	1.3	0.2	9.6	0.1	Below LOD	0.3	0.1	1140.0	1071.0
Chrysocolla_5	24.0	1.4	3.5	0.1	1.4	0.2	10.6	0.1	0.0	0.5	0.1	1130.0	1150.0
Chrysocolla_6	Below LOD	1.3	3.6	0.1	2.8	Below LOD	14.5	Below LOD	0.0	0.6	0.1	1250.0	1400.0
Chrysocolla_7	37.4	1.6	3.9	0.0	1.8	Below LOD	13.4	Below LOD	0.0	0.6	0.2	1320.0	1400.0
Chrysocolla_8	Below LOD	1.7	4.1	0.1	2.2	Below LOD	13.2	0.1	Below LOD	0.5	0.1	1300.0	1420.0
Chrysocolla_9	22.0	1.5	Below LOD	0.0	1.4	0.1	7.4	0.1	0.0	0.4	0.1	1200.0	724.0
Chrysocolla_10	Below LOD	2.1	6.0	0.1	3.5	0.2	17.9	0.2	0.0	0.9	0.2	1290.0	1180.0

Table 6 Trace elements analyses (ppm) of pseudomalachite

Sample	Li	Na	Mg	Si	Ca	Sc	Ti	Cr	Fe	Co	Ni	Rb	Sr
Pseudomalachite_1	Below LOD	77.9	60.2	2780.0	1050.0	Below LOD	Below LOD	7.7	Below LOD	Below LOD	7.9	Below LOD	27.2
Pseudomalachite_2	4.1	81.3	48.2	2590.0	1050.0	0.4	Below LOD	7.2	12.0	Below LOD	7.7	Below LOD	15.4
Pseudomalachite_3	Below LOD	158.0	50.7	2460.0	1040.0	1.2	1.9	7.4	Below LOD	Below LOD	5.1	Below LOD	16.5
Pseudomalachite_4	Below LOD	65.0	50.6	3120.0	1130.0	0.5	Below LOD	13.1	Below LOD	Below LOD	4.8	0.3	25.5
Pseudomalachite_5	Below LOD	68.9	48.8	2630.0	1110.0	Below LOD	Below LOD	11.4	Below LOD	Below LOD	Below LOD	Below LOD	21.2
Pseudomalachite_6	Below LOD	70.6	42.4	2370.0	1170.0	Below LOD	1.5	10.5	Below LOD	0.1	Below LOD	Below LOD	13.5
Pseudomalachite_7	5.4	148.0	58.7	2460.0	1310.0	1.4	Below LOD	14.6	Below LOD	Below LOD	Below LOD	Below LOD	32.7
Pseudomalachite_8	9.9	157.0	60.3	2700.0	1520.0	1.4	Below LOD	30.0	Below LOD	Below LOD	6.7	Below LOD	33.7
Pseudomalachite_9	10.2	147.0	84.3	2380.0	1500.0	2.0	1.3	31.3	Below LOD	Below LOD	Below LOD	Below LOD	36.9
Pseudomalachite_10	8.8	137.7	78.4	2080.0	1340.0	1.9	Below LOD	15.2	Below LOD	0.1	Below LOD	Below LOD	31.9
Sample	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U	Mn	
Pseudomalachite_1	52.0	Below LOD	Below LOD	Below LOD	Below LOD	4.6	Below LOD	Below LOD	Below LOD	Below LOD	430.0	5.4	
Pseudomalachite_2	55.0	Below LOD	Below LOD	Below LOD	Below LOD	4.0	Below LOD	Below LOD	Below LOD	Below LOD	419.0	5.3	
Pseudomalachite_3	77.0	2.0	Below LOD	Below LOD	Below LOD	4.0	Below LOD	Below LOD	Below LOD	Below LOD	722.0	10.9	
Pseudomalachite_4	55.4	Below LOD	Below LOD	Below LOD	Below LOD	4.4	Below LOD	Below LOD	Below LOD	0.0	442.0	5.3	
Pseudomalachite_5	57.0	Below LOD	Below LOD	Below LOD	Below LOD	4.9	Below LOD	Below LOD	0.0	Below LOD	449.0	4.8	
Pseudomalachite_6	60.0	Below LOD	Below LOD	Below LOD	Below LOD	4.0	0.0	Below LOD	Below LOD	Below LOD	428.0	4.2	
Pseudomalachite_7	90.0	Below LOD	Below LOD	Below LOD	Below LOD	5.7	0.0	0.0	Below LOD	Below LOD	772.0	13.0	
Pseudomalachite_8	92.0	Below LOD	Below LOD	Below LOD	Below LOD	5.6	0.0	Below LOD	Below LOD	0.0	838.0	14.2	
Pseudomalachite_9	93.0	Below LOD	Below LOD	Below LOD	Below LOD	5.4	Below LOD	Below LOD	0.0	0.0	1034.0	17.5	
Pseudomalachite_10	87.0	Below LOD	Below LOD	Below LOD	Below LOD	5.6	Below LOD	Below LOD	Below LOD	0.0	1031.0	15.5	

Damiana exotic copper deposition

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_bedrock_1	2.600	4.000	0.600	4.300	1.000	0.200	1.030	0.147	0.890	0.209	0.540	0.103	0.290	0.053
Chrysocolla_bedrock_2	2.500	4.400	0.630	3.000	0.530	0.180	0.460	0.096	0.640	0.121	0.320	0.097	0.490	0.069
Chrysocolla_bedrock_3	2.200	2.600	0.360	1.900	Below LOD	Below LOD	Below LOD	0.043	0.410	0.078	0.410	0.029	0.190	0.033
Chrysocolla_bedrock_4	4.500	12.000	1.110	4.500	0.430	Below LOD	0.710	0.123	0.490	0.130	0.430	Below LOD	0.680	0.081
Chrysocolla_bedrock_5	0.460	1.400	0.190	1.700	0.340	0.103	Below LOD	0.110	0.490	0.067	0.290	0.037	0.190	0.018
Chrysocolla_bedrock_6	3.200	4.200	0.480	2.400	0.980	0.290	1.670	0.180	0.540	0.220	0.650	Below LOD	0.570	0.041
Chrysocolla_bedrock_7	2.500	4.300	0.470	2.430	0.680	Below LOD	Below LOD	0.074	0.530	0.150	0.290	Below LOD	0.540	0.068
Chrysocolla_bedrock_8	1.800	3.100	0.480	1.800	Below LOD	Below LOD	Below LOD	0.066	0.350	0.088	0.370	0.029	0.400	0.034
Chrysocolla_bedrock_9	3.700	6.800	0.860	2.700	0.710	Below LOD	Below LOD	0.068	0.900	0.145	0.370	Below LOD	Below LOD	0.089
Chrysocolla_bedrock_10	2.300	3.500	0.450	2.600	0.780	0.100	Below LOD	0.095	0.520	0.090	0.240	0.073	0.190	0.050
Chrysocolla_gravels_1	Below LOD	Below LOD	0.043	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.021	Below LOD	Below LOD	0.130	Below LOD
Chrysocolla_gravels_2	Below LOD	0.089	0.045	Below LOD	Below LOD	0.020	0.127	Below LOD	0.034	Below LOD	0.080	Below LOD	0.011	Below LOD
Chrysocolla_gravels_3	4.100	0.037	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.008	Below LOD	0.013	Below LOD	Below LOD	0.070	Below LOD
Chrysocolla_gravels_4	Below LOD	Below LOD	Below LOD	0.060	Below LOD	Below LOD	Below LOD	0.009	Below LOD	0.004	0.038	Below LOD	0.075	Below LOD
Chrysocolla_gravels_5	0.026	0.028	Below LOD	0.006	0.021	Below LOD	Below LOD	0.008	Below LOD	Below LOD	0.046	Below LOD	Below LOD	Below LOD
Chrysocolla_gravels_6	0.036	0.069	0.026	Below LOD	0.015	Below LOD	Below LOD	Below LOD	0.030	Below LOD	0.150	Below LOD	0.036	Below LOD
Chrysocolla_gravels_7	Below LOD	0.028	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.052	Below LOD	0.043	Below LOD
Chrysocolla_gravels_8	Below LOD	Below LOD	Below LOD	0.037	Below LOD	Below LOD	Below LOD	Below LOD	0.053	Below LOD	Below LOD	Below LOD	0.095	Below LOD
Chrysocolla_gravels_9	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.019	Below LOD	0.009	Below LOD	0.016	Below LOD
Chrysocolla_gravels_10	Below LOD	0.046	Below LOD	Below LOD	0.050	Below LOD	Below LOD	0.006	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Pseudomalachite_bedrock_1	0.520	1.160	0.253	3.700	1.100	0.450	1.230	0.450	4.200	0.834	2.900	0.727	4.800	0.450
Pseudomalachite_bedrock_2	2.220	5.200	0.420	4.440	1.800	0.830	3.700	1.220	9.100	1.200	3.800	0.740	6.950	0.750
Pseudomalachite_bedrock_3	0.360	1.900	0.320	2.700	0.890	1.220	10.000	0.720	9.800	1.270	4.200	0.650	5.800	0.490
Pseudomalachite_bedrock_4	Below LOD	3.300	0.056	14.000	Below LOD	5.300	Below LOD	0.000	8.400	1.100	22.000	1.100	2.500	0.740
Pseudomalachite_bedrock_5	1.000	1.600	0.380	2.400	0.950	Below LOD	3.000	0.510	1.600	0.420	Below LOD	Below LOD	5.400	0.500
Pseudomalachite_bedrock_6	3.800	8.100	0.670	3.500	1.600	0.370	3.300	0.260	3.200	0.790	2.700	0.280	1.900	0.320
Pseudomalachite_bedrock_7	6.200	4.000	0.630	10.000	0.730	0.200	2.500	0.510	5.300	0.330	2.600	0.310	1.200	0.780
Pseudomalachite_bedrock_8	3.600	6.820	0.800	3.200	1.120	0.370	3.310	0.670	3.800	0.650	2.600	0.330	2.800	0.480
Pseudomalachite_bedrock_9	2.270	3.400	0.440	2.600	0.710	0.700	4.700	0.850	4.800	0.730	2.600	0.550	2.800	0.570
Pseudomalachite_bedrock_10	2.300	1.900	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.560	2.500	Below LOD	0.000	0.720
Pseudomalachite_gravels_1	0.415	0.474	0.170	0.840	Below LOD	0.108	Below LOD	0.092	0.590	0.137	0.510	0.064	0.480	0.111
Pseudomalachite_gravels_2	0.338	0.544	0.167	0.910	0.280	0.132	Below LOD	0.072	0.498	0.191	0.454	0.077	0.401	0.071
Pseudomalachite_gravels_3	0.405	0.560	0.154	0.950	0.219	0.132	Below LOD	0.085	0.660	0.192	0.490	0.053	0.540	0.078
Pseudomalachite_gravels_4	0.460	0.805	0.163	0.880	0.200	0.096	0.540	0.081	0.600	0.131	0.456	Below LOD	0.390	0.069
Pseudomalachite_gravels_5	0.376	0.870	0.154	0.740	0.330	0.118	0.620	0.089	0.710	0.170	0.540	0.062	0.450	0.096
Pseudomalachite_gravels_6	0.370	1.238	0.130	0.650	0.200	Below LOD	0.450	0.047	0.390	0.069	0.252	0.036	0.370	Below LOD
Pseudomalachite_gravels_7	0.361	1.040	0.131	0.570	0.200	0.057	Below LOD	0.055	0.295	0.091	0.200	0.044	0.260	0.052
Pseudomalachite_gravels_8	0.340	0.980	0.101	0.480	0.190	0.119	Below LOD	0.051	0.278	0.066	0.246	0.040	0.380	0.035
Pseudomalachite_gravels_9	0.318	1.160	0.135	0.830	0.279	0.097	0.360	0.057	0.348	0.087	0.300	0.033	0.324	0.041
Pseudomalachite_gravels_10	0.450	1.280	0.156	0.650	0.120	0.093	0.570	0.058	0.409	0.136	Below LOD	0.021	0.300	0.064

Damiana exotic copper deposition

Table 9 Trace elements analyses of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Chrysocolla_bedrock_1	Below LOD	42000.0	7200.0	1800.0	20000.0	2.3	130.0	53.0	138.0	540.0	0.5	Below LOD	65.0
Chrysocolla_bedrock_2	Below LOD	38000.0	10100.0	710.0	22000.0	2.7	149.0	71.0	150.0	630.0	0.5	Below LOD	27.0
Chrysocolla_bedrock_3	Below LOD	27000.0	6100.0	138.0	15200.0	2.0	81.0	61.0	101.0	300.0	0.3	Below LOD	40.0
Chrysocolla_bedrock_4	Below LOD	75000.0	12300.0	170.0	35000.0	3.1	217.3	80.0	191.0	1060.0	0.4	5.5	2.9
Chrysocolla_bedrock_5	Below LOD	1520.0	1630.0	2400.0	6600.0	1.9	6.9	27.0	137.0	68.0	0.5	Below LOD	114.0
Chrysocolla_bedrock_6	Below LOD	23000.0	70000.0	1100.0	19000.0	2.6	60.0	130.0	161.0	700.0	0.6	6.7	35.0
Chrysocolla_bedrock_7	Below LOD	28000.0	8200.0	820.0	18100.0	2.5	135.0	78.0	132.0	350.0	0.6	Below LOD	39.0
Chrysocolla_bedrock_8	Below LOD	23000.0	7900.0	400.0	18000.0	2.3	99.0	83.0	117.0	600.0	0.4	8.3	41.0
Chrysocolla_bedrock_9	Below LOD	32000.0	12000.0	600.0	37000.0	3.4	150.0	117.0	160.0	750.0	0.6	Below LOD	23.0
Chrysocolla_bedrock_10	Below LOD	42000.0	9600.0	690.0	26000.0	2.9	150.0	100.0	119.0	330.0	0.3	Below LOD	28.0
Chrysocolla_gravels_1	Below LOD	1590.0	1215.0	104.6	4860.0	1.6	5.2	11.9	49.2	150.0	0.8	34.9	1410.0
Chrysocolla_gravels_2	Below LOD	1300.0	1550.0	52.0	4240.0	1.6	11.0	11.5	31.0	800.0	0.9	34.6	1240.0
Chrysocolla_gravels_3	Below LOD	1830.0	1110.0	79.0	3550.0	1.4	5.5	12.7	17.4	222.0	0.3	29.6	1240.0
Chrysocolla_gravels_4	Below LOD	2320.0	1160.0	50.5	4240.0	1.4	5.4	7.1	16.0	183.0	0.3	24.5	1190.0
Chrysocolla_gravels_5	Below LOD	2940.0	1002.0	890.0	5500.0	1.3	8.4	Below LOD	36.8	268.0	0.5	10.4	1058.0
Chrysocolla_gravels_6	Below LOD	2700.0	1028.0	121.0	4310.0	1.5	5.7	7.6	38.9	260.0	0.4	8.5	882.0
Chrysocolla_gravels_7	Below LOD	2770.0	1050.0	70.0	4110.0	1.6	1.9	6.4	39.7	121.0	0.4	9.8	853.0
Chrysocolla_gravels_8	Below LOD	2650.0	1031.0	217.0	4180.0	1.4	4.9	5.1	46.7	169.0	0.5	8.9	820.0
Chrysocolla_gravels_9	Below LOD	2420.0	1110.0	97.0	4440.0	1.2	2.2	7.2	34.6	96.0	0.4	10.9	831.0
Chrysocolla_gravels_10	Below LOD	2500.0	981.0	87.0	3880.0	1.1	Below LOD	6.6	37.0	71.0	0.4	8.2	741.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Chrysocolla_bedrock_1	5.8	43.0	5.8	34.0	0.5	9.1	0.3	29.0	1.1	0.1	3.2	0.6	0.7
Chrysocolla_bedrock_2	6.0	43.0	3.2	38.0	0.5	13.8	0.6	30.0	1.5	0.1	6.0	0.8	0.9
Chrysocolla_bedrock_3	5.8	Below LOD	1.6	24.0	0.3	7.0	0.8	22.0	0.9	Below LOD	3.1	0.5	0.3
Chrysocolla_bedrock_4	5.2	Below LOD	7.1	83.0	1.4	25.0	0.3	52.0	2.0	0.1	12.2	1.6	1.3
Chrysocolla_bedrock_5	6.5	32.0	3.0	Below LOD	Below LOD	Below LOD	1.2	2.7	Below LOD	Below LOD	0.5	0.1	0.3
Chrysocolla_bedrock_6	3.8	Below LOD	3.3	20.0	0.2	13.0	0.6	16.0	1.0	0.1	4.5	0.6	0.3
Chrysocolla_bedrock_7	5.4	Below LOD	4.1	30.0	0.5	8.3	0.7	23.0	1.3	0.0	6.2	1.0	1.5
Chrysocolla_bedrock_8	7.2	37.0	2.8	32.0	0.4	6.1	0.6	22.0	1.7	0.1	4.1	0.8	0.5
Chrysocolla_bedrock_9	6.4	67.0	4.6	54.0	0.6	15.0	Below LOD	39.0	0.8	0.2	7.4	1.1	0.6
Chrysocolla_bedrock_10	6.4	57.4	4.1	37.0	0.6	8.9	0.6	28.0	0.9	0.1	5.3	0.8	0.5
Chrysocolla_gravels_1	1.2	53.0	0.3	Below LOD	0.0	Below LOD	0.6	13.4	Below LOD	Below LOD	0.6	Below LOD	2.3
Chrysocolla_gravels_2	2.2	Below LOD	0.3	Below LOD	0.0	Below LOD	0.5	5.7	Below LOD	0.0	0.4	0.0	2.2
Chrysocolla_gravels_3	2.4	43.1	0.2	Below LOD	Below LOD	Below LOD	0.7	3.7	Below LOD	Below LOD	0.2	Below LOD	2.5
Chrysocolla_gravels_4	2.5	45.5	0.2	Below LOD	Below LOD	Below LOD	0.7	3.4	Below LOD	Below LOD	0.4	0.0	3.0
Chrysocolla_gravels_5	1.6	58.4	0.2	Below LOD	0.0	Below LOD	0.5	6.4	Below LOD	Below LOD	0.6	0.0	3.0
Chrysocolla_gravels_6	2.5	58.0	0.3	Below LOD	0.0	Below LOD	0.7	8.1	Below LOD	Below LOD	0.8	0.0	3.9
Chrysocolla_gravels_7	1.9	48.0	0.2	Below LOD	Below LOD	Below LOD	0.4	6.8	Below LOD	Below LOD	0.5	0.0	3.4
Chrysocolla_gravels_8	2.2	45.6	0.3	Below LOD	Below LOD	Below LOD	0.5	6.0	Below LOD	0.0	0.6	0.0	3.5
Chrysocolla_gravels_9	1.5	43.8	0.2	Below LOD	Below LOD	Below LOD	0.4	4.9	Below LOD	Below LOD	0.7	0.0	3.0
Chrysocolla_gravels_10	2.3	42.7	0.2	Below LOD	0.0	Below LOD	0.5	5.0	Below LOD	Below LOD	0.6	0.0	4.1

Damiana exotic copper deposition

Table 10 Trace elements analyses of pseudomalachite

Sample	Li	Na	Mg	Si	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Pseudomalachite_bedrock_1	Below LOD	250.0	97.0	5400.0	1200.0	1.8	Below LOD	250.0	650.0	124.0	2.8	Below LOD	1700.0
Pseudomalachite_bedrock_2	Below LOD	260.0	75.0	5600.0	3300.0	2.2	11.0	230.0	542.0	130.0	2.9	Below LOD	3800.0
Pseudomalachite_bedrock_3	Below LOD	640.0	120.0	100000.0	2900.0	Below LOD	25.0	1500.0	710.0	240.0	4.7	21.0	1800.0
Pseudomalachite_bedrock_4	Below LOD	2600.0	2100.0	46000.0	15000.0	3.6	Below LOD	3400.0	360.0	730.0	3.6	Below LOD	1300.0
Pseudomalachite_bedrock_5	Below LOD	310.0	160.0	8300.0	4400.0	5.6	Below LOD	430.0	470.0	Below LOD	1.5	Below LOD	1900.0
Pseudomalachite_bedrock_6	12.0	430.0	160.0	5000.0	2900.0	Below LOD	13.0	110.0	810.0	200.0	3.5	Below LOD	4400.0
Pseudomalachite_bedrock_7	Below LOD	1900.0	320.0	25000.0	10000.0	15.0	17.0	1700.0	490.0	800.0	8.7	Below LOD	2800.0
Pseudomalachite_bedrock_8	Below LOD	106.0	81.0	6600.0	4400.0	Below LOD	16.0	200.0	790.0	200.0	4.6	16.0	5300.0
Pseudomalachite_bedrock_9	Below LOD	Below LOD	106.0	11000.0	5300.0	1.7	Below LOD	610.0	490.0	60.0	2.0	Below LOD	4500.0
Pseudomalachite_bedrock_10	40.0	620.0	300.0	27000.0	10000.0	Below LOD	Below LOD	1300.0	610.0	490.0	16.0	Below LOD	3700.0
Pseudomalachite_gravels_1	Below LOD	258.0	421.0	7600.0	1930.0	0.4	5.2	5.9	5.4	Below LOD	Below LOD	152.0	12800.0
Pseudomalachite_gravels_2	Below LOD	201.0	398.0	6600.0	1950.0	Below LOD	3.3	Below LOD	6.4	Below LOD	Below LOD	144.0	12570.0
Pseudomalachite_gravels_3	Below LOD	218.0	404.0	6540.0	1920.0	Below LOD	Below LOD	Below LOD	5.2	Below LOD	Below LOD	134.0	12100.0
Pseudomalachite_gravels_4	Below LOD	206.0	427.0	6120.0	2110.0	0.4	4.1	6.3	10.5	Below LOD	Below LOD	130.3	12300.0
Pseudomalachite_gravels_5	Below LOD	227.0	438.0	6200.0	2210.0	Below LOD	5.0	Below LOD	9.4	Below LOD	Below LOD	134.8	12420.0
Pseudomalachite_gravels_6	2.5	166.0	577.0	2380.0	4410.0	0.2	5.3	Below LOD	9.7	Below LOD	Below LOD	103.0	13700.0
Pseudomalachite_gravels_7	Below LOD	52.9	437.0	1280.0	4130.0	0.6	7.3	Below LOD	27.3	Below LOD	Below LOD	81.1	11700.0
Pseudomalachite_gravels_8	Below LOD	53.0	479.0	1480.0	4310.0	0.4	5.3	Below LOD	42.9	Below LOD	Below LOD	100.3	14650.0
Pseudomalachite_gravels_9	Below LOD	100.0	522.0	2130.0	3940.0	Below LOD	6.3	Below LOD	27.7	Below LOD	Below LOD	95.0	13400.0
Pseudomalachite_gravels_10	Below LOD	197.0	543.0	2810.0	4160.0	Below LOD	6.0	7.5	30.3	Below LOD	Below LOD	101.5	13200.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Pseudomalachite_bedrock_1	Below LOD	Below LOD	27.3	Below LOD	0.2	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.4	0.0	0.6
Pseudomalachite_bedrock_2	Below LOD	70.0	48.0	Below LOD	0.1	Below LOD	Below LOD	Below LOD	0.0	Below LOD	2.2	0.0	0.7
Pseudomalachite_bedrock_3	2.7	50.0	37.0	Below LOD	0.1	2.5	1.3	Below LOD	0.0	Below LOD	0.6	0.2	0.9
Pseudomalachite_bedrock_4	Below LOD	380.0	41.0	Below LOD	1.9	Below LOD	5.3	Below LOD	Below LOD	Below LOD	2.7	Below LOD	0.4
Pseudomalachite_bedrock_5	1.1	Below LOD	27.0	Below LOD	0.1	Below LOD	0.8	Below LOD	Below LOD	Below LOD	0.6	0.1	1.1
Pseudomalachite_bedrock_6	Below LOD	Below LOD	32.0	Below LOD	0.2	3.3	Below LOD	4.3	Below LOD	Below LOD	0.8	0.0	1.2
Pseudomalachite_bedrock_7	Below LOD	Below LOD	39.0	31.0	0.2	11.0	2.6	1.7	Below LOD	Below LOD	8.0	2.0	2.0
Pseudomalachite_bedrock_8	Below LOD	60.0	34.0	Below LOD	0.1	Below LOD	Below LOD	7.5	Below LOD	Below LOD	1.0	0.0	1.4
Pseudomalachite_bedrock_9	Below LOD	Below LOD	32.0	Below LOD	Below LOD	3.5	Below LOD	Below LOD	Below LOD	0.0	0.6	0.0	0.9
Pseudomalachite_bedrock_10	Below LOD	Below LOD	22.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.0	Below LOD	3.9	Below LOD	0.2
Pseudomalachite_gravels_1	Below LOD	16.6	3.7	Below LOD	0.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.3	0.0	1.2
Pseudomalachite_gravels_2	Below LOD	Below LOD	3.6	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	Below LOD	0.2	Below LOD	0.9
Pseudomalachite_gravels_3	Below LOD	Below LOD	3.7	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.2	0.0	0.9
Pseudomalachite_gravels_4	Below LOD	Below LOD	4.0	Below LOD	Below LOD	Below LOD	Below LOD	0.6	Below LOD	0.0	0.2	0.0	0.9
Pseudomalachite_gravels_5	Below LOD	Below LOD	4.1	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	Below LOD	0.3	0.0	0.9
Pseudomalachite_gravels_6	Below LOD	22.5	2.7	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.1	0.0	1.1
Pseudomalachite_gravels_7	Below LOD	Below LOD	2.6	1.8	Below LOD	0.3	Below LOD	Below LOD	0.0	Below LOD	Below LOD	0.0	1.7
Pseudomalachite_gravels_8	0.2	31.7	2.3	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	1.4
Pseudomalachite_gravels_9	Below LOD	24.0	2.8	Below LOD	Below LOD	Below LOD	Below LOD	0.5	Below LOD	0.0	Below LOD	0.0	1.2
Pseudomalachite_gravels_10	Below LOD	25.4	3.5	Below LOD	Below LOD	Below LOD	Below LOD	0.6	Below LOD	Below LOD	0.1	0.0	1.1

El Cobre exotic copper deposition

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_1	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.076	Below LOD	0.075	Below LOD	0.077	0.221	Below LOD	0.220	0.051
Chrysocolla_2	1.130	3.670	0.317	1.620	0.530	0.244	1.180	0.123	0.990	0.205	0.350	0.064	0.440	0.062
Chrysocolla_3	0.198	4.030	0.091	Below LOD	0.270	0.136	0.450	0.091	0.510	0.094	0.288	0.046	0.286	0.058
Chrysocolla_4	Below LOD	Below LOD	Below LOD	Below LOD	0.280	Below LOD	0.460	0.074	0.540	0.091	Below LOD	Below LOD	0.330	0.065
Chrysocolla_5	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.067	Below LOD	0.087	0.188	0.060	0.383	0.054
Chrysocolla_6	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.085	0.176	0.051	0.226	0.046
Chrysocolla_7	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.127	0.670	0.131	0.460	0.117	0.317	0.044	0.340	0.077
Chrysocolla_8	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.100	Below LOD	Below LOD	Below LOD	Below LOD	0.148	Below LOD	0.247	0.045
Chrysocolla_9	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.420	0.078	0.390	0.074	0.211	0.046	0.275	0.028
Chrysocolla_10	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.440	0.093	0.221	0.034	0.275	0.068

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Pseudomalachite_1	44.600	4.200	5.900	33.500	8.000	2.680	21.400	2.580	14.900	3.630	8.300	0.910	3.560	0.530
Pseudomalachite_2	49.300	8.100	9.100	51.500	13.500	4.420	30.300	3.980	23.400	5.170	11.600	1.400	5.600	0.710
Pseudomalachite_3	56.300	9.700	11.900	63.400	17.000	6.140	38.500	4.880	25.500	5.690	13.700	1.530	6.540	0.866
Pseudomalachite_4	36.900	7.700	5.120	29.500	7.900	2.660	20.200	2.540	13.100	3.110	7.870	0.750	3.700	0.494
Pseudomalachite_5	52.800	6.750	9.000	48.900	11.500	4.240	30.700	3.400	17.800	4.150	10.300	1.210	4.950	0.631
Pseudomalachite_6	51.400	10.200	11.100	60.600	15.400	5.700	37.400	4.520	22.400	4.930	11.700	1.370	5.960	0.890
Pseudomalachite_7	33.000	3.870	4.370	23.400	5.390	2.180	17.600	1.980	10.390	2.650	6.460	0.700	2.870	0.426
Pseudomalachite_8	37.700	10.200	8.380	46.300	12.600	4.410	32.800	3.780	18.800	4.220	10.610	1.173	5.270	0.667
Pseudomalachite_9	32.800	3.960	5.620	29.200	7.300	2.800	22.200	2.570	13.100	3.310	7.670	0.890	4.090	0.578

Gaby *in situ* copper deposition

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_1	0.459	0.272	0.310	1.820	1.000	0.172	0.800	0.177	1.039	0.173	0.242	0.079	0.380	0.102
Chrysocolla_2	0.560	0.242	0.378	1.530	0.500	0.193	1.120	0.177	1.030	0.212	0.361	0.055	0.700	0.078
Chrysocolla_3	0.518	0.144	0.365	1.290	0.440	0.149	0.940	0.179	1.040	0.170	0.281	0.066	0.400	0.044
Chrysocolla_4	0.535	0.058	0.358	1.330	0.560	0.143	1.040	0.168	0.990	0.207	0.590	0.045	0.410	0.130
Chrysocolla_5	0.725	0.076	0.313	1.380	0.430	0.167	0.870	0.172	0.900	0.189	0.464	0.072	0.520	0.060
Chrysocolla_6	0.640	Below LOD	0.414	1.570	0.620	0.170	0.940	0.181	1.140	0.159	0.230	0.059	0.470	0.058
Chrysocolla_7	0.481	0.134	0.311	1.370	0.450	0.131	Below LOD	0.118	0.820	0.148	0.440	0.045	0.370	0.065
Chrysocolla_8	0.490	0.203	0.273	1.130	0.320	0.105	0.610	0.123	0.860	0.098	0.348	0.027	0.350	0.057
Chrysocolla_9	0.650	0.063	0.353	1.680	0.610	0.070	1.170	0.131	0.970	0.196	0.310	0.041	0.270	0.053
Chrysocolla_10	0.760	Below LOD	0.423	1.430	0.520	0.168	0.750	0.180	0.920	0.176	0.420	0.045	0.350	0.095

El Cobre exotic copper deposition

Table 14 Trace elements analyses of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Chrysocolla_1	Below LOD	Below LOD	Below LOD	197.0	Below LOD	Below LOD	Below LOD	54.0	Below LOD	Below LOD	0.7	Below LOD	395.0
Chrysocolla_2	Below LOD	680.0	323.0	2860.0	2090.0	1.4	Below LOD	22.3	15.5	44.0	0.7	Below LOD	502.0
Chrysocolla_3	Below LOD	691.0	329.0	53.0	2280.0	1.5	Below LOD	20.1	16.9	61.0	0.5	Below LOD	440.0
Chrysocolla_4	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.8	Below LOD	357.0
Chrysocolla_5	Below LOD	Below LOD	Below LOD	54.0	Below LOD	Below LOD	Below LOD	29.6	Below LOD	Below LOD	0.8	4.3	373.0
Chrysocolla_6	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	27.0	Below LOD	Below LOD	1.5	Below LOD	451.0
Chrysocolla_7	Below LOD	Below LOD	Below LOD	960.0	Below LOD	1.7	Below LOD	Below LOD	Below LOD	Below LOD	2.6	Below LOD	536.0
Chrysocolla_8	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	42.0	Below LOD	Below LOD	1.1	3.8	620.0
Chrysocolla_9	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	29.6	Below LOD	Below LOD	0.7	3.6	444.0
Chrysocolla_10	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.4	Below LOD	Below LOD	Below LOD	Below LOD	0.8	4.8	447.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Chrysocolla_1	Below LOD	57.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.4	Below LOD	2.0
Chrysocolla_2	Below LOD	42.0	6.0	Below LOD	Below LOD	1.0	Below LOD	1.8	Below LOD	0.0	1.6	0.0	2.6
Chrysocolla_3	0.8	Below LOD	1.9	Below LOD	Below LOD	0.5	Below LOD	2.0	0.0	Below LOD	1.2	0.0	2.6
Chrysocolla_4	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.2	Below LOD	2.7
Chrysocolla_5	Below LOD	45.6	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.5	Below LOD	2.7
Chrysocolla_6	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.1	Below LOD	Below LOD	Below LOD	1.1	Below LOD	2.1
Chrysocolla_7	Below LOD	26.9	3.7	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.3	Below LOD	2.4
Chrysocolla_8	Below LOD	99.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.0	Below LOD	2.5
Chrysocolla_9	Below LOD	48.0	1.9	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.2	Below LOD	2.5
Chrysocolla_10	Below LOD	24.5	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	1.2	Below LOD	2.6

Table 15 Trace elements analyses of pseudomalachite

Sample	Li	Na	Mg	Si	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Pseudomalachite_1	Below LOD	Below LOD	141.0	2110.0	1650.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	19.8	1610.0
Pseudomalachite_2	Below LOD	Below LOD	95.0	2420.0	1560.0	0.7	Below LOD	3.8	1.6	Below LOD	Below LOD	17.8	1640.0
Pseudomalachite_3	1.6	40.0	97.0	2770.0	1740.0	0.8	Below LOD	3.5	Below LOD	22.0	Below LOD	17.8	1620.0
Pseudomalachite_4	2.2	38.0	59.0	2220.0	1270.0	0.5	Below LOD	Below LOD	1.9	19.8	0.2	18.7	1350.0
Pseudomalachite_5	Below LOD	22.0	169.0	2370.0	1900.0	0.6	Below LOD	Below LOD	Below LOD	25.0	Below LOD	19.3	1640.0
Pseudomalachite_6	Below LOD	Below LOD	97.0	4120.0	1590.0	1.0	0.9	Below LOD	1.7	102.0	0.1	19.1	1780.0
Pseudomalachite_7	Below LOD	Below LOD	186.0	2120.0	2440.0	0.8	Below LOD	Below LOD	Below LOD	Below LOD	0.1	21.0	1490.0
Pseudomalachite_8	Below LOD	20.7	74.0	3410.0	1370.0	0.8	Below LOD	Below LOD	1.5	Below LOD	0.1	19.6	1560.0
Pseudomalachite_9	Below LOD	Below LOD	143.0	2580.0	1920.0	0.5	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	18.7	1880.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Pseudomalachite_1	Below LOD	Below LOD	128.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	Below LOD	18.1	0.0	2.7
Pseudomalachite_2	Below LOD	Below LOD	149.0	Below LOD	Below LOD	Below LOD	Below LOD	0.4	0.0	Below LOD	20.5	0.0	2.7
Pseudomalachite_3	Below LOD	Below LOD	168.0	Below LOD	Below LOD	Below LOD	Below LOD	0.5	0.1	Below LOD	21.5	0.0	2.9
Pseudomalachite_4	Below LOD	Below LOD	131.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	0.0	21.8	0.0	1.7
Pseudomalachite_5	Below LOD	Below LOD	163.0	Below LOD	0.0	Below LOD	Below LOD	0.5	0.0	Below LOD	20.0	Below LOD	2.3
Pseudomalachite_6	Below LOD	Below LOD	177.0	Below LOD	Below LOD	Below LOD	Below LOD	0.8	Below LOD	Below LOD	20.8	Below LOD	2.5
Pseudomalachite_7	Below LOD	Below LOD	147.0	Below LOD	Below LOD	Below LOD	Below LOD	0.7	Below LOD	Below LOD	15.1	0.0	1.7
Pseudomalachite_8	Below LOD	Below LOD	162.0	Below LOD	0.0	Below LOD	Below LOD	Below LOD	0.0	Below LOD	22.3	0.0	2.6
Pseudomalachite_9	Below LOD	Below LOD	174.0	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.0	0.0	15.9	Below LOD	2.5

Gaby *in situ* copper deposition

Table 16 Trace elements analyses of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Chrysocolla_1	Below LOD	442.0	1050.0	127.0	6500.0	2.0	Below LOD	Below LOD	64.0	163.0	0.3	Below LOD	163.0
Chrysocolla_2	Below LOD	510.0	1099.0	33.2	6460.0	2.8	Below LOD	7.0	19.7	156.0	Below LOD	Below LOD	202.0
Chrysocolla_3	Below LOD	485.0	920.0	19.0	6100.0	2.2	Below LOD	Below LOD	17.8	126.0	0.2	Below LOD	193.0
Chrysocolla_4	Below LOD	365.0	863.0	22.3	6250.0	1.3	Below LOD	Below LOD	9.0	38.0	Below LOD	2.4	204.0
Chrysocolla_5	Below LOD	358.0	910.0	33.0	6800.0	0.9	Below LOD	Below LOD	62.7	Below LOD	0.2	2.9	208.0
Chrysocolla_6	Below LOD	385.0	853.0	45.0	6600.0	1.3	1.0	5.4	20.9	108.0	Below LOD	Below LOD	222.0
Chrysocolla_7	Below LOD	480.0	890.0	51.5	6800.0	1.7	0.7	8.1	32.7	740.0	Below LOD	4.8	215.0
Chrysocolla_8	Below LOD	435.0	880.0	33.0	6940.0	2.5	Below LOD	6.0	39.1	810.0	0.3	Below LOD	198.0
Chrysocolla_9	Below LOD	442.0	850.0	35.7	6480.0	1.4	Below LOD	Below LOD	17.6	141.0	Below LOD	Below LOD	217.0
Chrysocolla_10	Below LOD	606.0	840.0	33.5	7130.0	1.0	0.9	Below LOD	266.0	Below LOD	0.8	Below LOD	247.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Chrysocolla_1	1.2	40.0	8.6	Below LOD	Below LOD	Below LOD	Below LOD	1.2	0.0	Below LOD	1.2	0.0	76.0
Chrysocolla_2	1.4	54.0	10.6	Below LOD	Below LOD	Below LOD	0.4	3.3	0.0	Below LOD	1.0	0.0	89.0
Chrysocolla_3	1.1	49.3	8.5	Below LOD	Below LOD	Below LOD	0.4	2.6	Below LOD	Below LOD	1.0	Below LOD	94.0
Chrysocolla_4	1.2	60.6	9.7	Below LOD	Below LOD	0.3	0.3	1.2	0.0	Below LOD	0.9	0.0	80.6
Chrysocolla_5	0.9	43.1	10.9	Below LOD	0.0	Below LOD	Below LOD	1.5	Below LOD	Below LOD	1.1	Below LOD	66.5
Chrysocolla_6	1.3	46.0	9.8	Below LOD	Below LOD	0.1	Below LOD	1.9	Below LOD	Below LOD	0.9	0.0	86.0
Chrysocolla_7	1.4	56.2	9.6	Below LOD	Below LOD	Below LOD	0.5	2.4	Below LOD	Below LOD	0.9	0.0	86.8
Chrysocolla_8	1.4	39.0	8.1	Below LOD	Below LOD	Below LOD	0.4	2.2	Below LOD	Below LOD	0.8	Below LOD	89.1
Chrysocolla_9	1.5	41.0	9.7	Below LOD	Below LOD	Below LOD	0.4	2.4	Below LOD	0.0	0.9	Below LOD	87.0
Chrysocolla_10	1.2	56.0	11.5	Below LOD	Below LOD	Below LOD	0.2	0.9	0.0	Below LOD	0.9	0.0	66.5

Zaldivar *in situ* copper deposition

Table 17 REE analyses of chrysocolla														
Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_1	Below LOD	7.780	0.008	Below LOD	0.056	Below LOD	Below LOD	0.014	0.160	Below LOD	0.077	0.021	Below LOD	Below LOD
Chrysocolla_2	Below LOD	9.500	0.012	Below LOD	Below LOD	Below LOD	Below LOD	0.011	0.120	0.035	0.067	0.011	0.205	0.013
Chrysocolla_3	Below LOD	9.700	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.019	Below LOD	0.014	0.076	0.016	0.095	Below LOD
Chrysocolla_4	Below LOD	9.390	Below LOD	0.043	Below LOD	Below LOD	Below LOD	0.007	0.056	0.024	0.122	Below LOD	Below LOD	0.025
Chrysocolla_5	0.030	10.100	0.014	Below LOD	Below LOD	Below LOD	Below LOD	Below LOD	0.065	0.028	0.090	Below LOD	Below LOD	Below LOD
Chrysocolla_6	0.043	9.900	0.026	0.080	Below LOD	Below LOD	Below LOD	0.017	0.166	0.034	0.095	0.014	0.104	0.028
Chrysocolla_7	0.028	9.220	Below LOD	Below LOD	0.015	Below LOD	Below LOD	Below LOD	0.100	0.016	Below LOD	Below LOD	0.150	0.019
Chrysocolla_8	Below LOD	9.700	0.012	Below LOD	0.085	0.030	Below LOD	0.016	0.130	0.028	0.046	Below LOD	0.110	Below LOD
Chrysocolla_9	Below LOD	8.610	0.014	0.042	0.039	Below LOD	Below LOD	0.012	0.125	0.023	0.102	Below LOD	0.103	0.011
Chrysocolla_10	0.117	18.300	0.093	0.350	Below LOD	Below LOD	Below LOD	0.046	0.201	0.039	0.115	0.022	0.200	0.016

Table 18 REE analyses of pseudomalachite														
Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Pseudomalachite_1	10.500	22.200	4.130	22.500	5.890	1.060	5.150	0.940	5.620	0.920	1.940	0.219	0.930	0.069
Pseudomalachite_2	10.800	21.700	4.000	21.400	4.850	0.990	5.400	0.890	4.470	0.740	1.480	0.093	0.720	0.048
Pseudomalachite_3	14.620	28.000	4.920	23.100	4.590	0.860	4.700	0.734	4.350	0.670	1.520	0.106	0.450	0.047
Pseudomalachite_4	13.400	30.300	5.930	36.400	11.300	2.190	13.300	2.270	12.700	2.630	5.830	0.551	2.480	0.256
Pseudomalachite_5	12.550	25.600	4.390	21.600	5.360	1.010	4.750	0.850	5.050	0.860	1.800	0.174	0.750	0.061
Pseudomalachite_6	13.000	25.900	3.900	20.500	4.940	1.000	5.470	0.711	3.970	0.710	1.680	0.144	0.850	0.066
Pseudomalachite_7	17.300	37.600	5.430	26.200	5.800	1.240	6.500	0.890	4.900	0.790	1.720	0.096	0.590	0.050
Pseudomalachite_8	14.900	37.000	6.370	37.100	11.300	2.520	15.600	2.660	14.500	2.670	6.950	0.730	3.180	0.340
Pseudomalachite_9	15.500	37.600	5.350	27.900	7.620	1.620	9.400	1.460	8.200	1.640	3.940	0.402	1.660	0.197
Pseudomalachite_10	15.200	30.200	5.090	25.800	8.300	1.530	8.060	1.146	6.490	1.050	2.120	0.198	1.190	0.105

Gaoua *in situ* copper deposition

Table 19 REE analyses of chrysocolla														
Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)
Chrysocolla_1	2.500	4.200	0.850	4.000	1.400	0.370	1.800	0.290	1.850	0.410	1.210	0.198	0.930	0.152
Chrysocolla_2	1.170	0.330	0.261	1.580	0.610	0.180	0.920	0.197	1.540	0.281	0.863	0.126	0.960	0.135
Chrysocolla_3	3.500	4.500	0.870	6.500	1.150	0.240	1.340	0.213	1.340	0.276	0.840	0.116	0.760	0.134
Chrysocolla_4	1.470	0.380	0.259	1.500	0.750	0.235	1.050	0.193	1.600	0.329	0.930	0.162	1.050	0.161
Chrysocolla_5	1.430	0.500	0.321	2.400	0.560	0.220	1.180	0.220	1.590	0.322	0.910	0.133	1.030	0.129
Chrysocolla_6	1.700	1.400	0.420	1.800	0.510	0.232	0.920	0.167	1.250	0.297	0.780	0.116	0.730	0.099
Chrysocolla_7	1.190	0.540	0.292	1.270	0.630	0.213	1.040	0.157	1.410	0.289	0.700	0.123	0.920	0.160
Chrysocolla_8	2.900	2.100	0.540	3.300	1.120	0.247	1.420	0.175	1.410	0.335	1.060	0.121	0.920	0.170

Zaldivar *in situ* copper deposition

Table 20 Trace elements analyses of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Chrysocolla_1	Below LOD	331.0	276.0	94.3	1460.0	2.5	Below LOD	9.0	650.0	510.0	2.6	Below LOD	617.0
Chrysocolla_2	Below LOD	290.0	397.0	53.0	1750.0	2.8	Below LOD	15.6	580.0	396.0	2.3	Below LOD	670.0
Chrysocolla_3	Below LOD	243.0	830.0	47.0	1330.0	2.0	Below LOD	44.0	251.0	383.0	0.3	Below LOD	600.0
Chrysocolla_4	Below LOD	232.0	790.0	52.9	1200.0	1.8	0.9	24.3	262.0	424.0	0.2	Below LOD	566.0
Chrysocolla_5	Below LOD	280.0	670.0	57.0	1370.0	2.4	Below LOD	20.5	276.0	418.0	0.4	Below LOD	580.0
Chrysocolla_6	Below LOD	350.0	830.0	45.0	1440.0	2.2	Below LOD	20.0	270.0	416.0	0.4	Below LOD	564.0
Chrysocolla_7	Below LOD	160.0	750.0	55.0	1630.0	1.7	Below LOD	16.7	236.0	416.0	0.3	Below LOD	545.0
Chrysocolla_8	Below LOD	205.0	800.0	58.0	1580.0	2.0	Below LOD	34.0	248.0	455.0	0.4	Below LOD	571.0
Chrysocolla_9	Below LOD	198.0	520.0	54.0	1650.0	1.7	Below LOD	17.8	350.0	394.0	1.1	Below LOD	523.0
Chrysocolla_10	Below LOD	239.0	322.0	210.0	2150.0	1.9	Below LOD	12.3	2200.0	27000.0	11.9	Below LOD	630.0
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Chrysocolla_1	0.850	Below LOD	0.5	Below LOD	Below LOD	Below LOD	Below LOD	11.7	0.0	Below LOD	0.3	0.0	1.7
Chrysocolla_2	0.490	Below LOD	0.5	Below LOD	Below LOD	Below LOD	0.1	10.2	Below LOD	0.0	0.4	0.0	2.0
Chrysocolla_3	0.364	Below LOD	0.5	Below LOD	Below LOD	Below LOD	0.1	Below LOD	Below LOD	Below LOD	0.2	0.0	1.7
Chrysocolla_4	0.680	Below LOD	0.4	Below LOD	Below LOD	0.5	Below LOD	0.5	0.0	Below LOD	0.3	0.0	1.6
Chrysocolla_5	0.830	16.0	0.3	Below LOD	0.0	Below LOD	0.1	2.6	0.0	Below LOD	0.3	0.0	1.6
Chrysocolla_6	0.770	Below LOD	0.4	Below LOD	0.0	1.1	Below LOD	2.5	Below LOD	Below LOD	0.5	0.0	1.6
Chrysocolla_7	0.710	Below LOD	0.4	Below LOD	0.0	Below LOD	Below LOD	1.2	0.0	Below LOD	0.2	0.0	1.6
Chrysocolla_8	0.750	Below LOD	0.4	Below LOD	Below LOD	0.8	Below LOD	1.2	Below LOD	0.0	0.2	0.0	1.7
Chrysocolla_9	0.900	Below LOD	0.4	Below LOD	Below LOD	1.0	Below LOD	6.3	0.0	Below LOD	0.3	0.0	1.5
Chrysocolla_10	0.740	Below LOD	0.8	Below LOD	Below LOD	4.3	Below LOD	16.2	Below LOD	Below LOD	82.0	0.0	1.9

Table 21 Trace elements analyses of pseudomalachite

Sample	Li	Na	Mg	Si	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Pseudomalachite_1	4.600	52.500	43.100	2690.000	540.000	0.330	Below LOD	Below LOD	1205.000	43.800	2.100	4.300	3930.000
Pseudomalachite_2	Below LOD	54.700	36.000	3230.000	500.000	Below LOD	1.100	Below LOD	1200.000	Below LOD	2.020	2.800	3280.000
Pseudomalachite_3	3.400	66.000	46.200	2940.000	610.000	Below LOD	0.890	Below LOD	1490.000	66.000	1.030	5.300	5560.000
Pseudomalachite_4	3.100	Below LOD	71.900	3620.000	728.000	0.400	Below LOD	Below LOD	1420.000	54.000	2.240	Below LOD	4460.000
Pseudomalachite_5	5.100	40.000	35.700	3100.000	450.000	0.460	Below LOD	Below LOD	1290.000	Below LOD	2.390	4.600	4010.000
Pseudomalachite_6	Below LOD	39.000	35.100	2860.000	410.000	Below LOD	1.400	Below LOD	1080.000	Below LOD	2.260	3.700	3430.000
Pseudomalachite_7	8.200	65.000	69.200	3290.000	580.000	0.350	1.400	Below LOD	1700.000	103.000	0.990	7.800	7900.000
Pseudomalachite_8	Below LOD	Below LOD	96.000	3630.000	800.000	0.420	Below LOD	6.100	1372.000	66.000	3.130	5.600	5360.000
Pseudomalachite_9	Below LOD	76.300	70.100	3510.000	432.000	Below LOD	1.130	4.100	1442.000	44.000	5.290	5.000	5370.000
Pseudomalachite_10	4.000	53.000	51.400	3430.000	450.000	Below LOD	Below LOD	2.900	1211.000	28.000	2.090	5.500	4830.000
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Pseudomalachite_1	Below LOD	Below LOD	22.500	Below LOD	Below LOD	Below LOD	Below LOD	1.810	Below LOD	Below LOD	15.000	0.001	0.365
Pseudomalachite_2	Below LOD	Below LOD	19.100	Below LOD	Below LOD	Below LOD	Below LOD	1.180	Below LOD	Below LOD	15.100	Below LOD	0.562
Pseudomalachite_3	Below LOD	Below LOD	20.800	Below LOD	Below LOD	Below LOD	Below LOD	1.720	Below LOD	Below LOD	13.470	Below LOD	0.319
Pseudomalachite_4	Below LOD	Below LOD	57.700	Below LOD	Below LOD	Below LOD	Below LOD	1.310	0.017	Below LOD	15.100	0.000	0.485
Pseudomalachite_5	Below LOD	Below LOD	23.500	Below LOD	Below LOD	Below LOD	Below LOD	1.450	Below LOD	Below LOD	18.200	0.000	0.490
Pseudomalachite_6	Below LOD	Below LOD	22.300	Below LOD	Below LOD	Below LOD	Below LOD	1.540	Below LOD	Below LOD	16.500	0.000	0.443
Pseudomalachite_7	Below LOD	Below LOD	26.000	Below LOD	0.013	Below LOD	0.130	2.040	0.013	Below LOD	15.700	0.000	0.369
Pseudomalachite_8	Below LOD	19.000	70.000	Below LOD	Below LOD	Below LOD	Below LOD	2.060	Below LOD	0.012	17.900	0.004	0.356
Pseudomalachite_9	Below LOD	Below LOD	43.300	Below LOD	0.027	Below LOD	Below LOD	2.290	Below LOD	Below LOD	19.500	0.001	0.558
Pseudomalachite_10	Below LOD	Below LOD	35.200	Below LOD	Below LOD	Below LOD	0.111	1.560	Below LOD	0.001	19.700	0.002	0.507

Gaoua *in situ* copper deposition

Table 22 Trace elements analyses of chrysocolla

Sample	Li	Na	Mg	P	Ca	Sc	Ti	Cr	Mn	Fe	Co	Ni	Zn
Chrysocolla_1	Below LOD	823.0	1210.0	113.0	3350.0	4.6	1100.0	95.0	20.7	254.0	2.6	22.5	25.3
Chrysocolla_2	Below LOD	712.0	1000.0	Below LOD	2960.0	3.0	19.6	79.0	20.9	280.0	2.2	17.9	21.1
Chrysocolla_3	Below LOD	750.0	1050.0	18.5	3100.0	2.8	20.8	69.4	23.5	194.0	2.4	22.4	21.4
Chrysocolla_4	Below LOD	768.0	1180.0	Below LOD	3280.0	2.5	27.5	78.9	31.9	206.0	2.8	23.3	26.7
Chrysocolla_5	Below LOD	759.0	1180.0	40.8	3210.0	2.6	23.3	79.5	27.3	252.0	2.7	23.2	25.2
Chrysocolla_6	Below LOD	740.0	972.0	Below LOD	2730.0	2.5	22.2	84.0	21.1	290.0	2.0	15.9	21.7
Chrysocolla_7	Below LOD	703.0	1100.0	29.4	3050.0	2.6	25.4	94.1	31.1	274.0	2.6	19.6	27.3
Chrysocolla_8	Below LOD	680.0	1030.0	33.2	2970.0	2.7	36.4	101.5	42.8	360.0	2.0	16.7	28.2
Sample	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba	Hf	Ta	Pb	Th	U
Chrysocolla_1	1.0	42.4	8.7	Below LOD	0.8	Below LOD	Below LOD	6.8	0.1	0.1	0.5	0.0	15.7
Chrysocolla_2	0.7	49.7	7.9	Below LOD	0.0	Below LOD	0.1	5.5	0.0	Below LOD	0.6	0.0	15.7
Chrysocolla_3	0.8	53.0	8.7	Below LOD	0.0	Below LOD	0.1	6.2	0.0	0.0	0.4	0.0	13.3
Chrysocolla_4	0.8	70.0	8.5	Below LOD	0.0	0.4	0.1	7.2	0.0	Below LOD	0.6	0.0	13.3
Chrysocolla_5	0.9	51.0	8.1	Below LOD	0.0	Below LOD	0.1	6.5	0.0	Below LOD	0.6	0.0	13.7
Chrysocolla_6	0.8	46.9	7.9	Below LOD	0.0	Below LOD	Below LOD	5.9	Below LOD	Below LOD	0.4	0.0	14.2
Chrysocolla_7	0.9	47.9	7.6	Below LOD	0.1	Below LOD	0.1	7.6	Below LOD	Below LOD	0.6	0.0	11.8
Chrysocolla_8	1.8	69.0	7.5	Below LOD	0.0	0.7	0.4	7.6	0.0	Below LOD	0.7	0.0	12.1

91500 zircon standard

Table 23 REE and trace elements analyses of 91500 zircon standard

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)	Hf(ppm)
91500_1	b.d.l	2.7	0.0	0.2	0.4	0.2	2.0	0.8	10.7	4.4	22.9	6.1	69.0	11.3	5250.0
91500_2	b.d.l	3.1	0.0	0.2	0.5	0.2	2.2	0.9	11.2	4.7	26.2	6.1	78.0	12.1	5140.0
91500_3	b.d.l	2.7	0.0	0.2	0.4	0.3	2.2	1.0	11.9	4.7	23.6	6.7	68.5	10.8	4650.0
91500_4	b.d.l	2.8	b.d.l	0.2	0.5	0.3	2.8	1.0	13.7	5.1	26.6	7.2	80.0	12.4	5270.0
91500_5	b.d.l	2.6	b.d.l	0.2	0.5	0.2	2.8	0.8	10.4	4.3	22.6	6.3	64.1	11.3	5510.0
91500_6	b.d.l	2.3	b.d.l	0.2	0.3	0.2	2.5	0.8	9.5	3.8	21.2	5.9	63.4	10.2	4870.0
91500_7	b.d.l	3.1	b.d.l	b.d.l	0.7	0.3	2.9	1.2	14.9	5.7	29.3	8.8	93.0	14.1	6360.0
91500_8	b.d.l	3.5	b.d.l	0.3	0.7	0.3	3.0	1.1	16.0	6.1	32.5	9.1	98.0	15.4	6950.0
91500_9	b.d.l	2.9	0.0	0.3	0.7	0.2	2.8	0.9	14.2	5.2	28.0	7.8	85.0	14.2	6430.0
91500_10	b.d.l	2.4	0.0	0.3	0.5	0.2	3.1	1.0	14.5	5.4	26.4	7.2	79.0	14.7	6170.0
91500_11	b.d.l	2.5	0.0	0.2	0.2	0.2	2.2	0.7	9.9	3.7	19.8	5.5	65.0	10.4	6170.0
91500_12	b.d.l	2.8	b.d.l	0.1	0.4	0.2	2.3	0.8	9.9	4.0	19.9	5.1	60.6	9.9	5120.0
91500_13	b.d.l	3.0	b.d.l	0.2	0.7	0.3	2.4	0.9	13.2	4.3	21.9	6.3	76.0	11.1	5880.0
91500_14	b.d.l	2.6	b.d.l	0.2	0.4	0.2	1.5	0.7	9.9	3.9	19.6	5.6	64.0	9.3	4770.0
91500_15	b.d.l	2.3	b.d.l	b.d.l	0.3	0.2	1.8	0.7	9.6	3.8	21.9	5.8	65.0	11.0	6880.0
91500_16	b.d.l	2.1	b.d.l	0.2	0.3	0.1	1.5	0.7	9.4	3.7	22.0	5.7	60.3	10.2	6530.0
91500_17	b.d.l	3.0	b.d.l	0.3	0.9	0.2	2.5	1.3	14.9	6.2	32.6	9.4	99.0	17.2	8820.0
91500_18	b.d.l	2.6	b.d.l	0.2	0.5	0.2	2.7	1.2	15.1	5.6	31.8	9.4	84.0	14.5	8700.0
91500_19	b.d.l	2.8	b.d.l	0.3	0.5	0.3	2.3	1.0	14.2	6.1	28.1	6.1	88.0	12.8	5480.0
91500_20	b.d.l	2.7	b.d.l	0.2	0.6	0.3	2.5	1.0	13.2	5.7	29.3	7.8	87.0	12.8	5600.0
91500_21	b.d.l	2.3	b.d.l	0.1	0.4	0.3	2.5	1.0	14.9	5.3	30.0	8.1	89.0	12.5	6200.0
91500_22	b.d.l	2.1	b.d.l	0.2	0.5	0.3	2.6	0.9	13.6	5.5	27.1	8.1	87.0	12.2	5400.0
91500_23	b.d.l	2.1	b.d.l	0.3	0.5	0.2	2.0	0.9	10.6	5.0	22.6	7.1	63.0	8.7	5150.0
91500_24	b.d.l	1.9	b.d.l	0.2	0.4	0.2	1.9	1.1	10.6	5.3	24.7	7.0	60.0	9.3	5250.0

Sample	Li (ppm)	Na (ppm)	Mg (ppm)	P (ppm)	Ca (ppm)	Sc (ppm)	Ti (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Rb (ppm)
91500_1	1.9	b.d.l	b.d.l	36.1	b.d.l	952.0	4.7	2.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.5	0.1
91500_2	*b.d.l	b.d.l	b.d.l	41.1	b.d.l	873.0	5.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	4.4	b.d.l
91500_3	b.d.l	b.d.l	1.7	33.2	80.0	899.0	5.1	3.4	b.d.l	b.d.l	b.d.l	b.d.l	1.7	0.7	b.d.l
91500_4	2.2	b.d.l	b.d.l	46.6	b.d.l	1007.0	5.4	3.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.3	b.d.l
91500_5	3.6	b.d.l	b.d.l	42.8	b.d.l	930.0	6.1	4.6	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_6	3.0	b.d.l	b.d.l	37.0	b.d.l	919.0	5.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_7	b.d.l	b.d.l	b.d.l	53.1	b.d.l	1361.0	5.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.5	b.d.l
91500_8	2.0	b.d.l	b.d.l	b.d.l	b.d.l	1572.0	5.2	b.d.l	b.d.l	17.3	b.d.l	b.d.l	b.d.l	10.6	b.d.l
91500_9	2.7	b.d.l	b.d.l	60.0	b.d.l	920.0	4.9	6.9	b.d.l	b.d.l	b.d.l	b.d.l	2.8	3.7	b.d.l
91500_10	2.0	b.d.l	b.d.l	47.5	b.d.l	885.0	6.3	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	2.1	b.d.l
91500_11	b.d.l	b.d.l	b.d.l	40.0	b.d.l	899.0	5.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_12	b.d.l	b.d.l	b.d.l	43.8	b.d.l	897.0	4.8	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	0.4	b.d.l
91500_13	5.9	b.d.l	b.d.l	42.0	b.d.l	870.0	4.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.1	b.d.l
91500_14	b.d.l	b.d.l	b.d.l	16.0	b.d.l	825.0	4.3	3.2	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_15	2.0	b.d.l	b.d.l	42.3	b.d.l	1015.0	4.7	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	3.2	1.0	b.d.l
91500_16	3.1	b.d.l	b.d.l	b.d.l	b.d.l	991.0	4.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.8	b.d.l	0.2
91500_17	4.4	b.d.l	b.d.l	37.5	b.d.l	910.0	4.1	7.5	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_18	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	958.0	6.0	5.6	b.d.l	b.d.l	b.d.l	b.d.l	2.8	b.d.l	b.d.l
91500_19	b.d.l	b.d.l	4.0	32.0	b.d.l	1110.0	4.9	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.4	32.0	b.d.l
91500_20	1.5	b.d.l	b.d.l	b.d.l	b.d.l	1080.0	4.3	4.6	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.2	0.1
91500_21	b.d.l	b.d.l	b.d.l	37.0	92.0	1100.0	6.9	8.4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_22	b.d.l	b.d.l	b.d.l	b.d.l	97.0	1032.0	7.4	10.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l
91500_23	b.d.l	b.d.l	b.d.l	38.6	b.d.l	1070.0	5.0	4.8	b.d.l	b.d.l	b.d.l	b.d.l	5.4	2.4	b.d.l
91500_24	b.d.l	b.d.l	b.d.l	20.6	b.d.l	1070.0	5.7	4.4	b.d.l	b.d.l	b.d.l	b.d.l	b.d.l	1.7	b.d.l

Sample	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Sn (ppm)	Cs (ppm)	Ba (ppm)	Ta (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
91500_1	b.d.l	127.0	445000.0	1.3	b.d.l	b.d.l	b.d.l	0.5	2.9	29.1	89.0
91500_2	b.d.l	143.0	476000.0	1.4	b.d.l	b.d.l	b.d.l	0.5	3.1	30.7	84.0
91500_3	b.d.l	128.0	457000.0	1.3	b.d.l	b.d.l	b.d.l	0.4	3.0	28.4	82.0
91500_4	b.d.l	139.0	433000.0	1.4	b.d.l	b.d.l	b.d.l	0.5	3.3	31.3	85.0
91500_5	b.d.l	118.0	422000.0	1.1	b.d.l	b.d.l	b.d.l	0.5	2.7	31.2	102.0
91500_6	b.d.l	115.0	411000.0	1.0	b.d.l	b.d.l	b.d.l	0.5	2.6	29.7	96.0
91500_7	b.d.l	161.0	509000.0	1.4	b.d.l	b.d.l	b.d.l	0.7	4.0	36.9	113.0
91500_8	b.d.l	178.0	610000.0	1.6	b.d.l	b.d.l	b.d.l	0.7	4.1	38.4	113.0
91500_9	10.4	134.0	495000.0	1.3	b.d.l	b.d.l	b.d.l	0.6	3.4	34.3	106.0
91500_10	b.d.l	139.0	517000.0	1.3	b.d.l	b.d.l	b.d.l	0.6	3.2	35.8	106.0
91500_11	b.d.l	118.0	511000.0	1.1	b.d.l	b.d.l	b.d.l	0.5	2.6	25.1	77.0
91500_12	b.d.l	126.0	479000.0	1.2	b.d.l	b.d.l	b.d.l	0.4	2.8	24.3	79.0
91500_13	b.d.l	89.0	427000.0	1.5	b.d.l	b.d.l	b.d.l	0.5	2.9	29.1	83.0
91500_14	b.d.l	75.6	414000.0	1.2	b.d.l	b.d.l	b.d.l	0.6	2.0	21.3	65.0
91500_15	b.d.l	118.0	486000.0	1.2	b.d.l	b.d.l	b.d.l	0.6	2.4	31.1	83.1
91500_16	b.d.l	112.0	463000.0	1.2	b.d.l	b.d.l	b.d.l	0.7	2.3	30.3	75.7
91500_17	10.0	147.0	619000.0	1.6	b.d.l	b.d.l	b.d.l	0.9	3.9	39.5	125.0
91500_18	10.0	132.0	519000.0	1.5	0.4	b.d.l	b.d.l	0.8	3.1	38.3	131.0
91500_19	11.6	150.0	503000.0	1.1	b.d.l	b.d.l	b.d.l	0.5	2.8	29.0	93.0
91500_20	b.d.l	145.0	506000.0	1.2	b.d.l	b.d.l	b.d.l	0.6	2.6	28.9	90.0
91500_21	b.d.l	123.0	499000.0	1.4	b.d.l	b.d.l	b.d.l	0.9	3.1	32.9	120.0
91500_22	b.d.l	122.0	511000.0	1.5	b.d.l	b.d.l	0.3	0.9	3.0	31.8	119.0
91500_23	b.d.l	110.0	429000.0	1.3	b.d.l	b.d.l	b.d.l	0.8	2.1	26.5	105.0
91500_24	9.5	114.0	457000.0	1.2	b.d.l	b.d.l	b.d.l	0.7	2.1	27.6	89.0

Durango apatite standard

Table 24 REE and trace elements analyses of Durango apatite standard

Sample	La(ppm)	Ce(ppm)	Pr(ppm)	Nd(ppm)	Sm(ppm)	Eu(ppm)	Gd(ppm)	Tb(ppm)	Dy(ppm)	Ho(ppm)	Er(ppm)	Tm(ppm)	Yb(ppm)	Lu(ppm)	Hf(ppm)
Durango_1	5400.0	6100.0	470.0	1570.0	229.0	24.6	174.0	22.7	144.0	24.0	62.0	8.3	54.0	5.6	b.d.l.
Durango_2	3420.0	4100.0	360.0	1070.0	138.0	15.7	144.0	17.4	95.0	18.2	46.0	4.8	30.9	4.1	b.d.l.
Durango_3	2910.0	3920.0	324.0	930.0	127.0	11.8	127.0	16.0	88.0	18.1	40.9	5.7	37.4	4.8	b.d.l.
Durango_4	4500.0	4900.0	404.0	1410.0	193.0	18.0	156.0	22.6	141.0	30.7	83.0	12.3	54.0	6.3	b.d.l.
Durango_5	3720.0	4400.0	366.0	1230.0	180.0	17.9	129.0	16.0	129.0	26.4	68.0	9.6	49.0	5.0	b.d.l.
Durango_6	2980.0	2950.0	233.0	830.0	111.0	12.8	100.0	10.9	91.0	19.1	51.0	7.1	41.0	4.1	b.d.l.
Durango_7	2480.0	2370.0	176.0	620.0	91.0	8.2	76.7	10.8	77.0	14.5	38.8	6.4	34.0	3.3	b.d.l.
Durango_8	2610.0	2780.0	210.0	710.0	110.0	10.0	87.0	14.0	76.0	12.8	36.7	4.6	23.6	2.8	b.d.l.
Durango_9	2580.0	3180.0	266.0	880.0	134.0	13.2	127.0	16.6	91.0	19.2	50.8	5.8	32.1	4.7	b.d.l.
Durango_10	4200.0	4400.0	293.0	1260.0	161.0	12.9	122.0	16.6	89.0	18.1	51.6	5.8	33.7	4.9	b.d.l.
Durango_11	3900.0	4800.0	330.0	1380.0	159.0	11.0	122.0	15.9	88.0	15.5	38.6	5.5	30.5	4.2	b.d.l.
Durango_12	3600.0	5200.0	444.0	1650.0	203.0	19.1	177.0	21.3	91.0	22.1	49.0	5.5	25.7	2.8	b.d.l.
Durango_13	4100.0	6500.0	520.0	1950.0	254.0	24.3	192.0	25.0	108.0	27.9	51.0	5.5	26.8	3.4	b.d.l.
Durango_14	2990.0	3700.0	331.0	950.0	111.0	13.3	133.0	16.1	92.0	25.3	62.3	7.9	49.9	6.7	b.d.l.
Durango_15	2380.0	3230.0	297.0	930.0	98.0	9.5	95.0	13.1	76.0	21.5	56.0	6.5	44.0	5.4	b.d.l.
Durango_16	4500.0	5400.0	390.0	1320.0	205.0	19.8	186.0	23.4	111.0	24.1	60.0	7.6	41.3	5.8	b.d.l.
Durango_17	5500.0	6000.0	500.0	1490.0	207.0	21.9	190.0	23.4	134.0	27.3	59.0	6.8	52.0	7.1	b.d.l.
Durango_18	4590.0	4600.0	370.0	1230.0	188.0	17.7	180.0	23.9	138.0	24.0	66.0	10.1	45.0	3.7	b.d.l.
Durango_19	4200.0	4700.0	400.0	1240.0	189.0	19.1	178.0	22.2	119.0	25.8	63.0	9.8	39.5	4.0	b.d.l.
Sample	U (ppm)	Na (ppm)	Mg(ppm)	Si(ppm)	Ca(ppm)	Sc(ppm)	Ti(ppm)	Cr(ppm)	Mn(ppm)	Fe(ppm)	Co(ppm)	Ni(ppm)	Cu(ppm)	Zn(ppm)	Rb(ppm)
Durango_1	b.d.l.	1740.0	185.0	1870.0	400000.0	b.d.l.	b.d.l.	b.d.l.	123.0	367.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_2	b.d.l.	1470.0	120.0	1550.0	295000.0	b.d.l.	b.d.l.	b.d.l.	96.0	247.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_3	b.d.l.	1060.0	146.0	1430.0	361000.0	b.d.l.	b.d.l.	b.d.l.	105.0	272.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_4	b.d.l.	2000.0	179.0	1910.0	434000.0	b.d.l.	b.d.l.	b.d.l.	112.0	310.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_5	b.d.l.	2060.0	195.0	2420.0	486000.0	b.d.l.	b.d.l.	b.d.l.	111.3	365.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_6	b.d.l.	1500.0	196.0	1790.0	390000.0	b.d.l.	b.d.l.	b.d.l.	107.0	368.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_7	b.d.l.	1520.0	195.0	1790.0	406000.0	b.d.l.	b.d.l.	b.d.l.	91.0	223.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_8	b.d.l.	1320.0	163.0	1890.0	358000.0	b.d.l.	b.d.l.	b.d.l.	72.9	217.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_9	b.d.l.	1250.0	182.0	1880.0	329000.0	b.d.l.	b.d.l.	b.d.l.	94.0	249.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_10	b.d.l.	1320.0	154.0	1830.0	325000.0	b.d.l.	b.d.l.	b.d.l.	98.0	220.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_11	b.d.l.	1410.0	155.0	1610.0	334000.0	b.d.l.	b.d.l.	b.d.l.	93.0	214.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_12	b.d.l.	1420.0	186.0	2170.0	320000.0	b.d.l.	b.d.l.	b.d.l.	81.0	200.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_13	b.d.l.	1700.0	170.0	1880.0	367000.0	b.d.l.	b.d.l.	b.d.l.	69.5	202.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_14	b.d.l.	1460.0	163.0	1820.0	-	b.d.l.	b.d.l.	b.d.l.	74.8	203.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_15	b.d.l.	1361.0	153.0	1330.0	-	b.d.l.	b.d.l.	b.d.l.	71.0	162.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_16	b.d.l.	1380.0	193.0	1360.0	380000.0	b.d.l.	b.d.l.	b.d.l.	129.0	257.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_17	b.d.l.	1680.0	220.0	1830.0	396000.0	b.d.l.	b.d.l.	b.d.l.	125.0	262.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_18	b.d.l.	1740.0	168.0	820.0	355000.0	b.d.l.	b.d.l.	b.d.l.	85.0	153.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Durango_19	b.d.l.	1750.0	200.0	1020.0	368000.0	b.d.l.	b.d.l.	b.d.l.	92.0	179.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Sample	Sr(ppm)	Y(ppm)	Zr(ppm)	Nb(ppm)	Sn(ppm)	Cs(ppm)	Ba(ppm)	Ta(ppm)	Pb(ppm)	Th(ppm)	U(ppm)				
Durango_1	617.0	589.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.1	299.0	16.3				
Durango_2	420.0	460.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.4	222.0	10.0				
Durango_3	327.0	445.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.7	192.0	8.8				
Durango_4	550.0	670.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.0	310.0	13.8				
Durango_5	520.0	660.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.9	295.0	15.1				
Durango_6	780.0	910.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.9	247.0	14.2				
Durango_7	622.0	820.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.0	262.0	12.9				
Durango_8	380.0	420.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.7	163.0	7.5				
Durango_9	362.0	450.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.6	224.0	12.5				
Durango_10	500.0	680.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.5	237.0	9.4				
Durango_11	540.0	740.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.7	195.0	9.1				
Durango_12	530.0	650.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.0	227.0	10.9				
Durango_13	511.0	820.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.7	217.0	10.0				
Durango_14	360.0	650.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.1	325.0	13.7				
Durango_15	362.0	560.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.0	267.0	13.4				
Durango_16	620.0	730.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.5	327.0	12.9				
Durango_17	610.0	860.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.1	410.0	13.9				
Durango_18	368.0	430.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.8	268.0	11.4				
Durango_19	360.0	460.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.0	279.0	11.3				

Table 25 Operating conditions for the ns-LA-ICP-MS equipment carried out on supergene copper minerals

	ns-LA-Q-ICP-MS
Laboratory & Sample preparation	
Laboratory name	Géosciences Environnement Toulouse
Sample preparation	Polished thin sections
Imaging	Back-scattered electron imaging (JEOL JSM 6360 LV, Géosciences Environnement Toulouse)
Laser ablation system	
Make, Model & type	ESI NWR213UC 213 nm
Ablation cell	ESI NWR TwoVol2
Laserwavelength	213 nm
Pulse width	< 5ns
Fluence	3.07 J/cm ²
Repetition rate	5 Hz
Spot size	40 µm (round spot)
Sampling mode / pattern	Single spot
Carrier gas	100% He and Ar make-up gas
Background collection	10 seconds
Ablation duration	40 seconds
Wash-out delay	65 seconds
Cell carrier gas flow (He)	450 mL/min
ICP-MS Instrument	
Make, Model & type	Thermo-Fisher Element-XR, HR-ICP-MS
Sample introduction	Via conventional tubing
RF power	1280 W
Sampler, skimmer cones	Ni
Extraction lenses	X type
Make-up gas flow (Ar)	0.96 L/min
Detection system	Single collector secondary electron multiplier
Data acquisition protocol	Time-resolved analysis
Scanning mode	Peak hopping, one point per peak
Detector mode	Pulse counting, dead time correction applied, and analog mode when signal intensity > ~ 10 ⁶ cps
Masses measured	7Li, 23Na, 24Mg, 31P, 43Ca, 45Sc, 49Ti, 52Cr, 55Mn, 57Fe, 59Co, 60Ni, 65Cu, 66Zn, 85Rb, 86Sr, 89Y, 91Zr, 93Nb, 118Sn, 133Cs, 137Ba, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 151Eu, 157Gd, 159Tb, 163Dy, 165Ho, 167Er, 169Tm, 173Yb, 175Lu, 177Hf, 181Ta, 208Pb, 232Th and 238U
Dwell time per isotope	depending on the masses
Data Processing	
Calibration strategy	NIST SRM 610 reference glass was used as primary reference material and 91500 zircon were used as secondary reference material for Mn-rich Chrysocolla and Chrysocolla and Durango apatite as secondary reference material for Pseudomalachite
Reference Material info	91500 Zircon (Wiedenbeck et al. 1995), Durango (McDowell et al. 2005)
Data Processing package	lomite (Paton et al. 2010)

Chapitre IV

Annexe 1: Copper isotope composition of chrysocolla from Zaldivar and Gaoua *in situ* oxidized ore (Table 1) and copper isotope composition of BHVO-2 secondary standard (Table 2)

Table 1: Copper isotope composition of chrysocolla from Zaldivar and Gaoua <i>in situ</i> oxidized ore				
Sample	Location	Elevation	Mineral type	$\delta^{65}\text{Cu}$ results (‰)
Zaldivar <i>in situ</i> oxidized ore				
Z1-1	Oxidized ore	3240 m	chrysocolla	1.47
Z1-2	Oxidized ore	3240 m	chrysocolla	1.49
Z1-3	Oxidized ore	3240 m	chrysocolla	1.47
Z1-4	Oxidized ore	3240 m	chrysocolla	1.48
Gaoua <i>in situ</i> oxidized ore				
GM1- 1	Oxidized ore	-	chrysocolla	3.08
GM1- 2	Oxidized ore	-	chrysocolla	3.17
GM1- 3	Oxidized ore	-	chrysocolla	3.17

Table 2: Copper isotope composition of BHVO-2								
Sample	^{62}Ni	^{63}Cu	^{64}Zn	^{65}Cu	^{66}Zn	^{67}Zn	^{68}Zn	$\delta^{65}\text{Cu}$ results (‰)
BHVO-2	0.008	2.328	3.250	1.091	1.879	0.280	1.295	14.726
BHVO-2	0.008	2.310	3.241	1.084	1.875	0.280	1.293	14.860
BHVO-2	0.008	2.279	3.201	1.069	1.852	0.276	1.278	14.820

Chapitre VI

ESM 1: Operating conditions for the ns- and fs- LA-ICP-MS U-Pb equipments carried out on chrysocolla, black chrysocolla and pseudomalachite from Mina Sur, Damiana and El Cobre exotic SCM at Toulouse and Rennes (Table 1) and Dublin (Table 2)

Table 1 Analytical conditions for the ns- and fs- LA-ICP-MS equipments carried out on chrysocolla, black chrysocolla and pseudomalachite		
	ns-LA-Q-ICP-MS	fs-LA-HR-ICP-MS
Laboratory & Sample preparation		
Laboratory name	Géosciences Rennes	Géosciences Environnement Toulouse
Sample preparation	Polished thin sections	Polished thin sections
Imaging	Back-scattered electron imaging (JEOL JSM 6360 LV, Géosciences Environnement Toulouse)	
Laser ablation system		
Make, Model & type	ESI NWR193UC, Excimer	Laser femtosecond, Pulsar 10, 800 nm, 50 fs, Amplitude technologies
Ablation cell	ESI NWR TwoVol2	ESI NWR 213
Laserwavelength	193 nm	800 nm
Pulse width	< 5ns	150-200 fs
Fluence	5.2 J/cm ²	2.14 J/cm ²
Repetition rate	4 Hz	6 Hz (Pseudomalachite) and 4 Hz (Chrysocolla)
Spot size	40 µm (round spot)	40 µm (Pseudomalachite) and 35 µm (Chrysocolla)
Sampling mode / pattern	Single spot	Single spot
Carrier gas	100% He, Ar make-up gas and N ₂ (3 mL/mn) combined using in-house smoothing device	100% He and Ar make-up gas
Background collection	20 seconds	15 seconds
Ablation duration	60 seconds	20-25 seconds
Wash-out delay	10 seconds	20 seconds
Cell carrier gas flow (He)	0.75 L/min	280 mL/min
ICP-MS Instrument		
Make, Model & type	Agilent 7700x, Q-ICP-MS	Thermo-Fisher Element-XR, HR-ICP-MS
Sample introduction	Via conventional tubing	Via conventional tubing
RF power	1350 W	1280 W
Sampler, skimmer cones	Ni	Ni
Extraction lenses	X type	X type
Make-up gas flow (Ar)	0.87 L/min	0.96 L/min
Detection system	Single collector secondary electron multiplier	Single collector secondary electron multiplier
Data acquisition protocol	Time-resolved analysis	Time-resolved analysis
Scanning mode	Peak hopping, one point per peak	Peak hopping, one point per peak
Detector mode	Pulse counting, dead time correction applied, and analog mode when signal intensity > ~ 10 ⁶ cps	
Masses measured	²⁰⁴ (Hg + Pb), ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³⁸ U, ²³⁵ U (only for black chrysocolla), ²³² Th	
Sensitivity / Efficiency	20000 cps/ppm Pb (50µm, 10 Hz)	1.2 10 ⁷ cps/ppm ²³⁸ U (20µm, 10 Hz)
Dwell time per isotope	10-30 ms depending on the masses	25 ms
Data Processing		
Gas blank	20 seconds on peak	15 seconds on peak
Calibration strategy	GJ-1 zircon was used as primary reference material and Plešovice zircon were used as secondary reference material for chrysocollas / Madagascar apatite was used as primary reference material and Durango apatite as secondary reference materials for Pseudomalachite	
Reference Material info	GJ-1 (Jackson et al. 2004), Plešovice (Sláma et al. 2008) / Madagascar (Thomson et al. 2012), Durango (McDowell et al. 2005)	
Data Processing package	Glitter (van Achterberg et al. 2001) for chrysocollas and lolite (Paton et al. 2010) with VizualAge_UcomPbine (Chew et al. 2014) for Pseudomalachite	
Quality control / Validation	Durango apatite : Weighted average ²⁰⁷ Pb-corrected age = 32.5 ± 1.1 Ma (MSWD = 0.33). Plešovice zircon : ²⁰⁶ Pb/ ²³⁸ U weighted average ages = 336.0 ± 3.3 Ma (MSWD = 0.10)	Durango apatite : Weighted average ²⁰⁷ Pb-corrected ages = 32.9 ± 0.7 (MSWD = 0.50). Plešovice zircon : ²⁰⁶ Pb/ ²³⁸ U weighted average ages = 338.2 ± 2.6 Ma (MSWD = 0.27)

ESM 1: (continued)

Table 2 Analytical conditions for the ns-LA-ICP-MS equipments carried out on chrysocolla, black chrysocolla and pseudomalachite		
	Mapping	ns-LA-ICP-MS Spot Ablation
Laboratory & Sample preparation		
Laboratory name	Trinity College Dublin	Trinity College Dublin
Sample preparation	Polished thin sections	Polished thin sections
Imaging	Back-scattered electron imaging (JEOL JSM 6360 LV, Géosciences Environnement Toulouse)	
Laser ablation system		
Make, Model & type	Ultra-short Pulse Excimer, Photon Machines	Ultra-short Pulse Excimer, Photon machines
Ablation cell	HelEx TwoVol2	HelEx TwoVol2
Laserwavelength	193nm	193nm
Pulse width	< 4ns	< 4ns
Fluence	1.2	1.2
Repetition rate	55 Hz and 61 Hz (only for REEs)	4 Hz
Spot size	12 * 12 µm	60 * 60 µm
Sampling mode / pattern	Successive linear rasters	Single spot
Carrier gas	Argon Fluoride (ArF) gas mixture	Argon Fluoride (ArF) gas mixture
Background collection	10 seconds	18s
Ablation duration	depend on the lenght of the line	30s
Wash-out delay	up to 10s	20s
Cell carrier gas flow (He)	0.5 L/min	0.5 L/min
ICP-MS Instrument		
Make, Model & type	Thermo-Fisher iCAP Qs, Q-ICP-MS	Thermo-Fisher iCAP Qs, Q-ICP-MS
Sample introduction	via PEEK tubing (narrow bore tubing for rapid wash-out)	via PEEK tubing (narrow bore tubing for rapid wash-out)
RF power	1550 W	1550 W
Sampler, skimmer cones	Ni	Ni
Extraction lenses	X type	X type
Make-up gas flow (Ar)	0.65 L/min	0.65 L/min
Detection system	Single collector secondary electron multiplier	Single collector secondary electron multiplier
Data acquisition protocol	Time-resolved analysis	Time-resolved analysis
Scanning mode	Peak hopping, one point per peak	Peak hopping, one point per peak
Detector mode	Pulse counting, dead time correction applied, and analog mode when signal intensity > ~ 10 ⁵ cps	
Masses measured	Al, Si, P, Mn, Y, La, Sm, Yb, ⁴⁴ Ca, Pb (204, 206, 207), ²³⁸ U	Si, P, Hg, Th, Na, Li, ⁴⁴ Ca, Pb (204, 206, 207), ²³⁸ U, ²³⁵ U
Sensitivity / Efficiency	205.10 ³ counts ²³⁸ U (20 µm, 10 Hz)	205.10 ³ counts ²³⁸ U (20 µm, 10 Hz)
Dwell time per isotope	depending on the masses	depending on the masses
Data Processing		
Gas blank	between 8 and 10 seconds on peak	between 8 and 10 seconds on peak
Calibration strategy	NIST 610, NIST 612 were used as primary reference material for chrysocolla, black chrysocolla and pseudomalachite. Madagascar and Durango apatites were used as secondary reference material for pseudomalachite and 91500 zircon was used as secondary reference material for chrysocolla and black chrysocolla	
Reference Material info	91500 zircon (Wiedenbeck et al. 1995) / Madagascar (Thomson et al. 2012) and Durango (McDowell et al. 2005) apatites	
Data Processing package	Iolite (Paton et al. 2010) with VizualAge_UcomPbine(Chew et al. 2014) for pseudomalachite and chrysocollas	

ESM 2: Representative table U-Th-Pb ns- and fs- LA-ICP-MS data carried out on chrysocolla, black chrysocolla and pseudomalachite from Mina Sur, Damiana and El Cobre exotic SCM

Table 1 U-Th-Pb ns-LA-Q-ICP-MS (Rennes) data carried out on chrysocolla									
Spot	²⁰⁴ Pb (cps)	Pb (ppm)	U (ppm)	Th (ppm)	²³⁸ U/ ²⁰⁶ Pb	±2σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±2σ (%)	Expected radiogenic Pb for t=19 Ma
19190417e	79	0.01	790	0	100000	0.0	0.10	17.12	2.330
20190417e	25	0.02	1099	0	50000	0.0	0.18	8.73	3.243
21190417e	204	0.01	1010	0	100000	0.0	0.02	54.83	2.978
22190417e	120	0.02	926	0	50000	0.0	0.14	15.28	2.731
23190417e	115	0.01	844	0	50000	0.0	0.07	18.34	2.489
24190417e	76	0.02	855	0	50000	0.0	0.24	9.68	2.521
27190417e	84	0.03	231	0	9091	0.0	0.18	7.09	0.681
28190417e	78	0.02	235	0	11111	0.0	0.16	9.65	0.693
29190417e	164	0.03	269	0	11111	0.0	0.22	6.41	0.793
30190417e	113	0.07	311	0	7143	0.0	0.31	6.39	0.917
31190417e	26	0.02	275	0	11111	0.0	0.11	9.34	0.810
32190417e	93	0.04	253	0	8333	0.0	0.23	5.82	0.745
20200417a	117	0.20	518	0	25000	0.0	0.11	5.06	1.528
21200417a	90	0.00	599	0	25000	0.0	0.09	5.35	1.767
22200417a	167	0.02	438	0	25000	0.0	0.15	4.12	1.292
23200417a	128	0.02	533	0	33333	0.0	0.11	6.07	1.573
24200417a	157	0.10	581	0	12500	0.0	0.49	1.73	1.713

Table 6 U-Th-Pb ns-LA-iCap-Q-ICP-MS (Dublin) data carried out on chrysocolla from Damiana							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				²³⁸ U/ ²⁰⁶ Pb	±2σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±2σ (%)
DG2_01	6.10	6.98	0.01	42.02	14.29	0.79	10.34
DG2_02	3.70	11.74	0.00	149.48	17.94	1.03	13.59
DG2_03	3.30	12.48	0.00	182.48	17.34	0.93	16.13
DG2_04	4.20	10.91	0.00	90.09	14.41	0.75	16.00
DG2_05	5.70	10.90	0.00	72.46	15.94	0.90	10.91
DG2_06	5.60	12.13	0.00	131.58	15.79	0.98	13.27

Table 7 U-Th-Pb fs-LA-HR-ICP-MS (Toulouse) data carried out chrysocolla from Damiana (sans squid)							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				²³⁸ U/ ²⁰⁶ Pb	±2σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±2σ (%)
DG2-1	10.9	1.743	0.048	56.50	22.03	1.22	20.08
DG2-2	41.1	1.721	0.47	14.93	16.42	1.43	14.69
DG2-3	14.3	1.445	0.345	43.29	23.38	0.76	32.24
DG2-4	14.7	1.54	0.059	38.61	18.53	0.99	27.78
DG2-5	16.8	1.648	0.119	42.19	17.72	0.99	27.27
DG2-6	12.9	1.154	0.29	46.51	25.12	1.50	18.67
DG2-7	14.3	1.701	0.152	39.53	18.58	0.79	27.22
DG2-8	15.8	2.05	0.069	50.25	16.58	1.50	22.00

Table 8 U-Th-Pb ns-LA-iCap-Q-ICP-MS (Dublin) data carried out on pseudomalachite from Damiana							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				²³⁸ U/ ²⁰⁶ Pb	±2σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±2σ (%)
DG2_01	-	10.48	0.01	29.24	20.18	0.87	10.48
DG2_02	-	10.85	0.01	35.34	15.19	0.89	10.85
DG2_03	-	8.94	0.01	18.02	12.79	0.78	8.94
DG2_04	-	11.61	0.02	37.04	20.00	0.78	11.61
DG2_05	-	12.50	0.00	53.48	11.23	0.88	12.50
DG2_06	-	11.16	0.00	51.28	9.74	0.87	11.16
DG2_07	-	9.63	0.17	26.32	39.47	0.81	9.63

ESM 2: (continued)

Table 9 U-Th-Pb fs-LA-HR-ICP-MS (Toulouse) data carried out on pseudomalachite from Damiana (sans squid)							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
DG2_01	0.17	2.94	0.06	63.29	16.5	1.01	34.7
DG2_02	0.19	3.95	0.05	74.07	12.6	0.94	23.4
DG2_03	0.23	1.67	0.00	24.88	11.9	0.97	16.5
DG2_04	0.37	2.09	0.00	22.12	9.3	0.96	11.5
DG2_05	0.32	2.13	0.00	28.41	10.5	0.99	13.1
DG2_06	0.49	2.02	0.04	17.04	11.6	0.97	14.4
DG2_07	0.31	1.86	0.02	24.69	11.6	1.10	15.5
DG2_08	0.41	2.03	0.02	23.47	11.5	1.15	13.9
DG2_09	0.22	3.39	0.00	66.67	14.0	1.44	22.9
DG2_10	0.44	1.90	0.02	17.64	9.9	0.93	11.8
DG2_11	0.29	1.80	0.01	27.55	12.1	0.96	37.5
DG2_12	0.49	1.93	0.01	15.34	11.8	0.96	15.6
DG2_13	0.32	1.99	0.00	22.08	11.7	0.88	12.5
DG2_14	0.36	1.95	0.00	21.14	11.2	0.99	15.2
DG2_15	0.53	0.44	0.10	2.79	17.5	0.97	13.4
DG2_16	0.27	2.45	0.01	31.06	11.8	1.03	20.4

Table 10 U-Th-Pb ns-LA-iCap-Q-ICP-MS (Dublin) data carried out on chrysocolla from El Cobre							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
CO27_1_01	13.23	5.09	0.00	6.71	9.40	0.87	5.99
CO27_1_02	10.60	3.69	0.00	5.61	9.54	0.80	5.22
CO27_1_03	11.20	3.77	0.00	5.84	9.35	0.81	4.32
CO27_1_04	12.13	4.26	0.00	6.67	10.00	0.82	4.99
CO27_1_05	7.73	2.46	0.00	6.23	10.59	0.86	5.72
CO27_1_06	13.40	3.71	0.00	5.19	9.85	0.82	4.64

Table 11 U-Th-Pb fs-LA-HR-ICP-MS (Toulouse) data carried out on chrysocolla from El Cobre							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$
C-CO27-1.FIN2	9.78	1.76	0.05	3.45	11.38	0.92	8.28
C-CO27-2.FIN2	9.50	2.07	0.02	4.42	7.52	0.86	6.72
C-CO27-3.FIN2	22.50	1.13	0.58	0.98	16.67	0.88	6.14
C-CO27-4.FIN2	10.90	2.15	0.19	3.82	17.94	0.94	10.64
C-CO27-5.FIN2	11.48	1.75	0.04	2.66	10.11	0.84	8.83
C-CO27-6.FIN2	8.50	2.37	0.00	5.95	9.52	0.95	8.35

Table 12 U-Th-Pb ns-LA-iCap-Q-ICP-MS (Dublin) data carried out on pseudomalachite from El Cobre							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
CO27_01	-	3.34	0.00	0.30	5.70	0.82	1.59
CO27_02	-	3.06	0.00	0.33	6.00	0.82	1.70
CO27_03	-	2.86	0.00	0.26	5.54	0.82	1.83
CO27_04	-	2.28	0.00	0.45	5.80	0.81	1.97
CO27_05	-	3.42	0.00	0.45	5.84	0.82	2.20
CO27_06	-	3.18	0.00	0.25	5.55	0.82	1.84
CO27_07	-	3.71	0.00	0.54	5.42	0.81	2.21

Table 13 U-Th-Pb fs-LA-HR-ICP-MS (Toulouse) data carried out on pseudomalachite from El Cobre							
Spot	Pb (ppm)	U (ppm)	Th (ppm)	Isotopic ratios			
				$^{238}\text{U}/^{206}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$
P-CO27-1.FIN2	-	1.49	0.00	0.35	4.91	0.54	3.33
P-CO27-2.FIN2	-	1.45	0.00	0.27	3.71	0.54	2.61
P-CO27-3.FIN2	-	1.44	0.00	0.22	3.91	0.53	2.82
P-CO27-4.FIN2	-	3.09	0.00	0.38	3.09	0.54	1.87
P-CO27-5.FIN2	-	3.61	0.00	0.52	2.96	0.54	2.06
P-CO27-6.FIN2	-	3.58	0.00	0.51	3.18	0.54	2.04

ESM 3: $\delta^{18}\text{O}$ isotope analyses data of black chrysocolla, chrysocolla and pseudomalachite from Mina Sur, Damiana and El Cobre exotic SCM

Table 1 Oxygen isotope analyses profile for black chrysocolla (Mina Sur exotic-Cu deposit)				
Clast 1				
Profile (in μm)	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
7300	1082217698.34	2224605.31	1.00	0.09
7340	1038605735.09	2138324.94	0.97	0.09
7380	1033483801.69	2127751.58	0.85	0.10
7420	1024876555.39	2110959.72	0.94	0.11
7460	1029393951.55	2120104.14	0.81	0.10
7500	1054685170.48	2170506.19	1.19	0.09
7540	1078091482.22	2218296.08	1.75	0.07
7580	1070232271.36	2200264.30	0.37	0.10
7620	1044531122.36	2150735.49	1.17	0.09
7660	1038594621.16	2138449.68	1.15	0.08
7700	1038678429.26	2138986.48	1.10	0.10
7740	1030887603.08	2123430.76	1.42	0.13
7780	1027034320.85	2116153.78	1.67	0.11
7820	1017902451.76	2097014.39	1.47	0.09
7860	1017188476.35	2096322.60	1.55	0.10
7900	1022322582.15	2106960.22	1.74	0.10
7940	1023218047.26	2109300.19	1.97	0.09
7980	1003996432.06	2070571.55	1.87	0.09
8020	1000188588.42	2063309.70	1.84	0.10
8060	998279223.04	2059537.01	1.75	0.10
8100	1010869376.26	2084838.21	2.39	0.10
8140	1002596379.48	2069195.54	2.48	0.10
8180	1004203287.23	2073962.44	3.14	0.10
8220	992747359.56	2051035.23	3.31	0.12
8260	991080686.09	2047262.55	3.36	0.11
8300	1062541281.53	2189430.11	2.56	0.10

Table 2 Oxygen isotope analyses profile for chrysocolla (Mina Sur exotic-Cu deposit)				
Profile (in μm)	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
2934	1137176188.88	2367143.34	15.31	0.06
2854	1167853920.75	2430148.73	15.39	0.09
2814	1165111350.94	2424364.95	15.69	0.09
2814	1165111350.94	2424364.95	15.69	0.09
2774	1157906047.35	2410068.05	15.55	0.11

Table 3 Oxygen isotope analyses profile for pseudomalachite (Mina Sur exotic-Cu deposit)				
Profile (in μm)	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
2832	1315585892.83	2643373.61	-17.50	0.07
2895	1306097017.12	2625436.33	-17.10	0.06
2910	1323558322.11	2663008.21	-15.85	0.09
2925	1323499350.24	2660233.51	-17.04	0.08
2940	1308842346.51	2632717.09	-16.76	0.07
3096	1313871966.26	2642640.59	-16.32	0.09
3231	1332417295.11	2678121.65	-16.79	0.08
3572	1363217053.38	2744941.31	-14.41	0.06
1201	1306935135.87	2626033.61	-17.53	0.09
1109	1329764733.01	2673188.42	-16.62	0.08
912	1336212890.75	2692108.56	-14.10	0.08
890	1326890572.77	2667189.17	-16.88	0.09
572	1347296464.01	2709550.63	-15.87	0.09
419	1343230694.05	2701937.21	-16.00	0.08
148	1333423256.86	2683954.57	-15.32	0.07
0	1321535360.28	2657273.58	-16.66	0.07

Table 4 Oxygen isotope analyses for chrysocolla (Damiana exotic-Cu deposit)				
Spots	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
DG2-C@1	1183666773.06	2455627.60	12.49	0.11
DG2-C@2	1127963989.52	2330471.15	7.09	0.13
DG2-C@3	1161284341.44	2413780.25	14.07	0.10
DG2-C@4	1114161094.99	2300924.74	6.04	0.09
DG2-C@5	1143253655.53	2372242.89	11.92	0.09
DG2-C@6	1080752398.67	2234078.61	6.09	0.10
DG2-C@8	1162081898.13	2410415.83	11.94	0.12
DG2-C@7	1104093652.35	2282957.22	7.26	0.09

Table 5 Oxygen isotope analyses for pseudomalachite (Damiana exotic-Cu deposit)				
Spots	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
DG2-P@1	1178998658.41	2388890.75	-11.88	0.10
DG2-P@2	1171800121.47	2373777.67	-12.22	0.09
DG2-P@3	1154868845.03	2340798.79	-12.12	0.08
DG2-P@4	1150127091.16	2332372.62	-11.72	0.11
DG2-P@5	1140817701.62	2313240.78	-11.96	0.07
DG2-P@6	1136509617.78	2304410.12	-11.87	0.07
DG2-P@7	1139044387.36	2308821.67	-12.09	0.09

Table 6 Oxygen isotope analyses for chrysocolla (El Cobre exotic-Cu deposit)				
Spots	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
CO27-1-C@9	545563924.50	1152670.68	0.68	0.18
CO27-1-C@8	710939031.49	1495002.36	9.06	0.18
CO27-1-C@6	755054788.37	1573669.32	2.57	0.16
CO27-1-C@5	766896208.05	1595677.92	1.45	0.15
CO27-1-C@4	620503746.65	1306681.50	6.21	0.14
CO27-1-C@3	642901450.48	1354396.04	6.40	0.15
CO27-1-C@2	658119669.79	1365072.75	6.72	0.15
CO27-1-C@1	729241328.21	1530461.08	8.46	0.14

Table 7 Oxygen isotope analyses for pseudomalachite (El Cobre exotic-Cu deposit)				
Spots	^{16}O	^{18}O	$\delta^{18}\text{O}$ (‰)	$\pm \sigma$ (‰)
CO27-1-P@1	724373465.26	1480739.48	-19.13	0.21
CO27-1-P@2	731052293.73	1494272.77	-18.77	0.15
CO27-1-P@3	741347874.32	1511692.15	-21.11	0.11
CO27-1-P@4	731151487.44	1495059.06	-18.73	0.13
CO27-1-P@5	731781730.36	1495773.53	-19.56	0.13
CO27-1-P@6	737896981.82	1507015.99	-19.58	0.16
CO27-1-P@7	790603331.77	1607060.25	-21.42	0.12
CO27-1-P@8	761687346.60	1549127.95	-22.29	0.10
CO27-1-P@9	736256031.70	1503005.14	-19.98	0.13

ESM 4: Summary of chrysocolla, black chrysocolla and pseudomalachite EPMA analyses from the exotic copper deposits

Table 1 Chemical composition of supergene copper minerals from Mina Sur exotic SCM				Table 2 Chemical composition of supergene copper minerals from Damiana exotic SCM (gravels)		
	Black chrysocolla	Chrysocolla	Pseudomalachite		Chrysocolla	Pseudomalachite
N	105	79	123	N	21	23
wt %				wt %		
Al ₂ O ₃	0.057	2.159	0.090	Al ₂ O ₃	2.463	0.212
SiO ₂	32.177	36.780	0.221	SiO ₂	47.617	1.521
K ₂ O	0.000	0.050	0.000	K ₂ O	0.036	0.012
CaO	0.420	0.442	0.124	CaO	0.960	0.278
Cl	0.153	0.119	0.016	Cl	0.033	0.015
MnO	6.385	0.038	0.014	MnO	0.022	0.006
FeO	0.066	0.049	0.011	FeO	0.111	0.040
Na ₂ O	0.000	0.063	0.000	Na ₂ O	0.036	0.004
MgO	0.152	0.121	0.005	MgO	0.203	0.037
BaO	0.179	0.077	0.032	BaO	0.015	0.017
P ₂ O ₅	0.080	0.030	24.189	P ₂ O ₅	0.206	22.673
SO ₃	0.341	0.099	1.327	SO ₃	0.064	0.428
CuO	49.047	50.782	68.441	CuO	41.070	65.806
Total	89.057	90.809	94.470	Total	92.836	91.048

Table 4 Chemical composition of supergene copper minerals from El Cobre exotic SCM				Table 3 Chemical composition of supergene copper minerals from Damiana exotic SCM (bedrock)		
	Chrysocolla	Pseudomalachite	Copper wad		Chrysocolla	Pseudomalachite
N	135	68	7	N	21	23
wt %				wt %		
Al ₂ O ₃	0.693	0.117	1.670	Al ₂ O ₃	0.025	0.525
SiO ₂	43.456	0.790	28.680	SiO ₂	43.247	0.222
K ₂ O	0.032	0.011	0.047	K ₂ O	0.015	0.025
CaO	0.414	0.175	0.800	CaO	0.276	0.228
Cl	0.073	0.005	0.029	Cl	0.052	0.010
MnO	0.052	0.016	13.529	MnO	0.014	0.044
FeO	0.086	0.036	1.510	FeO	0.013	0.022
Na ₂ O	0.023	0.000	0.098	Na ₂ O	0.005	0.003
MgO	0.089	0.021	0.084	MgO	0.106	0.008
BaO	0.015	0.026	0.032	BaO	0.013	0.006
P ₂ O ₅	0.038	22.401	0.057	P ₂ O ₅	0.034	28.506
SO ₃	0.098	0.067	0.106	SO ₃	0.056	0.065
CuO	49.229	67.156	41.713	CuO	52.629	62.814
Total	94.299	90.820	88.354	Total	96.486	92.475

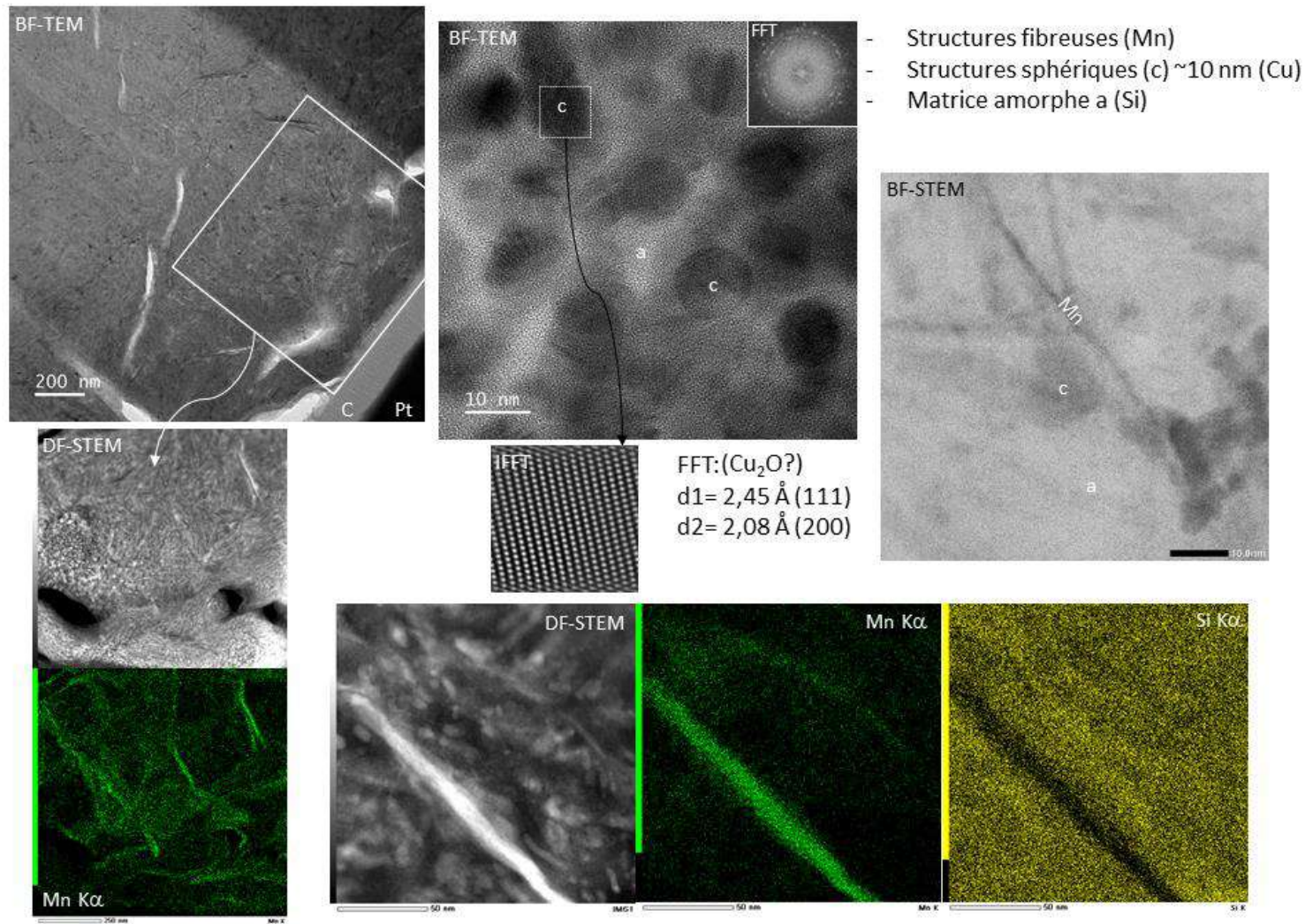
Images - Microscope Electronique à Transmission (FIB-MET)

La caractérisation cristallographique à l'échelle nanométrique a été réalisée via un microscope électronique à transmission MET JEOL NEO-ARM au Consortium Lyon Saint-Etienne de microscopies (CLYM) par Anne-Magali Seydoux-Guillaume (CR, CNRS).

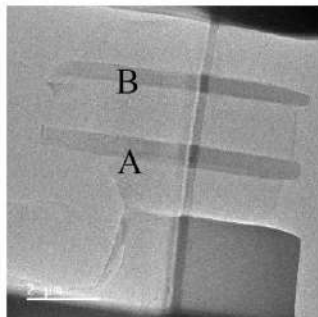
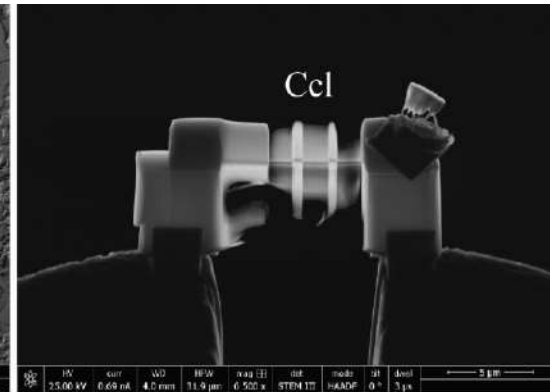
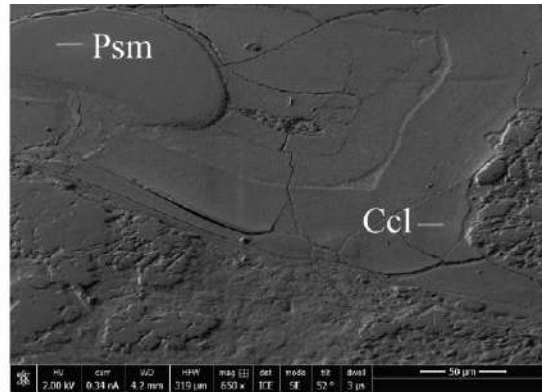
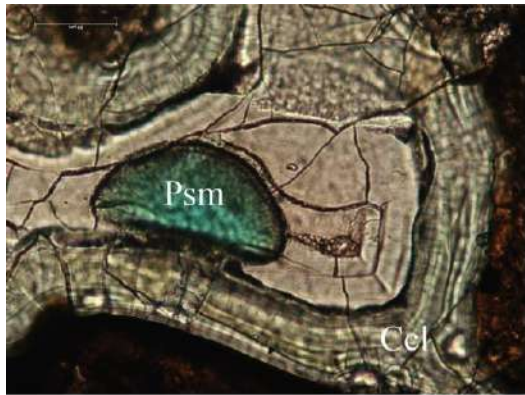
Cette étude a eu pour objectif de mettre en évidence la répartition à l'échelle nanométrique de l'uranium et du plomb dans la structure (amorphe ou cristalline) de la chrysocolle et de la pseudomalachite. Ceci pour relier les informations structurales aux analyses géochronologiques afin de contraindre les processus perturbateurs du chronomètre U-Pb dans la chrysocolle et la pseudomalachite. Pour cela, des coupes FIB (Focused Ion Beam, FIB Manutech-USD, Université Jean Monnet, Saint-Etienne) ont été réalisées aux interfaces entre les phases cristallines. Les résultats préliminaires ont montré, dans les clastes de chrysocolle noire, deux types de phases nanocristallines baignant dans une matrice amorphe. Dans les bandes de chrysocolle et de pseudomalachite, les analyses au MET ont montré des nano-cristaux sphériques dans une matrice amorphe.

Clastes de chrysocolle noire

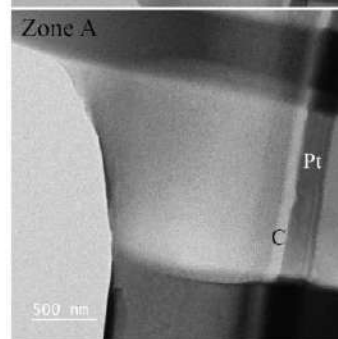
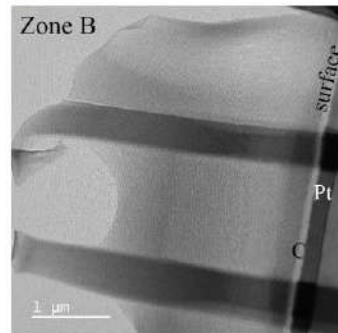
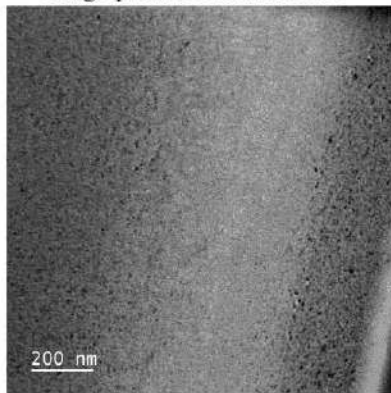
Chrysocolle noire 2 types de nano-phases cristallisées le tout dans une matrice amorphe (Si)



Lits de chrysocolle



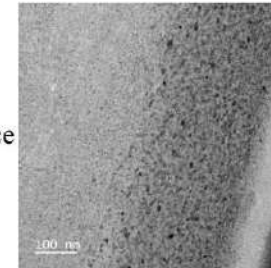
Litage parallèle à la surface



C (carbone) Pt (Protection FIB)

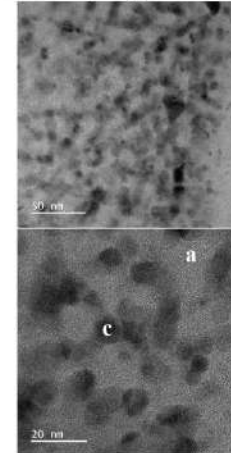
BF-TEM

Un seul type nanocristaux
(sphériques) dans une matrice
amorphe

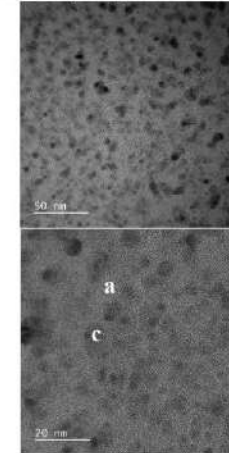


Chrysocolle

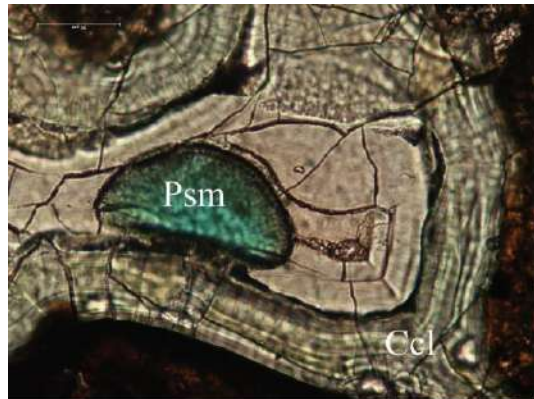
Bande à plus gros cristaux



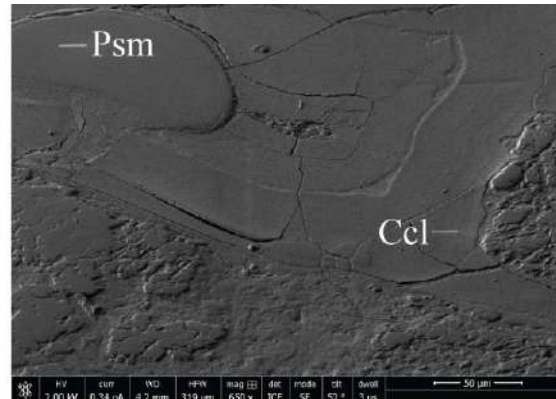
Bande à plus petits cristaux



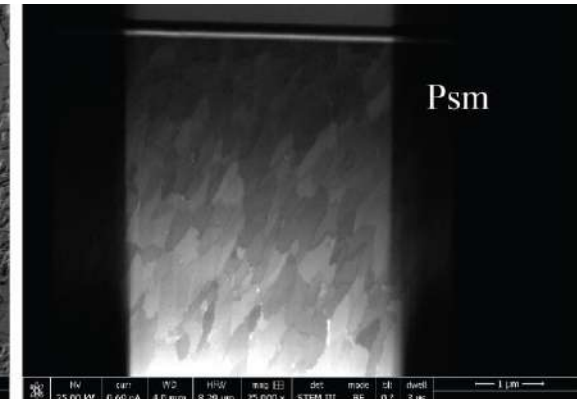
Pseudomalachite (Annexe 1)



BF-TEM

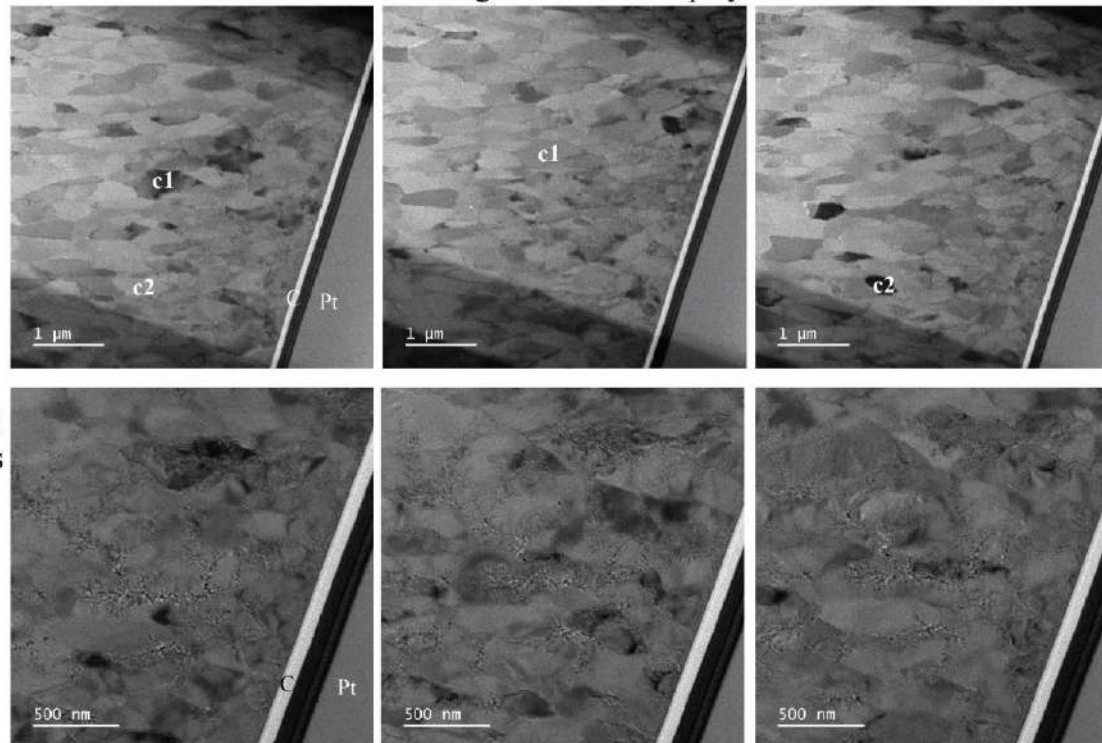


Lame FIB à faible grandissement et polycristallins



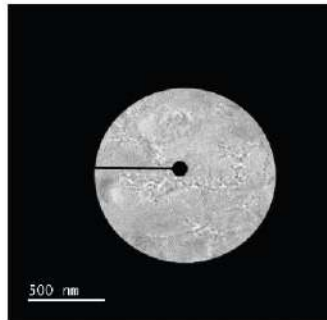
Pseudomalachite

En zoomant, on voit des grappes le long des joints de grains. Certains sont noirs quand d'autres sont gris

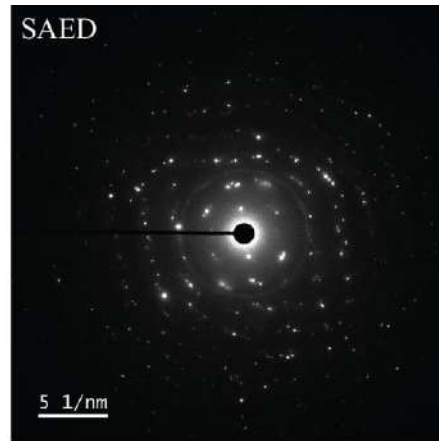


Pseudomalachite (Annexe 2)

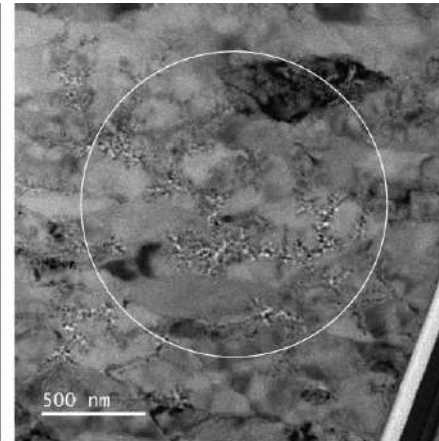
BF-TEM



SAED

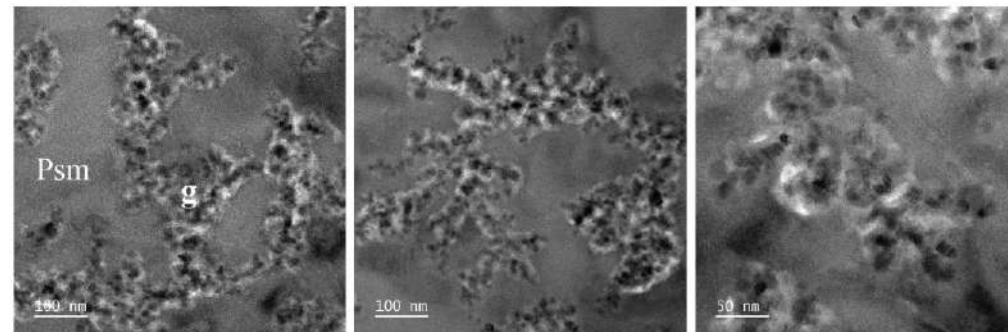


Pseudomalachite

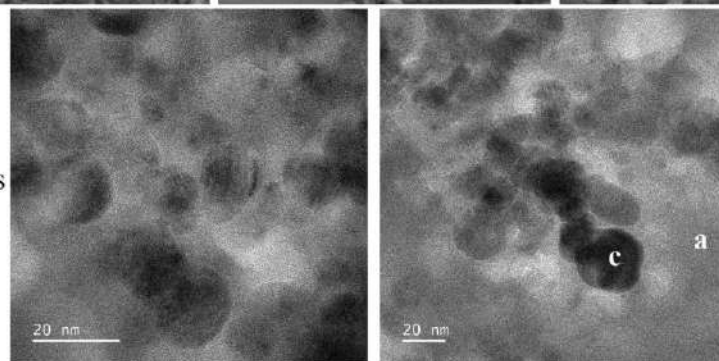


Dans la diffraction (SAED) on note:

- un anneau fin de petites tâches qui correspond à la diffraction des petits cristaux dans les grappes
- de plus gros cristaux avec des orientations différentes



En zoomant dans les grappes (g), on observe des agglomérations de nanocristaux sphériques dans une matrice amorphe



Abstract

Supergene copper mineralization (SCM) are nowadays the economic viability of many porphyry copper deposits worldwide. These mineralization are derived from supergene processes, defined as sulfide oxidation and leaching of ore deposits in the weathering environment, and any attendant secondary sulfide enrichment. For supergene copper mineralization to form, favorable tectonics, climate and geomorphologic conditions are required. Tectonics control the uplift needed to induce groundwater lowering and leaching of sulphides from a porphyry copper deposit. Climate controls copper leaching in the supergene environment and groundwater circulation towards the locus where supergene copper-bearing minerals precipitate. In Atacama Desert of northern Chile, SCM seem to take place during specific Tertiary climatic periods and relief formation. But many uncertainties remain regarding the genesis and the exact timing for SCM formation.

We present mineralogical and chemical data on supergene copper-bearing minerals sampled from *in situ* and exotic SCM from two geologically and climatically distinct areas, namely the Atacama Desert of northern Chile and the Gaoua porphyry Cu-Au district in Burkina Faso. Although both areas have experienced different geological conditions, they both underwent similar geological and climatic controls to form and preserve SCM.

Chrysocolla and pseudomalachite are the most common copper-bearing minerals found in SCM from the Atacama Desert of northern Chile. This led us to test the potential of both minerals as dating materials to place the SCM formation in a geochronological context. However, variation of U content from one mineral to another, common Pb contribution and the absence of matrix-matched-standard for both minerals made U-Pb LA-ICP-MS dating of chrysocolla and pseudomalachite challenging. A mixed approach combining texturally-controlled *in situ* LA-ICP-MS U-Pb dating and multi-elements mapping together with SIMS oxygen isotope analyses were applied to Mina Sur, Damiana and El Cobre exotic copper deposits and the *in situ* SCM of the Gaoua porphyry Cu-Au district.

Regardless their location, the results demonstrate the important role played by the local geological parameters on the control of the U-Pb chronometer in supergene copper minerals. Initial high U content of the porphyry source can promote U-rich supergene copper minerals as it is the case at Mina Sur. Additionally, a long-term supergene alteration will favor long term water circulation in the depositional environment which can leached U from the porphyry source and allow the formation of U-low supergene copper minerals during recent times.

The promising results obtained represent a new tool to understand the physico-chemical, climatic and geological conditions that prevailed during the formation of supergene copper deposits and a proxy for their prospection around the world.

Key words: Supergene copper mineralization; Atacama Desert; Gaoua Cu-Au district; textural and chemical characterization; U-Pb LA-ICP-MS dating, chrysocolla; pseudomalachite

Résumé

Les minéralisations cuprifères supergènes (MCS) représentent la viabilité économique de nombreux porphyres cuprifères de par le monde. Ces minéralisations dérivent de processus supergènes, définis comme étant l'altération en conditions oxydantes des sulfures primaires et tout enrichissement en sulfures secondaires qui en découle. Des conditions tectoniques, climatiques et géomorphologiques favorables sont requises pour la formation des minéralisations cuprifères supergènes. La tectonique contrôle le soulèvement nécessaire pour induire la baisse de la nappe phréatique et l'oxydation des sulfures primaires. Le climat contrôle le lessivage du cuivre dans l'environnement supergène et la circulation des eaux météoriques dans le milieu de dépôt. Dans le désert d'Atacama, les MCS semblent se former pendant des périodes climatiques spécifiques du Tertiaire durant la formation du relief Andin. Cependant, de nombreuses incertitudes persistent quant à la genèse et au moment précis de la formation de ces MCS.

Ce travail de thèse présente des données minéralogiques et chimiques de minéraux échantillonnés dans des MCS *in situ* et exotiques provenant de deux zones géologiques et climatiques distinctes, à savoir le désert d'Atacama au nord du Chili, et le district minier de Gaoua, au Burkina Faso. Bien que ces deux régions aient connu une histoire géologique et climatique différente, elles ont toutes deux subi un contrôle géologique et climatique similaire pour former et préserver les MCS.

La chrysocolle et la pseudomalachite sont les minéraux les plus abondants dans les MCS du désert d'Atacama. Ceci nous a poussé à tester le potentiel de ces deux minéraux comme géochronomètre pour replacer la formation des MCS dans un contexte géochronologique. Cependant, la variation de la teneur en U d'un minéral à l'autre, la contribution du Pb commun et l'absence de standards spécifiques à ces minéraux ont représenté un challenge pour la datation de ces deux minéraux. Une approche mixte combinant la datation *in situ* U-Pb LA-ICP-MS et la cartographie isotopique ainsi que les analyses isotopiques de l'oxygène au SIMS a été appliquée aux dépôts exotiques de cuivre de Mina Sur, Damiana et El Cobre et à la minéralisation cuprifère supergène *in situ* du district minier de Gaoua.

Quelle que soit leur localisation, les résultats démontrent le rôle important joué par les paramètres géologiques locaux sur le contrôle du chronomètre U-Pb dans les minéraux supergènes de cuivre. La teneur initiale élevée en U du porphyre source peut favoriser la présence de minéraux cuprifères supergènes riches en U, comme c'est le cas à Mina Sur. En outre, une altération supergène à long terme favorisera une circulation continue des eaux météoriques dans l'environnement de dépôt, ce qui peut entraîner le lessivage de l'U du porphyre source et permettre la formation de minéraux cuprifères supergènes pauvres en U, à une époque relativement récente.

Les résultats prometteurs obtenus pendant cette thèse représentent de nouveaux outils pour comprendre les conditions physico-chimiques, climatiques et géologiques qui ont prévalu lors de la formation des minéralisations cuprifères supergènes dans le désert d'Atacama, mais aussi dans la région de Gaoua au Burkina Faso, et fournissent des indications quant à leur prospection dans le monde entier.

Mots clés : Minéralisations cuprifères supergènes ; désert d'Atacama ; district Cu-Au de Gaoua ; caractérisation texturale et chimique ; datation U-Pb LA-ICP-MS, chrysocolle ; pseudomalachite