Sommaire

Introduction générale

INTRODUCTION GENERALE

Les compositions isotopiques des éléments métalliques dans les émanations volcaniques sont très peu connues. Leur étude peut cependant fournir de précieuses informations sur l'origine et le comportement des métaux au cours des interactions complexes fluides/solides ainsi que sur les processus de fractionnement isotopiques susceptibles de se produire au sein des édifices volcaniques actifs. Ce travail, qui se situe à la croisée des chemins entre la géochimie isotopique et la volcanologie, vise à explorer les compositions isotopiques du zinc (Zn) du strontium (Sr) et du plomb (Pb) dans les gaz volcaniques et dans les différentes composantes des systèmes volcaniques susceptibles d'interagir avec ces fluides. Cette étude présente aussi une analyse critique des différentes techniques actuelles de prélèvement des gaz volcaniques, tout en proposant de nouvelles méthodologies d'échantillonnage de ces émanations.

1. Géochimie des gaz volcaniques :

Les magmas sont constitués d'un mélange de composés silicatés et de gaz dissous à haute température et à haute pression. Lors de leur mise en place dans les niveaux superficiels de la croûte terrestre, ces magmas sont soumis à une forte diminution de pression qui engendre une différentiation entre une phase liquide (lave) et une phase gazeuse qui migre vers la surface de l'édifice volcanique avant son émission à l'atmosphère. Au cours de cette migration, la phase gazeuse initiale subit de profondes modifications physico-chimiques liées à son refroidissement et à des interactions complexes avec la roche encaissante ou des fluides extérieurs infiltrés dans l'édifice volcanique, comme les eaux météoriques ou l'eau de mer (cas des systèmes hydro-volcaniques). La composition élémentaire et isotopique des gaz émis en surface (constitués en proportions variables d'H_2O, CO_2, H_2S, H_2, CO, CH_4, SO_2, HCl, HF, d'autres gaz en traces et d'éléments métalliques) est par conséquent une véritable mine d'informations car elle est la résultante de l'ensemble de ces processus. Elle est susceptible de nous renseigner sur l'état d'activité du volcan, sur les sources des éléments, mais aussi sur la nature et l'amplitude des processus se produisant au sein de l'édifice volcanique.

Plusieurs approches visant à caractériser les phases en présence et à quantifier ces processus et interactions sont décrites dans la littérature. Les paragraphes suivants ne prétendent pas lister de manière exhaustive l'ensemble de ces approches, mais présentent les méthodologies qui sont en relation directe avec ce travail.

. Étude des condensations gaz/particules :

Le gaz volcanique étant soumis a un refroidissement plus ou moins important avant son émission en surface, il se sature par rapport à des espèces minérales variées qui précipitent sous forme solide en réponse à la décroissance de température. Ces phénomènes de condensation gaz-particule sont étudiés à l'aide de tubes de silice insérés dans un évent fumerolien [*Le Guern and Bernard*, 1982]. Ces tubes permettent de recréer artificiellement en surface les processus de condensation gaz/particules rencontrés dans l'édifice volcanique. En effet, un gradient de température s'installe dans le tube et des minéraux, appelés improprement sublimés, et contenant quantité de métaux, précipitent successivement en réponse à leurs températures de saturation respectives. Ces minéraux condensés peuvent alors êtres identifiées par différentes méthodes analytiques (Diffraction des Rayons X, Microscopie Electronique à Balayage, Analyse par Activation Neutronique Instrumentale ou INAA). Associée à la composition globale des gaz volcaniques et à la modélisation thermodynamique des processus de condensation, ce type d'approche a permis une meilleure compréhension des processus de transport des éléments volatils par les gaz volcaniques et a fourni de précieuses informations sur le rôle des fluides magmatiques dans la formation des gîtes minéraux. [*Bernard*, 1985; *Le Guern and Bernard*, 1982; *Quisefit et al.*, 1989; *Symonds et al.*, 1987; *Taran et al.*, 2001].

. Étude des gaz fumeroliens et des panaches volcaniques :

Les gaz fumeroliens sont généralement collectés à l'aide de deux méthodologies d'échantillonnages complémentaires :

- Les ampoules à NaOH sous vide artificiel [*Giggenbach*, 1975] qui donnent accès à la composition des gaz majeurs (CO_2, H_2S, HCl….).
- Les condensats acides [*Chevrier and Le Guern*, 1982] qui sont généralement employés pour la mesure des compositions isotopiques et des teneurs en éléments trace.

Dans le cas où les champs fumeroliens ne sont pas accessibles, un échantillonnage du panache s'avère être la seule possibilité pour l'obtention de données sur la phase gazeuse. Dans ce

cadre, les méthodes citées ci-dessus sont inadaptées, mais des techniques alternatives ont été proposées dans la littérature:

- Des filtres imprégnés de ^{7}LiOH peuvent être utilisés pour l'estimation des teneurs en gaz acides dans le panache [*Faivre-Pierret*, 1983; *Finnegan et al.*, 1989].
- La filtration sur membrane synthétique, qui est généralement employée pour la détermination des teneurs en éléments trace métalliques [*Toutain et al.*, 1995; *Vié le Sage*, 1983].

L'ensemble de ces méthodes d'échantillonnage des émanations volcaniques présentent cependant plusieurs inconvénients. En effet, plusieurs prélèvements (parfois difficiles à mettre en oeuvre sur le terrain) sont nécessaires à l'obtention de données complètes sur la phase gazeuse. Les techniques analytiques nécessaires sont parfois lourdes et indisponibles dans la majorité des laboratoires (INAA). De plus, la représentativité de ces modes d'échantillonnage est parfois mise en doute dans la littérature, le prélèvement non-quantitatif des espèces les plus volatiles et/ou le piégeage d'éléments en trace lors de la précipitation de soufre solide lors de l'échantillonnage (cas des condensats acides) étant les processus les plus fréquemment mis en évidence [*Bichler and Sortino*, 1995; *Finnegan et al.*, 1989; *Fischer et al.*, 1998b]. De plus, ces problèmes d'échantillonnage peuvent induire des fractionnements isotopiques indésirables sur certains éléments, qui seront discutés plus loin. Il apparaît donc clairement que des progrès doivent êtres effectués dans le domaine des méthodes d'échantillonnage des émanations volcaniques pour augmenter la représentativité des prélèvements et faciliter les analyses.

Les études élémentaires réalisées sur les espèces majeures contenues dans les gaz volcaniques (CO_2, SO_2, HCl, HF…) ont permis d'évaluer l'ampleur des apports volcaniques à l'atmosphère (gaz à effet de serre) et leur impact sur les variations climatiques [*Dessert*, 2002; *Fischer et al.*, 1998a; *Halmer et al.*, 2002]. Les variations des flux d'émission de SO_2 de même que les rapports S/Cl et F/Cl sont très largement utilisés comme marqueurs de l'activité volcanique ou comme traceurs des processus d'assimilation ou de mélanges de magmas [*Fischer et al.*, 1996; *Goff et al.*, 1998]. En ce qui concerne les concentrations en éléments trace, les calculs de facteurs d'enrichissement dans les gaz volcaniques par rapport à la roche ont permis de décrire le comportement des éléments dans ces fluides de haute température. Les éléments en trace ont ainsi été classifiés comme étant plus ou moins réfractaires (cas du Sr) ou volatils (cas du Zn et du Pb) [*Symonds et al.*, 1987; *Taran et al.*, 2001]. L'étude de ces

concentrations a aussi permis d'évaluer l'ampleur des apports volcaniques en éléments trace à l'atmosphère et leur impact sur l'environnement [*Dongarra and Varrica*, 1998].

Du point de vue de la géochimie isotopique, les émanations volcaniques sont principalement étudiées à l'aide des isotopes stables des éléments légers : δD, $\delta^{18}O$, $\delta^{13}C$, $\delta^{34}S$ et plus récemment $\delta^{11}B$. Ces études, très nombreuses, ont conduit a des avancées majeures dans l'identification de l'origine de ces éléments dans les gaz volcaniques et dans la compréhension des interactions fluides roches se produisant au sein des édifices volcaniques [*Bolognesi*, 1996; *Capasso et al.*, 1999; *Chiodini et al.*, 1995; *Cortecci et al.*, 2001; *Leeman et al.*, 2005; *Pennisi et al.*, 2000]. En ce qui concerne les éléments métalliques, il n'existe que quelques données sur les compositions isotopiques du Pb dans les aérosols et les incrustations volcaniques obtenues sur le Masaya (Nicaragua) et le Vulcano [*Ferrara et al.*, 1995; *Monna et al.*, 1999; *Vallelonga and Mather*, 2003]. Ces travaux suggèrent que le Pb contenu dans les émanations possède une signature identique au magma. À l'exception de ces quelques études, les données concernant les compositions isotopiques des éléments métalliques dans les gaz volcaniques sont inexistantes. Ces fluides étant constitués en majeure partie d'H_2O, CO_2 et d'espèces soufrées H_2S+SO_2, l'étude des isotopes stables des éléments légers nous renseignent sur le comportement de la « phase porteuse » des gaz volcaniques, mais ne permettent pas de décrire précisément l'origine et les comportements individuels des métaux contenus dans ces gaz. Seule une étude élémentaire et isotopique spécifique des éléments métalliques dans les gaz volcaniques est susceptible d'apporter des informations précises sur ces questions.

2. Géochimie isotopique du Sr, du Pb et du Zn

Le Sr possède 4 isotopes ^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr, d'abondances respectives 0,56%, 9,86%, 7% et 82,58%. Le ^{87}Sr est radiogénique (désintégration radioactive du ^{87}Rb). Le Pb possède aussi 4 isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, d'abondances respectives 1,4%, 24,1%, 22,1% et 52,4% [*Rosman and Taylor*, 1998]. Les isotopes ^{206}Pb, ^{207}Pb et ^{208}Pb sont radiogéniques (désintégration radioactive du ^{238}U, ^{235}U et ^{232}Th, respectivement). Par comparaison aux variations isotopiques issues des désintégrations radioactives, les processus naturels n'induisent pas de fractionnements isotopiques significatifs pour ces deux éléments [*Barbieri and Morotti*, 2003; *Bollhöfer and Rosman*, 2001]. Leurs compositions isotopiques sont par

conséquent de puissants traceurs, très largement utilisés en géochimie pour leur aptitude à identifier les sources naturelles ou anthropiques [*Bollhöfer and Rosman*, 2001; *Freydier and Viers*, 2003; *Monna et al.*, 1999; *Monna et al.*, 1997], pour l'étude des interactions eaux roches [*Barbieri and Morotti*, 2003; *Goff et al.*, 1991; *Möller et al.*, 2004; *Pennisi et al.*, 2000] ou pour la description de l'évolution des magmas [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997; *De Astis et al.*, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003]. Les travaux citées ci-dessus ne constituent que quelques exemples d'application, pour la plupart en relation directe avec ce travail, car lister l'ensemble des publications basées sur l'utilisation des isotopes du Sr et du Pb prendrait plusieurs pages. Comme nous l'avons vu plus haut, les compositions isotopiques de ces éléments dans les gaz volcaniques sont très peu connues et sont susceptibles de fournir de précieuses informations sur leur origine et leur comportement dans les gaz volcaniques.

Les compositions isotopiques du Sr et du Pb sont généralement mesurées à l'aide de spectromètres de masse à thermo-ionisation (TIMS). Bien que les TIMS permettent l'étude de nombreux systèmes isotopiques (Sr, Pb, Nd, Th, Os…), certains éléments ne peuvent êtres analysés convenablement du fait des limitations de la source d'ions à thermo-ionisation. Cette source est basée sur l'éjection d'ions à partir de la surface d'un échantillon déposé sur un filament porté sous vide à haute température (typiquement 1500 à 3000°K). De telles températures sont trop faibles pour ioniser efficacement les éléments à haute énergie de première ionisation (>7 eV) comme le zinc (Zn), le magnésium (Mg), le cuivre (Cu), ou encore le fer (Fe).

L'avancée technique la plus significative de ces quinze dernières années dans le domaine de la spectrométrie de masse est sans conteste la mise au point de l'analyse des rapports isotopiques par MC-ICP-MS (Multiple Collector Inductively Coupled Plasma Mass Spectrometer), dont le premier prototype a été fabriqué en 1990 [*Rehkämper et al.*, 2000]. Cet instrument (Fig.1) est basé sur le couplage d'une source d'ions à plasma induit (ICP) et d'un secteur magnétique à cages de Faraday multiples, équivalent à ceux qui sont utilisés dans la plupart des TIMS. Avec des températures de plasma pouvant atteindre 10000°K, ces sources d'ions, souvent rencontrées dans les instruments prédestinés à l'analyse des concentrations comme les ICP-MS quadrupolaires, permettent une ionisation très efficace des éléments à haute énergie de première ionisation cités plus haut.

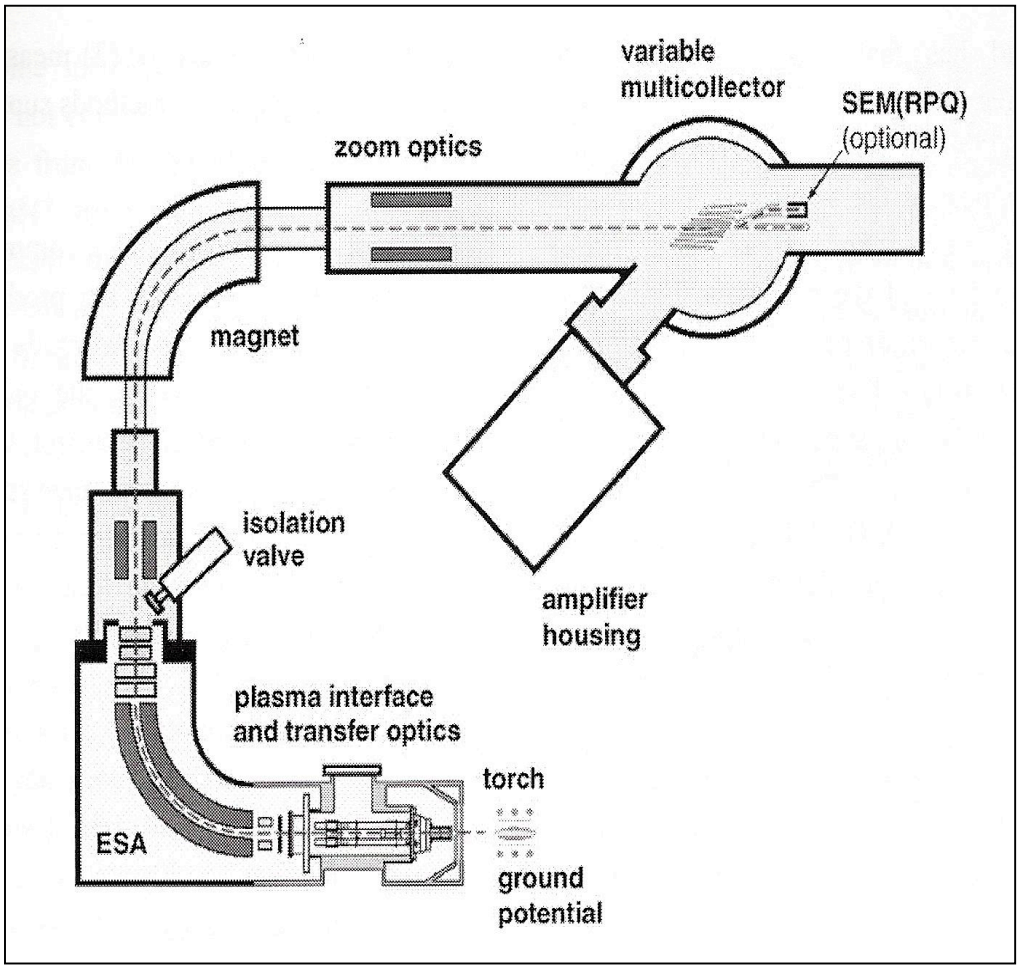

Fig .1 : Schéma simplifié du Neptune d'après [*Weyer and Schwieters*, 2003]. Cet MC-ICP-MS a été reçu au LMTG fin 2003.

Grâce à ces caractéristiques techniques, cette nouvelle génération d'instruments permet d'étudier avec précision les variations isotopiques encore inexplorées d'un grand nombre d'éléments (métalliques ou non métalliques). L'une des applications les plus novatrices de cette technique est sans doute l'étude des isotopes stables des éléments dits « non traditionnels ». Ces dix dernières années, le nombre de publications concernant ces nouveaux systèmes stables n'a cessé de croître [*Reviews in Mineralogy*, 2004]. Concernant les métaux, des variations isotopiques significatives ont été mesurées par MC-ICP-MS pour un grand nombre d'éléments, par exemple le Mg, le Fe, le Cr, le Mo, le Cu ou encore le Zn. De plus, les études de ces variations commencent à trouver des applications de première importance dans un grand nombre de domaines scientifiques. Par exemple, les études réalisées sur le Mg ont permis de caractériser les compositions isotopiques des différents réservoirs terrestres (eau de mer, croûte terrestre, manteau, carbonates…) et peuvent être utilisées pour décrire son comportement lors des interactions entre ces différentes composantes [*Young and Galy*, 2004]. Les isotopes du Fe peuvent êtres utilisés dans la description des processus d'accrétion

des planètes du système solaire [*Poitrasson et al.*, 2004], mais aussi comme traceurs du métabolisme [*Anbar*, 2004].

Parmi ces métaux, le Zn, qui fait partie des éléments de transition, présente des caractéristiques particulièrement adaptées à la présente étude. Cet élément possède 5 isotopes stables non radiogéniques de masses ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn et ^{70}Zn et d'abondances respectives 48.63%, 27.90%, 4.10%, 18.75% et 0.62% [*Rosman and Taylor*, 1998]. Contrairement au Sr et au Pb, les fractionnements isotopiques naturels sont mesurables pour cet élément. Le Zn présente cependant une faible amplitude de variations isotopiques (0,84‰ par unité de masse atomique) dans les échantillons naturels terrestres analysés à ce jour [*Weiss et al.*, 2005]. Par comparaison, le Cu, très proche en termes de masse atomique, présente des variations isotopiques 10 fois plus importantes. Cet effet est très probablement relié au fait que le Zn est pratiquement insensible aux changements de conditions d'oxydo-réduction qui sont capables d'engendrer d'importants fractionnements isotopiques. En effet, le Zn ne possède que 2 états d'oxydation (0 et +2), le degré d'oxydation +2 étant largement prédominant dans la nature car « moins coûteux » d'un point de vue énergétique. Cette caractéristique importante peut donc nous permettre de restreindre les causes des potentielles variations isotopiques observées dans nos échantillons (nature des fractionnements isotopiques, effets de sources), en nous affranchissants des possibles fractionnements isotopiques induits par les changements de conditions d'oxydo-réduction. De plus, le Zn est présent en quantité significative dans les roches, mais aussi dans les gaz volcaniques et dans les sublimés du fait de son caractère volatil [*Symonds et al.*, 1987]. Les processus de changement de phase pouvant produire d'importants fractionnements isotopiques (cinétiques ou à l'équilibre), des variations isotopiques significatives sont susceptibles d'être observées lors de la formation des sublimés (Condensations gaz-particules) mais aussi lors du dégazage magmatique. Cependant, ces changements de phases se produisent à des températures élevées, et l'amplitude de certains processus de fractionnements isotopiques (à l'équilibre) diminue avec la température (dépendance en $1/T^2$). Si ces fractionnements à l'équilibre sont dominants au cours des processus des changements de phase décrits ci-dessus, la principale question est donc de savoir si la précision des mesures sera suffisante pour les détecter.

Malgré leur faible amplitude dans les échantillons terrestres, les variations isotopiques du Zn sont mesurables avec une très grande précision (<0.05‰) par MC-ICP-MS grâce aux protocoles de purification et d'analyse mis au point par [*Marechal*, 1998]. Les études

postérieures ont permis de déterminer les compositions isotopiques du Zn dans plusieurs minerais et échantillons biologiques [*Marechal et al.*, 1999], dans certains nodules ferro-manganesifères, sédiments et carbonates marins [*Marechal et al.*, 2000; *Pichat et al.*, 2003]. Ces travaux suggèrent que les isotopes du Zn peuvent être utilisés en tant que traceurs des processus biogéochimiques marins et ont par conséquent un important potentiel d'applications en océanographie et paléo-océanographie. Cependant, les bases de données relatives aux isotopes stables du Zn sont encore très incomplètes, en particulier sur les échantillons naturels. De plus, les processus responsables des variations observées (fractionnements isotopiques, effets de source) sont encore mal connus [*Albarède*, 2004]. Il est par conséquent nécessaire de compléter ces bases de données et d'identifier clairement les causes des variations observées pour pouvoir profiter pleinement du potentiel de cet élément. À ce stade, il est important de signaler qu'aucune investigation n'a été effectuée sur les variations isotopiques du Zn dans les gaz volcaniques ou dans les sublimés.

3. Démarche et objectifs de la thèse :

Cette thèse comporte deux objectifs:

1) Le premier objectif de cette thèse est le développement de la géochimie des isotopes stables et radiogéniques des éléments métalliques dans les gaz volcaniques afin d'évaluer ses apports, tant dans le cadre strict de la compréhension des processus volcaniques que dans le cadre plus général de la géochimie des isotopes stables « non traditionnels ».

- Pour atteindre cet objectif, nous avons choisi d'effectuer une étude élémentaire et isotopique couplée Sr/Pb (élément réfractaire/élément volatil) dans les gaz fumeroliens et les eaux thermales du Vulcano (Iles Eoliennes, Italie). Ce site est un système hydro-volcanique très complexe, où des interactions multiples se produisent entre les gaz magmatiques, la roche encaissante, et des aquifères plus ou moins profonds alimentés par des infiltrations d'eau météorique ou d'eau de mer. Le Sr et le Pb n'étant pas soumis à des fractionnements isotopiques significatifs, le problème de l'échantillonnage des gaz volcaniques ne se pose pas dans cette étude car il n'est pas à même de modifier significativement la composition isotopique des gaz prélevés. L'ensemble des échantillons de gaz fumeroliens utilisés dans cette étude ont été prélevés par la méthode des condensats acides. Pour mener à bien ce

travail, les procédures de purifications des échantillons et d'analyses TIMS ont été testées et validées. Cette étude a été réalisée dans le but d'évaluer le potentiel des traceurs radiogéniques Sr/Pb pour l'identification des sources de ces éléments et des processus contrôlant leur transfert dans un système hydro-volcanique complexe.

-Nous avons choisi d'étudier les variations isotopiques du Zn dans les gaz volcaniques, les sublimés et les roches du Merapi (Java, Indonésie). Ce site est moins complexe que Vulcano en termes d'interactions entre fluides. En effet, du fait de sa position géographique, les infiltrations d'eau de mer dans l'édifice peuvent être négligées. De plus, le climat de l'île de Java est typiquement tropical, avec deux saisons très marquées (saison des pluies et saison sèche). Ce contexte volcanique est donc plus adapté pour pouvoir discriminer entre les différentes causes possibles (fractionnements isotopiques/effets de source) des variations isotopiques observées. Le Zn étant susceptible de fractionner lors du prélèvement des gaz fumeroliens, plusieurs techniques d'échantillonnage ont été utilisées pour évaluer l'impact du mode de prélèvement sur les compositions isotopiques mesurées. Pour mener à bien ce travail, les protocoles de mise en solutions et de purifications des échantillons ont été adaptés, testés et validés. Cette étude présente des données obtenues sur 2 MC-ICP-MS : le Plasma 54 de l'ENS Lyon, et le Thermo Finnigan Neptune (reçu au LMTG en 2003) dont la mise au point pour l'analyse des compositions isotopiques Zn, a été effectuée durant ce travail (optimisation des paramètres machine, test des effets de matrice, corrections d'interférences, comparaison et sélection des méthodes de corrections du fractionnement instrumental). Cette étude a été réalisée pour documenter la variabilité isotopique du Zn en contexte volcanique et pour identifier les processus responsables des variations isotopiques observées.

2) Le deuxième objectif de cette thèse est de proposer de nouvelles méthodologies d'échantillonnage et d'analyse des émanations volcaniques permettant d'améliorer la représentativité des prélèvements et de faciliter l'obtention de données complètes sur les gaz volcaniques.

Dans ce cadre, deux méthodologies nouvelles d'échantillonnage des gaz et des panaches volcaniques sont présentées dans ce travail. Ces deux méthodes sont basées sur l'utilisation de solutions d'ammoniac qui sont utilisées pour piéger l'ensemble des constituants des émanations volcaniques. De nombreux protocoles ont été mis au point pour permettre

l'analyse de ces solutions d'ammoniac par des techniques courantes (HPLC, GC, titrage, ICP-MS). Les résultats obtenus par ces deux nouveaux modes de prélèvement ont ensuite été validés par comparaison aux méthodes d'échantillonnage de référence.

Les échantillons utilisés dans cette thèse proviennent de cinq campagnes de prélèvement qui ont été effectuées entre 1999 et 2002 sur le Merapi et le Vulcano à l'exception des 4 échantillons de roches du Mérapi (Chapitre 4) qui nous ont été gracieusement fournis par N.Metrich et M.Condomines.

4. Organisation du manuscrit :

Ce manuscrit est organisé autour de quatre articles publiés ou soumis dans des revues scientifiques internationales, d'une conclusion générale, et deux annexes :

- Le **chapitre I** présente la description et les tests d'un nouveau dispositif mis au point pour l'échantillonnage des panaches volcaniques : le VES (Venturi Effect Sytem). Ce travail, réalisé à Vulcano (Iles Eoliennes, Italie), a été publié en 2003: Toutain, et al., (2003), A new collector for sampling volcanic aerosols, *J. Volcanol. Geotherm. Res.*, *123* (1-2), 95-103.

- Le **chapitre II** présente les résultats d'expérimentations sur une nouvelle procédure développée pour l'échantillonnage et l'analyse des gaz fumeroliens. Ce travail, réalisé à Vulcano (Iles Eoliennes, Italie) et au Mérapi (Indonésie) fait l'objet d'une publication soumise : Sortino et al., (submitted), Giggenbach's 1975 revisited: using ammoniac to sample volcanic gases, *J. Volcanol. Geotherm. Res*.

- Le **chapitre III** présente la première étude isotopique couplée Sr/Pb des gaz fumeroliens et des eaux thermales de Vulcano (Iles Eoliennes, Italie). Ce travail fait l'objet d'une publication sous presse : Nonell et al., (in press.), First coupled Sr and Pb isotopic measurements in volcanic gas condensates and groundwaters of Vulcano island (Italy), *Geochem. Geophys. Geosyst.*, 2005GC000980.

- Le **chapitre IV** présente les premières mesures isotopiques du Zn dans les gaz volcaniques, les sublimés et les roches du volcan Mérapi (Ile de Java, Indonésie). Ce travail fait l'objet d'une publication soumise : Nonell et al., (submitted), Evidence for Zn isotopic variations at Merapi active volcanic system, *Earth Planet. Sci. Lett.*

- La **conclusion générale** résume de manière synthétique l'ensemble des résultats obtenus dans ce travail, et présente de manière détaillée les apports et les perspectives des études réalisées.

- Annexe 1 : Nouveau chapitre de thèse, valorisation des compétences :
Ce document, réalisé suivant les recommandations de l'école doctorale SDU2E et en collaboration avec un professionnel du recrutement, a pour objectif de porter un regard rétrospectif et lucide sur le cadre général de la thèse, son déroulement et son coût, ainsi que sur les compétences et les savoir-faire acquis personnellement par le futur docteur. Ce travail vise aussi à évaluer la place et les retombées de la thèse sur le laboratoire et dans le contexte scientifique national et international.

- Annexe 2 : Cette annexe présente les premiers résultats et interprétations sur les variations isotopiques du Zn dans les plantes, les litières, les roches, et les différents horizons de sols du bassin versant d'Nsimi (Cameroun). Ce travail résulte de ma collaboration analytique avec les membres de l'équipe « Eaux, sols, érosion : milieu naturel et anthropisé » du L.M.T.G. et fait l'objet d'une publication en cours de révision : Viers et al., (under revision), Measurements of Zn isotopic compositions in a soil-plant system of a tropical watershed : a new tool to constrain the biogeochemical cycles of metals ? *Earth Planet. Sci. Lett.*

Chapitre 1 :
Nouvelle méthodologie d'échantillonnage des panaches volcaniques.

I-1 VERSION ABREGEE DE L'ARTICLE EN FRANÇAIS

I-1-1 Introduction

L'objectif de cette étude est de présenter un nouveau dispositif, appelé le VES (Venturi Effect System), destiné à l'échantillonnage des panaches volcaniques. Cet appareil a été élaboré pour faciliter l'accès à la composition chimique des panaches volcaniques (gaz acides, éléments en trace métalliques). En effet, les méthodes classiquement utilisées pour l'obtention de ces compositions reposent essentiellement sur des techniques de filtrations qui présentent plusieurs désavantages. Ces méthodes nécessitent l'utilisation d'un appareillage complexe, qui se révèle souvent peu pratique à utiliser dans les conditions de terrain. De plus, les techniques analytiques requises pour l'obtention des données sont lourdes (Induced Neutron Activation Analysis, INAA) et la représentativité de ces modes d'échantillonnage est contestée dans la littérature, le prélèvement non-quantitatif des espèces les plus volatiles étant le plus souvent mis souvent en évidence [*Finnegan et al.*, 1989; *Vié le Sage*, 1983].

. *Principe de fonctionnement :*

Le principe de fonctionnement du VES (Fig.2, page 33) est basé sur l'aspiration, à l'aide d'une pompe électrique 12V, de l'échantillon de panache volcanique dans une solution d'ammoniac (NH_4OH 5N, ultra-pure, MERCK), permettant la dissolution de l'eau, des gaz acides et des éléments en trace métalliques (MTE). L'échantillon ainsi obtenu permet d'accéder à la composition chimique du panache volcanique par des méthodes analytiques largement répandues, comme l'HPLC (High Pressure Liquid Chromatography) pour les analyses S, Cl, F ou L'ICP-MS (Inductively Coupled Plasma Mass Spectrometry) pour l'analyse des compositions en éléments trace.

. *Échantillonnage :*

Dans le but de tester et de valider ce nouveau mode d'échantillonnage, deux campagnes de prélèvements ont été effectuées sur le Vulcano (Iles Eoliennes, Italie) en 2000 et 2001. Durant ces campagnes, nous avons sélectionné une fumerolle isolée : F0 (Fig.1, page 32), et effectué des échantillonnages en parallèle en utilisant plusieurs méthodes de prélèvements. Des échantillonnages directs de la fumerolle par ampoules à soude [*Giggenbach*, 1975] et à ammoniac [*Sortino et al.,* submitted *;* cf. chapitre II] nous ont permis d'obtenir la composition

de référence de la fumerolle sélectionnée. Le VES a, quant à lui, été placé à 3 à 5 mètres sous le vent de la fumerolle pendant les prélèvements. Durant la campagne effectuée en 2000, des prélèvements de panache ont aussi été effectués en plaçant un filtre à l'entrée du VES. L'ensemble de ces échantillons nous a permis de comparer les données obtenues à l'aide du VES (seul ou avec filtre) aux données du gaz de référence obtenues par les ampoules NaOH et NH_4OH.

I-1-2 Résultats

. *Gaz acides*

La comparaison des rapports Cl/F et Cl/SO_4 obtenus par HPLC dans les échantillons VES et dans les ampoules NaOH (Fig. 3, page 34) nous ont permis de valider la méthode pour l'échantillonnage des gaz acides. En effet, les rapports obtenus entre les deux techniques sont très comparables, ce qui confirme l'efficacité des prélèvements par VES. Il est aussi démontré que les échantillons de panache obtenus par ajout d'un filtre à l'entrée du VES présentent des rapports Cl/SO_4 sensiblement différents. Ce phénomène est attribué à un fractionnement du soufre lors de la filtration, ce qui confirme la non-représentativité de cette méthodologie d'échantillonnage.

. *Éléments en trace*

La validation de la méthode VES pour l'analyse des éléments en trace a été obtenue par comparaison des facteurs d'enrichissements (EF) par rapport à l'aluminium (page 35) entre un échantillon de gaz prélevé directement sur l'évent fumerolien à l'aide d'une ampoule NH_4OH et de la moyenne de 5 échantillons VES (Fig. 4 ; page 35). Les diagrammes d'enrichissements obtenus par les deux méthodes sont globalement similaires. Cependant, il est observé que les facteurs d'enrichissement dans le panache sont systématiquement égaux ou inférieurs à ceux qui sont obtenus dans l'ampoule NH_4OH. Ces différences sont attribuées aux comportements variables des éléments trace à l'interface volcan-atmosphère, certains d'entre eux pouvant précipiter sous forme d'incrustations, classiquement observées sur les évents fumeroliens.

I-1-3 Conclusion :

Le VES s'est avéré être un outil simple et efficace pour l'obtention de données représentatives sur les compositions en gaz acides (rapports S, Cl, F) et en éléments trace des panaches volcaniques. Ce dispositif, testé en conditions réelles, a présenté un grand nombre d'avantages :

1) Un seul échantillon VES est nécessaire pour l'obtention de la composition en gaz acides et en éléments en trace du panache volcanique.
2) L'utilisation de solutions d'ammoniac permet d'analyser les échantillons VES par des méthodes très largement répandues (HPLC, ICP-MS).
3) Ce nouveau dispositif s'est avéré être un outil robuste et aisément transportable (dimensions : 0.43 x0.33x0.3m, pour un poids total de 5kg) dans les conditions de terrain. Par conséquent, il semble être très adapté à la surveillance géochimique en continu des panaches volcaniques, principalement dans les cas où l'accès aux champs fumeroliens s'avère difficile.

I-2 A NEW COLLECTOR FOR SAMPLING VOLCANIC AEROSOLS

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A new collector for sampling volcanic aerosols

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Abstract

A new apparatus, Venturi Effect System (VES), designed for sampling volcanic plumes is described and tested at Vulcano (Italy). This device, together with purified basic NH_4OH solutions, supplies optimal conditions to obtain reliable S_{total}/Cl/F ratios and enrichment factors for metallic trace elements (MTE). Good concordance for acid gas ratios and metal enrichment factors in both the gas phase and the related plume allows the procedure to be validated. The VES appears in Vulcano conditions as a simple, robust and easily portable apparatus that allows reliable collection of both acid gases and MTE within a single sample and the analysis with current chemical methods (High Pressure Liquid Chromatography, Inductively Coupled Plasma–Mass Spectrometry). This apparatus may be suitable for more difficult volcanoes where only the plume can be sampled.

Keywords: volcanic plume; acid gases; metallic trace elements; sampling; monitoring

1. Introduction

A major objective in volcano surveillance is to detect changes of volatile chemistry and interpret them in terms of changing magmatic processes and degassing conditions. But investigations regarding volcanic volatiles also provide a clue to various processes such as climate changes, mineral deposition processes and geothermal activity. Accurate data are needed at active volcanoes and continuous and regular sampling of high temperature gases is generally considered to be responsible for supplying the most complete and comprehensive set of data under optimal conditions. Because access to fumaroles may be very hazardous and is sometimes impossible, sampling of the vapour plume is the only way to obtain reliable chemical parameters such as the contents of total sulphur (S_t), halogens (HCl, HF) and metallic trace elements (MTE).

Sulphur species, halogens and MTE, besides water and CO_2, are the main components of volcanic fluids. Their study provides important data

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for degassing and magmatic processes and therefore constitutes critical arguments for evaluating volcanic hazards (Symonds et al., 1994). Fluorine and chlorine display contrasted behaviours in magmatic environments and can reach several mol% in the gas phase. Sulphur is exsolved mainly as SO_2 and H_2S, depending mainly on pressure conditions. SO_2 emission rates are known to correlate with fluctuations in activity (Fischer et al., 1996) and S/Cl and F/Cl ratios are largely used to forecast eruptive activity and detect events such as magma mixing, assimilation processes, vaporisation of acid crater lakes, shallow degassing (e.g. Italiano et al., 1991; Goff et al., 1998; Schevenell and Goff, 2000). MTE are commonly enriched in high temperature gases as the result of distillation acting at the magma level and subsequent vapour transportation of species (Symonds et al., 1987; Quisefit et al., 1989; Toutain et al., 1990).

The techniques commonly used for sampling and analysing total sulphur (St), halogens and MTE contents in volcanic plumes display several serious disadvantages. MTE are usually sampled by using bulk filtration through synthetic membranes (Vié le Sage, 1983; Toutain et al., 1995). The most common method used for acid gases is based on the use of impregnated filters (Faivre-Pierret, 1983; Finnegan et al., 1989). However, these techniques require complex sampling conditions, difficult analytical techniques (Induced Neutron Activation Analysis) and non-quantitative trapping of some species is often observed (Finnegan et al., 1989). Aerosol collection in plumes is based on the assumption that fast gas-to-particle processes occur and that chemical elements are either in the solid or liquid state. Plumes usually display a very high variability of chemical composition which increases with the degree of volatility of the elements (Vié le Sage, 1983) suggesting that very volatile elements may not be retained quantitatively by filters. This is confirmed by Finnegan et al. (1989) who established that many volatile elements (Se, As, In, Sb) are not trapped by particle filters because of their speciation at filtering level, at least partially dominated by volatile species. Moreover, some compounds based on elements such as Se are known to display significant vapour pressures even at atmospheric temperatures (Mosher and Duce, 1985). It is highly probable that other MTE, such as As, Tl, Pb, and Hg, may display a similar behaviour. This leads to important fractionation between metals that makes plume acid gases and MTE data processing uncertain in some cases.

There is therefore a need for a more reliable method allowing one-step, fast, simple and quantitative sampling and anlyzing of S_t, HCl, HF, and MTE in plumes. This is especially true for volcanoes where fumaroles are not accessible. In this paper, we will present a new device named Venturi Effect System (VES) and test it in very simple conditions (safety, small distance to fumaroles) at Vulcano (Italy).

2. Sampling and analytical methods

In this section, we shall describe the VES allowing quantitative sampling of acid gases and MTE in plumes. To validate this device, we shall compare S_t/Cl and Cl/F ratios, and MTE enrichment factors (EF) in the plume and in the bulk gas phase. For this purpose, we chose an isolated fumarolic fissure at Vulcano island (South Italy) that allows rather homogeneous sampling conditions of the related plume.

2.1. The Venturi Effect System

We designed a new apparatus allowing the complete dissolution of a mixed gas–solid–liquid phase in plume conditions. The process is based on the continuous injection of such a mixed plume phase into NH_4OH occurring as a spray of microdroplets generated by a Venturi effect (Fig. 2A). Continuous pumping with a 12-V electrical pump allows both injection of the sample and the nebulisation of the NH_4OH solution. Dissolution of gases, liquids and already condensed particles is expected to be much more efficient than normal bubbling in solutions, as the surface exchange between plume mixture and trapping solution is much higher due to the small size of droplets in the spray. Pumping rates were chosen to minimise the loss of alkaline solution and to insure the continuous spraying (spraying stops be-

low 3 l min^{-1} with the selected geometry of the device). To insure a good resistance with respect to alkaline solutions and to avoid contamination with MTE, we used fused quartz for the spray chamber and the container of the solution. This device is immersed in a Pyrex container of ice water (Fig. 2) which is regularly supplied during sampling. Packaging of the bulk apparatus (quartz and Pyrex devices, pump, 12-V battery) in a case results in a total size of $0.43 \times 0.33 \times 0.30$ m weighing 5 kg. One sample needs about 2 l of ice water carried as ice in bottles. About 4 samples can be collected with a 7-Amp-hour battery.

Effective and complete dissolution of condensable species (H_2O, CO_2, SO_2, H_2S, HCl, HF) has been demonstrated in NaOH solutions by Giggenbach (1975) and many other volcanic gas geochemists (i.e. Giggenbach and Matsuo, 1991; Sortino et al., 1991). This procedure, used for collecting major and trace gases, has been used recently to analyse MTE (Fischer et al., 1998). However, it requires high dilution rates (250 ideally for samples from Kudryavy Volcano) and sector-field Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) to obtain a high mass resolution and reduce interferences. Recently, we established (Sortino et al., in prep.) the efficiency of trapping major gases and MTE in NH_4OH. These solutions require only minor dilutions (factor 2) and multi-collection ICP–MS allows analysis of more than 40 elements with very low detection limits (extreme values are 4 and 600 ppt for U and Li, respectively). In this work, we followed this method and used 5N NH_4OH solution from ultra-pure MERCK NH_4OH (25%) diluted with 50% ultra-pure water.

2.2. Fumarolic gas collection with NaOH and NH_4OH bottles

In order to validate the efficiency of this device, we compared elemental ratios and EF in samples collected by VES with those in the bulk gas phase collected by bottles partially filled with either NaOH or NH_4OH. NaOH bottles (see Section 2.1) were used to sample St, HCl and HF (Giggenbach, 1975; Sortino et al., 1991).

NH_4OH bottles were used for sampling MTE (Sortino et al., in prep.). We favoured this technique, rather than the classic 'acid condensate' technique which consists of direct condensation of the bulk gas phase in an ether or acetone device (Quisefit et al., 1989). These latter samples often display a very high variability of MTE concentrations that can be easily explained by sulphur behaviour upon condensing and cooling during sampling. First, the 'acid condensate' method does not trap H_2S and results in samples with artificially low S_t/Cl ratios. Moreover, progressive solid S precipitation occurs leading to floating aggregates in solution and adsorption of S on bottle inner walls. Subsequent incorporation of metals within solid S particles occurs as the result of chemical affinities (Greenland and Aruscavage, 1986; Fischer et al., 1998), as well as possible adsorption on the mineral surfaces. Moreover, as acid condensing is performed in an 'open system' because of off-line pumping, revolatilisation of volatile elements is believed to occur. These factors lead to possibly large fractionation of MTE within the solution during 'acid condensates' sampling. Our method allows the complete dissolution of MTE and a significant enrichment of the trapping solution by gases (typically 30 g of fumarolic fluid trapped in bottles filled with 100 g of NH_4OH).

Advantages of sampling method are: (1) as the solution used is alkaline, it allows quantitative trapping of acid gases with the same efficiency as well-known NaOH solutions, and (2) it allows analysis of dissolved trace elements with classic ICP–MS techniques as only elements of small atomic mass are present in the matrix.

3. Site and procedure

3.1. Site

We chose Vulcano to verify the efficiency of VES. Vulcano, in the Eolian Archipelago, displays well-developed fumarolic activity located on both the crater rim and the inner slope of the summit Fossa crater. We selected an isolated fumarole (F0) located at the centre of a recent

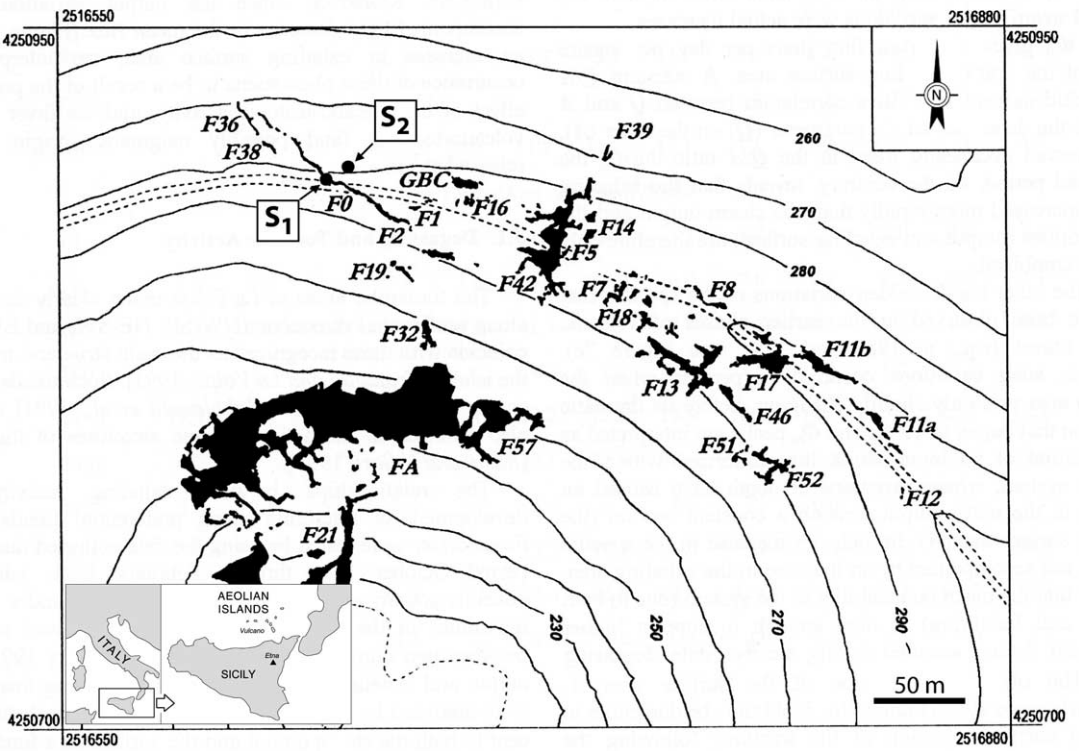

Fig. 1. Precise mapping of fumaroles at Vulcano (Italy). Legend: (S1) sampling site of fumarolic gases; (S2) site for plume sampling with VES. Modified from Italiano and Pecoraino, 1998.

fracture trending NW–SW (Fig. 1). F0 fumarole is the hottest vent from the fracture, located roughly at its centre, and was at 313 and 307°C during our experiments (May 2000 and April 2001, respectively). The VES was emplaced 3–5 m downwind of F0, so that only limited other fumarolic vapours from the fissure and from the crater were expected to contribute to the plume. With these conditions, heterogeneities during sampling consisted mostly in the variable density of the F0 plume over the sample as a function of wind direction and speed, with more or less limited mixing with other fumarolic gases emitted from the same fissure.

3.2. Field procedures

The duration for VES sampling was about 60 min, with pumping rates of about 5 l min^{-1}. Seven plume samples were collected in 2000 and 5 in 2001. Moreover, to underline the fractionation processes due to the above-mentioned membrane filtration process, three of the 7 VES samples of 2000 were performed with a 2-μm silica filter placed in-line. In this case, sampling duration was 120 min with higher pumping rates (about 8 l min^{-1}) to obtain measurable concentrations of the expected elements in solution. Samples were stored in cleaned polyethylene bottles and analysed about 1 month after collection.

3.3. Laboratory and analytical procedures

• *Acid gases*. Samples from VES, NH_4OH and NaOH bottles underwent the following processing: (1) adding of ultra-pure H_2O_2 and thunder-

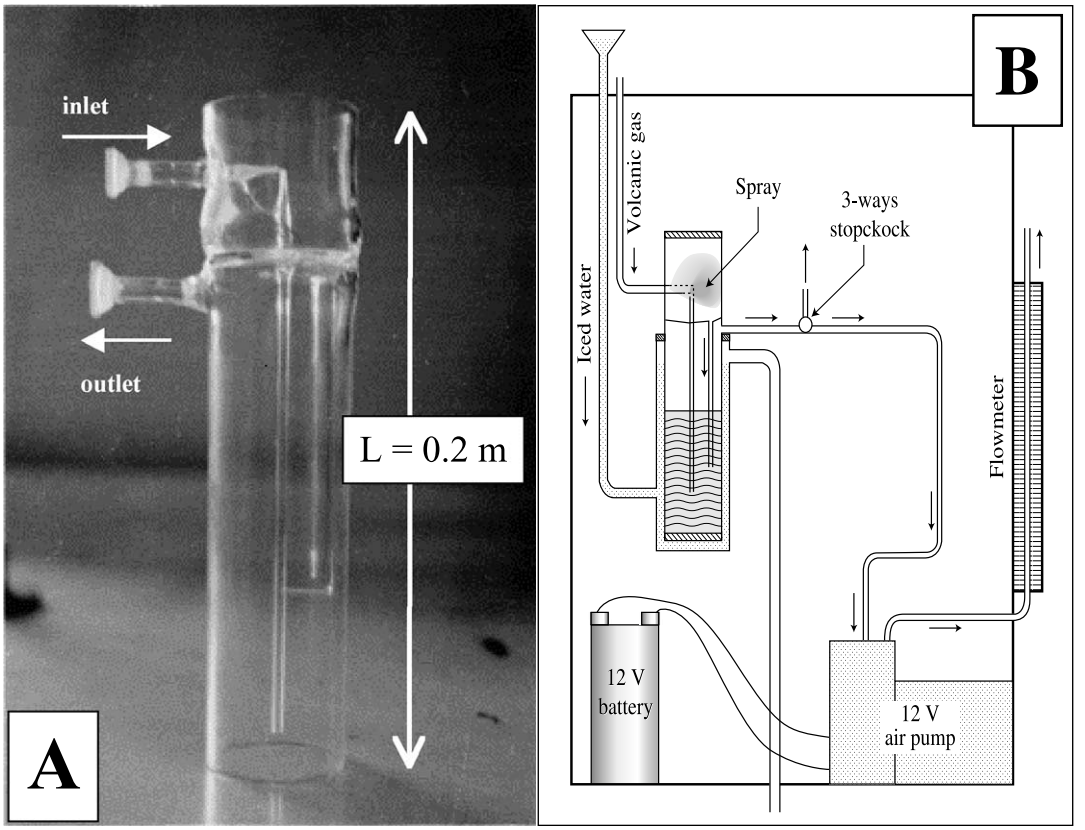

Fig. 2. VES used at Vulcano. (A) Quartz cell with the inlet system. The length of the cell is 0.2 m. (B) Schematic draft of the complete apparatus. Note the weak dimension of the device (0.43×0.33×0.3 m).

lightning of solutions to oxidise reduced S species to sulphates, and (2) gentle warming (30°C) to remove excess H_2O_2. F^-, Cl^- and SO_4^- ions are analysed by High-Pressure Liquid Chromatography (HPLC) after pH neutralisation by means of a 50WX 4–50 hydrogen ion exchange resin (DOWEX)

• *MTE*. For ICP–MS analysis, oxidised alkaline solutions are acidified with purified 14N HNO_3 down to pH = 1. ICP–MS analysis was performed on an Elan 6000 (Perkin Elmer). Concentrations were calculated by using both multi-elemental standard solutions in double-distilled HNO_3 (2%) and laboratory-made standards for Cl and Br. An internal standard (In–Re) was used to correct temporal drifts. Routine corrections for oxide and hydroxide interferences were performed using the procedure described in Aries et al. (2000).

4. Results

4.1. Acid gases

Fig. 3 displays Cl/F and Cl/SO_4 ratios for both the 2000 and 2001 sampling campaigns. In 2000 we performed an experiment placing a 2-μm silica filter in-line to observe the potential fractionation effects on major elements due to membrane filtration. Mean ratios of the bulk fluid (NaOH bottles) are displayed as diamonds and as squares for plume (VES samples) (Fig. 3).

Cl/F mean ratios (in meq/l of solution) of the 2000 and 2001 plume are 6.42 ± 1.23 and 4.98 ± 0.14, respectively. These values are close to the same ratios of F0 fumarolic gas which are 6.0 ± 0.17 and 4.31 in 2000 and 2001, respectively. Filtration does not induce significant frac-

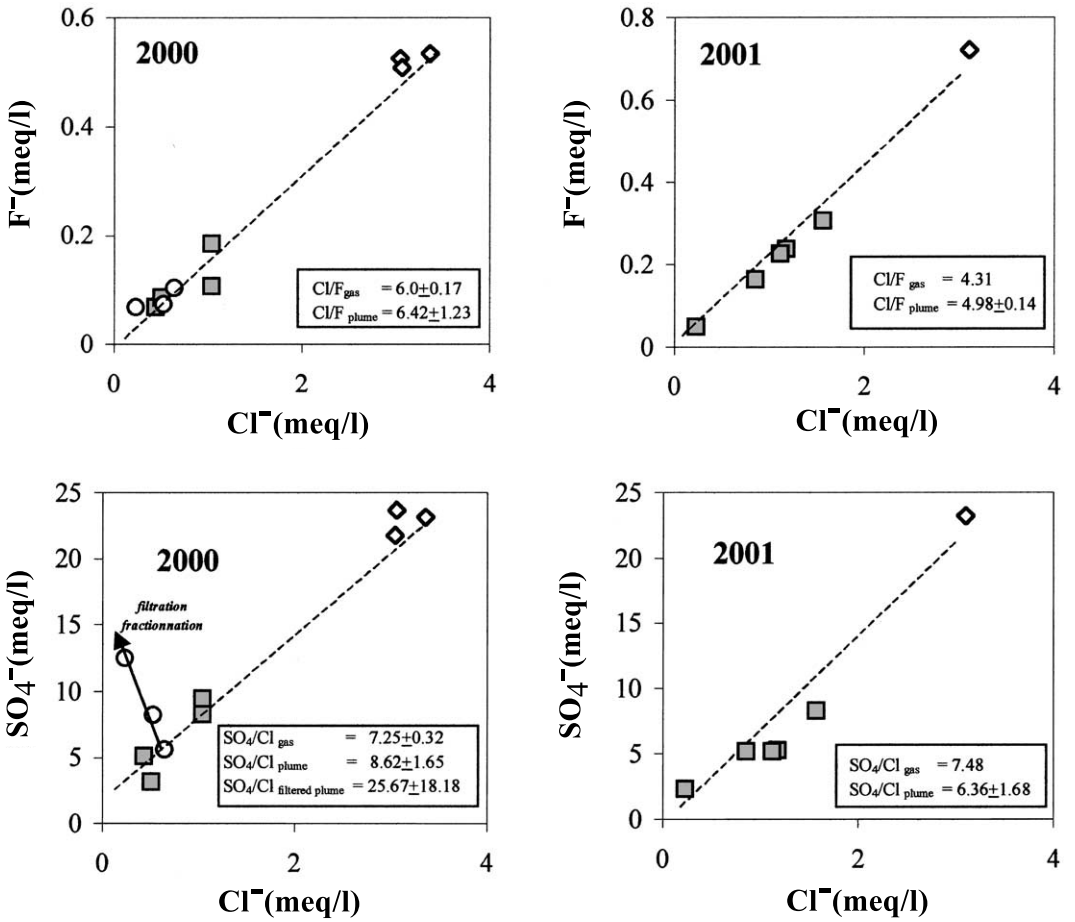

Fig. 3. Graphical representation of Stotal/Cl and F/Cl ratios in VES (plume samples displayed as grey squares) and NaOH bottles (F0 fumarole displayed as diamonds) for the 2000 and 2001 field seasons. Note the drastic fractionation of S with respect to Cl due to filtration prior sampling in VES (filtered plume samples displayed as open circles).

tionation between Cl and F (mean Cl/F ratios of 5.68 ± 1.47 and 6.42 ± 1.23 for filtered and non-filtered samples, respectively). SO_4/Cl ratios of the 2000 and 2001 plume are more scattered. They are 8.62 ± 1.65 and 6.36 ± 1.68, respectively. These ratios are also similar to fumarolic gas values (7.25 ± 0.32 and 7.48 for the 2000 and 2001 samples, respectively).

The filtration process of the plume produces a very strong fractionation effect in the S/Cl ratio. Residual solutions are highly enriched in SO_4 (mean SO_4/Cl ratios of 25.67 ± 18.18 and 8.62 ± 1.65 for filtered and non-filtered samples, respectively) with respect to chlorine. This demonstrates that filtration is not a quantitative sampling method, at least for S-bearing species. This is likely the result of S speciation in the Vulcano plume, with solid S, H_2S and SO_2 being present in the collected phase. Gaseous SO_2 (and to a lesser extent H_2S) at the filter level is not trapped, inducing a strong fractionation effect. Such an effect may also occur for many volatile trace elements. SO_4/Cl ratios of non-filtered samples appear slightly more scattered than Cl/F, especially for the 2001 samples. This is probably due to gas-particle conversion of sulphur and subsequent deposition in the fumarolic zone, in agreement with visual observations.

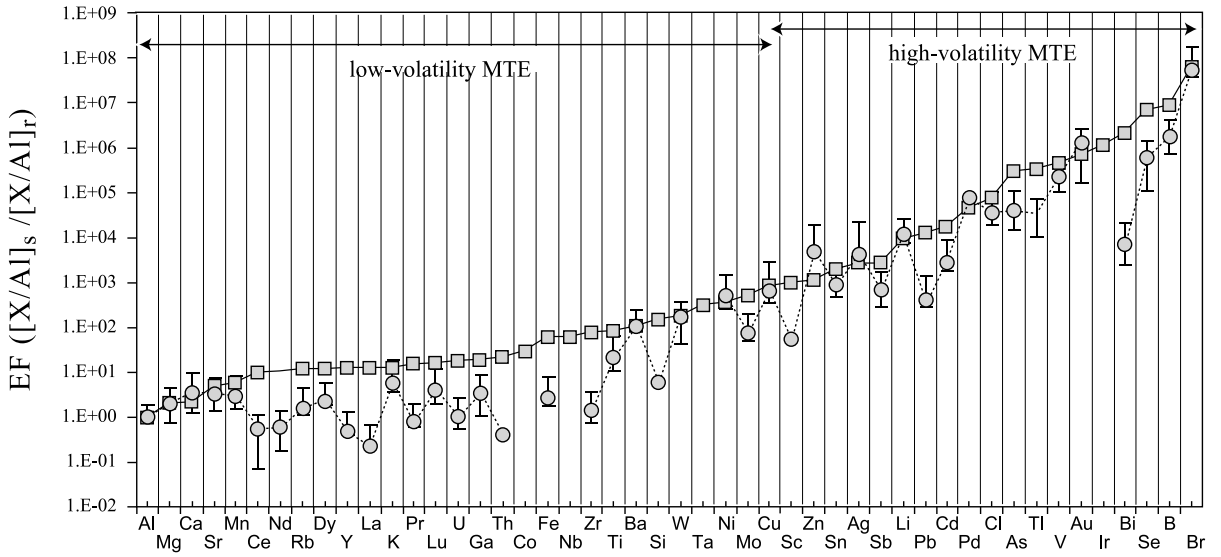

Fig. 4. Comparison of EF calculated in the fumarolic fluid (1 NH_4OH sample, plain squares) and VES samples (plain circles). Mean, maximum and minimum values are displayed for VES samples ($n = 5$).

4.2. MTE

Fig. 4 displays comparative results of fluid sampled in a NH_4OH bottle, and VES samples (5 samples). Because of both the high variability of trace elements in volcanic volatile phases and the presence of an erosive contribution due to dust contamination, their contents are often expressed as EF that are:

$$EF_X = [(X/Al)_s/(X/Al)_r] \quad (1)$$

for an element X, s and r being the volcanic sample and the rock, respectively (Quisefit et al., 1989). Al is chosen because of its refractory behaviour in volcanic fluids. Ti or Zr may also be chosen, but this is likely of little effect for global results. EF were calculated by using a chemical analysis of Vulcano rocks (1988–1990 trachyte; Clochiatti et al., 1994). When elements were lacking in the reference rock of Clochiatti et al. (1994), we arbitrary selected trace contents from AGV-1 which is a typical andesite used as an international standard (Govindaraju, 1989). Because our current purpose is only to compare trace patterns between fumarolic fluids and the related plume, concentrations of trace elements in the reference rock are not of major importance. Fumarolic fluid data are displayed in Fig. 4 with the elements arranged following EF values. Data are consistent with the level of volatility of elements in high temperature volcanic medium deduced from studies of silica tube sublimates (Quisefit et al., 1989; Symonds et al., 1987, 1994). Mean EF values of the 5 VES samples are displayed as circles on Fig. 4 together with minimum and maximum values.

The precise geochemical behaviour of elements at the volcano–atmosphere interface is beyond the scope of this paper. However, some main features should be noted:

(1) The general trend (EF as a function of element) of the fumarolic fluid is globally conserved in plume samples.

(2) EF are equal to or significantly lower in plume samples than in the fluid, except for Zn which displays a slightly higher EF in the plume with respect to the gas phase.

(3) Low volatility elements (from Al to Sc on Fig. 4) show almost systematically lower EF in the plume than in the gas phase. This may be due to scavenging of these elements from the fu-

marolic fluid by adsorption processes on mineral surfaces available in vents.

(4) High volatility elements (from Zn to Br on Fig. 4) are closer to the gas EF values. Within volatile elements, one can note peculiar compositions of the plume for elements Pb, Cd, Bi, and, to a lesser extent, Se. These elements occur in known sulphosalts in Vulcano sublimates (Mozgova et al., 1985; Ferrara et al., 1995). Moreover, these sulfosalts were shown to be highly enriched in selenium with Se contents up to 5.25 wt% in pure phases (Mozgova et al., 1985). If these trends were confirmed, they may indicate that surface condensation of incrustations may modulate the overall budget of MTE elements to the atmosphere. On the other hand, heterogeneity of the plume may also be significant. Lower temperature areas of the F0 fissure may also contribute the plume in proportions varying according to wind direction and speed.

It must be noted that for some elements (e.g. Ce, Au, Ag), concentrations display a large variability (up to ± 2 log units). This is likely due to the very low concentrations in solution for these elements, along with heterogeneities in plume conditions.

5. Perspectives in volcanology

The main advantages of VES are: (1) only one sample allows the determination of all compounds of interest in plumes (acid gases, MTE), (2) NH_4OH solutions are very simple to use and need only classical and easily available analytical techniques (HPLC, ICP–MS or AAS) for elemental analysis, and (3) the packaging of VES is adapted for rough volcanological conditions. Such a device may be used for the following purposes: (1) continuous monitoring of plumes when fumaroles are not accessible, (2) checking the reliability of remote Fourier Transformed Infrared Spectrometry (FTIR) measurements which are starting to be extensively used for general monitoring purposes, (3) supplying reliable data for volatile budgets at plume-emitting volcanoes, and (4) studying the mean isotopic signature of degassing volcanoes for Cl, Cu, Zn, and Se.

6. Conclusion

Volcanic aerosols were easily and reliably sampled with a new device (VES) at Vulcano, Italy. This apparatus allows quantitative sampling of all plume components (gas, solid, liquid) and subsequent simple analysis using ultrapure NH_4OH solutions and chemical techniques (HPLC, MC ICP–MS) which are widely available. The chemistry of the plume sampled by VES has been compared to the original gas phase in a controlled fumarolic context (F0 fumarole, Vulcano). S/Cl and F/Cl ratios are similar in plume and gas samples, showing the efficiency of the device for major acid gases. EF for metallic trace elements follow the general trend of elements in the gas phase, which is mainly related to volatility. This confirms that the apparatus is also reliable for sampling MTE. Some differences in EF between gas and plume are interpreted in terms of fractionation of the gas phase within the fumarolic vent.

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References

Aries, S., Valladon, M., Polve, M., Dupré, B., 2000. A routine method for oxide and hydroxide interference corrections in ICP–MS chemical analysis of environmental and geologic samples. Geostand. Newslett. 24, 19–31.

Clochiatti, R., Del Moro, A., Gioncada, A., Joron, J.L., Mosbah, M., Pinarelli, L., Sbrana, A., 1994. Assessment of a

shallow magmatic system: the 1888–90 eruption, Vulcano Island, Italy. Bull. Volcanol. 56, 466–486.

Faivre-Pierret, R., 1983. SO_2, HCl and HF detection and dosing in the volcanic gas phase. In: Tazieff, Sabroux (Eds.), Forecasting Volcanic Events. Elsevier, pp. 399–408.

Ferrara, G., Garavelli, A., Pinarelli, L., Vurro, F., 1995. Lead isotope composition of the sublimates from the fumaroles of Vulcano (Aeolian Islands, Italy): inference on the deep fluid circulation. Bull. Volcanol. 56, 621–625.

Finnegan, D.L., Kotra, J.P., Hermann, D.M., Zoller, W.H., 1989. The use of ^{7}LiOH-impregnated filters for the collection of acidic gases and analysis by instrumental neutron activation analysis. Bull. Volcanol. 51, 83–87.

Fischer, T.P., Arehart, G.B., Sturchio, N.C., Williams, S.N., 1996. The relationship between fumarole gas composition and eruptive activity at Galeras Volcano, Columbia. Geology 24, 531–534.

Fischer, T.P., Shuttleworth, S., O'Day, P.A., 1998. Determination of trace and platinium-group elements in high ionic-strength volcanic fluids by sector-field inductively coupled plasma mass spectrometry (ICP–MS). Ar. J. Anal. Chem. 362, 457–464.

Giggenbach, W., 1975. A simple method for the collection and analysis of volcanic gas samples. Bull. Volcanol. 39, 132–145.

Giggenbach, W., Matsuo, S., 1991. Evaluation of results from second and third IAVCEI field workshops on volcanic gases, Mt Usu, Japan, and White Island, New Zealand. App. Geochem. 6, 125–141.

Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T., Johnson, L., 1998. Geochemical surveillance of magmatic volatiles at Popocatepetl volcano, Mexico. G.S.A. Bull. 110, 695–710.

Govindaraju, K,., 1989. Compilation of working values and sample desciption for 272 geostandards. Geostand. Newslett. 13, 1–113.

Greenland, L.P., Aruscavage, P., 1986. Volcanic emission of Se, Te, and As from Kilauea volcano, Hawaii. J. Volcanol. Geotherm. Res. 27, 195–201.

Italiano, F., Nuccio, P.M., Pecoraino, G., Valenza, M., 1991. Monitoring of acid gases at the crater of Vulcano using the method of alkaline traps. Acta Vulcanol. 1, 249–254.

Italiano, F., Pecoraino, G., 1998. Steam output from fumaroles of an active volcano: tectonic and magmatic–hydrothermal controls on the degassing system at Vulcano (Aeolian Arc). J. Geophys. Res. 103, 29829–29842.

Mosher, B.W., Duce, R.A., 1985. Vapour phase and particulate selenium in the marine atmosphere. J. Geophys. Res. 88, 6761–6768.

Mozgova, N., Kuzmina, O., Organova, N., Laputina, I., 1985. New data on sulfosalts assemblages at Vulcano (Italy). Rend. Soc. Ital. Miner. Petrol. 40, 277–283.

Quisefit, J.P., Toutain, J.P., Bergametti, G., Javoy, M., Cheynet, B., Person, A., 1989. Evolution versus cooling of gaseous volcanic emissions from Momotombo volcano, Nicaragua: thermochemical model and observations. Geochim. Cosmochim. Acta 53, 2591–2608.

Schevenell, L., Goff, F., 2000. Temporal geochemical variations in volatile emissions from Mount St Helens, USA, 1980–1994. J. Volcanol. Geotherm. Res. 99, 123–138.

Sortino, F., Inguaggiato, S., Francofonte, S., 1991. Determination of HF, HCl and total sulfur in fumarolic fluids by ion chromatography. Acta Vulanol. 1, 89–94.

Sortino, F., Toutain, J.P., Nonell, A., Munoz, M., in prep. A new and accurate method for sampling and analyzing trace metals in high temperature volcanic gases.

Symonds, R.B., Rose, W.I., Bluth, G.J.S., Gerlach, T.M., 1994. Volcanic gas studies: methods, results and applications. In: Reviews of Mineralogy, Volatiles in Magmas, pp. 1–66.

Symonds, R.B., Rose, W.I., Reed, M.H., Lichte, F.E., Finnegan, D.L., 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi volcano, Indonesia. Geochim. Cosmochim. Acta 51, 2083–2101.

Toutain, J.P., Aloupogiannis, P., Delorme, H., Person, A., Blanc, P., Robaye, G., 1990. Vapor deposition of trace elements from degassed basaltic lava, Piton de la Fournaise volcano, Reunion Island. J. Volcanol. Geotherm. Res. 40, 257–268.

Toutain, J.P., Quisefit, J.P., Briole, P., Aloupogiannis, P., Robaye, G., Blanc, P., 1995. Mineralogy and chemistry of solid aerosols emitted from Mount Etna. Geochem. J. 29, 163–173.

Vié le Sage, R., 1983. Chemistry of the volcanic aerosol. In: Tazieff, H., Sabroux, J.C. (Eds.), Forecasting Volcanic Events. Elsevier, Amsterdam, pp. 445–474.

Chapitre 2 :
Utilisation des ampoules à ammoniac sous vide pour l'échantillonnage des gaz fumeroliens.

II-1 VERSION ABREGEE DE L'ARTICLE EN FRANÇAIS

II-1-1 Introduction

Les gaz fumeroliens sont classiquement échantillonnés par la méthode des ampoules NaOH sous vide artificiel [*Giggenbach*, 1975]. Ces échantillons permettent d'effectuer des mesures précises et représentatives des teneurs en gaz acides (S_t, HCl, HF, CO_2) et incondensables (He, H_2, CO, CH_4…) contenus dans ces émanations gazeuses. Cependant, cette méthode d'échantillonnage implique la dilution de l'échantillon de gaz dans une solution concentrée de soude (NaOH, 4N), qui rend difficile l'analyse des teneurs en éléments en trace par des techniques analytiques conventionnelles (ICP-MS quadrupolaire). Pour déterminer ces teneurs, l'échantillonnage par ampoules à soude est souvent couplé à un échantillonnage du gaz par condensats acides [*Chevrier and Le Guern*, 1982]. Par opposition aux ampoules à soudes, où l'échantillonnage se fait en système fermé, l'échantillonnage par la méthode des condensats acides requiers l'utilisation d'un système de pompage en relation directe avec l'atmosphère (système ouvert). L'utilisation d'un tel dispositif est susceptible de nuire à la représentativité de l'échantillonnage des gaz fumeroliens. En effet, certains des éléments les plus volatils peuvent êtres évacués vers l'atmosphère via le système de pompage. De plus, une précipitation de soufre est systématiquement observée dans ces phases condensées. Ce soufre est susceptible de piéger une partie des éléments en trace présents dans l'échantillon [*Fischer et al.*, 1998b].

Dans ce travail, nous proposons une nouvelle méthode de prélèvement des gaz fumeroliens qui permet d'accéder à l'aide d'un seul échantillonnage à la composition globale de ces émanations, de manière représentative, et par l'utilisation de méthodes analytiques largement répandues. Cette méthode repose sur le même principe que les ampoules à soude (prélèvement en système fermé), mais en utilisant des solutions d'ammoniac ultrapures 4N en substitution de la soude 4N généralement utilisée. L'échantillon ainsi obtenu présente tous les avantages des ampoules à soude classiques (pas de pertes à l'atmosphère ou de précipitations indésirables de soufre) et permet d'accéder à la composition en éléments trace de l'échantillon, les solutions NH_4OH étant aisément analysables par ICP-MS quadrupolaire.

. Échantillonnage

Dans le but de valider ce nouveau mode de prélèvement des gaz fumeroliens, plusieurs campagnes d'échantillonnage ont été effectuées entre 2001 et 2002 sur les volcans Mérapi

(Indonésie) et Vulcano (Italie). Durant ces campagnes, plusieurs fumerolles ont été échantillonnées à l'aide des 3 méthodes décrites ci-dessus (Table 1, page 63). Les résultats analytiques obtenus dans les échantillons NH_4OH ont ainsi pu êtres validés par comparaison aux modes de prélèvements de référence (ampoules NaOH et condensats acides).

II-1-2 Résultats

. *Gaz acides*

Les résultats obtenus par HPLC sur les concentrations SO_4, Cl, F sont présentés dans la Table 3, page 64 et dans la Figure 1 page 65. Les résultats de reproductibilité analytique (Table 3) montrent que la précision des mesures SO_4, Cl, F obtenue dans les échantillons NH_4OH est comparable à celle obtenue dans les ampoules à soude. La comparaison des rapports SO_4/Cl (Fig.1, A) et F/Cl (Fig.1 B et C) entre les ampoules NH_4OH, NaOH et condensats acides sont en bon accord, ce qui confirme la validité de l'échantillonnage des gaz acides par les ampoules NH_4OH.

.*CO_2 et gaz incondensables*

Les résultats d'analyse CO_2 présentés dans la Table 4 (page 64) montrent que la précision des mesures CO_2 est comparable entre les ampoules NaOH et NH_4OH. La comparaison des deux techniques d'échantillonnage sur une même fumerolle donne des résultats similaires. Les résultats de la Table 5 (page 64) montrent que les gaz incondensables peuvent êtres analysés précisément dans les ampoules NH_4OH. L'ensemble de ces résultats confirme la fiabilité des ampoules NH_4OH pour la détermination de teneurs en CO_2 et gaz incondensables.

. *Éléments en trace*

Des standards multi-élémentaires ont été analysés dans une matrice de référence HNO_3 2% et dans une matrice 0.3N NH_4OH/0.6N HNO_3 (correspondant aux matrices des échantillons NH_4OH analysés par ICP-MS) dans le but de vérifier la fiabilité de l'utilisation des solutions ammoniac pour l'analyse des élément en trace. La linéarité de réponse entre les deux matrices (Fig.2, page 66) montre que les solutions NH_4OH sont parfaitement adaptées à des analyses multi-élémentaires par ICP-MS quadrupolaire et ne requièrent pas l'utilisation de standards spécifiques. Une procédure simple de correction des interférences isobariques S, Cl, pouvant s'appliquer aussi bien aux condensats acides qu'aux ampoules NH_4OH est aussi proposée (Figure 3, page 67).

La figure 4 (page 68) montre que les éléments les plus volatils sont majoritairement enrichis (80% des cas) dans les échantillons NH_4OH par rapport aux condensats acides correspondants. Ceci confirme les pertes en éléments volatils liées au système d'aspiration et/ou au piégeage d'éléments en trace par les précipitations de S solide lors des prélèvements par condenats acides. Ce résultat démontre la meilleure représentativité des prélèvements des éléments volatils par les ampoules NH_4OH. Cependant, 20% des résultats obtenus montrent que certains éléments (Pb, Bi, Tl et Cd) peuvent êtres appauvris dans l'ampoule NH_4OH par rapport au condensat acide correspondant. Ce phénomène est attribué à une aspiration insuffisante du gaz dans l'ampoule NH_4OH due à un vide de mauvaise qualité, ce qui entraîne la précipitation de sublimés riches en Pb, Bi, Tl et Cd avant l'entrée du gaz dans l'ampoule.

II-1-3 Conclusion

L'ensemble des tests et comparaisons réalisés dans ce travail ont permis de démontrer l'efficacité des prélèvements des gaz fumeroliens par l'utilisation des ampoules à ammoniac sous vide artificiel.

Ce seul mode de prélèvement permet d'accéder de manière représentative à la composition en gaz acides (St, HCl, HF, CO_2), incondensables (He, H_2, CO, CH_4) et en éléments trace des gaz fumeroliens, en utilisant des techniques analytiques largement répendues (HPLC, GC, titration, ICP-MS quadrupolaire). Une attention toute particulière doit cependant être apportée à la qualité du vide dans l'ampoule pour éviter les précipitations indésirables de sublimés pendant l'échantillonnage.

II-2 GIGGENBACH'S 1975 REVISITED : USING AMMONIAC TO SAMPLE VOLCANIC GASES

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GIGGENBACH'S 1975 REVISITED: USING AMMONIAC TO SAMPLE VOLCANIC GASES

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ABSTRACT

A new method using ammonia solutions in pre-evacuated quartz bottles has been experimented for volcanic gas sampling and analysing. Various tests (reproducibility, variability and comparison with known methods such as NaOH pre-evacuated bottles and acid condensates) have been performed to check for their efficiency. By using ammonia solutions, acid gases (St, HCl, HF), carbon dioxide, incondensable gases (N_2, Ar, ...) and metallic trace elements (MTE) can be measured with standard methods (HPLC, GC, titrimetry, ICP-MS).

Results show that acid gases, CO_2 and incondensable gases are sampled and analyzed with similar efficiency in NH_4OH bottles than by using the known and accurate NaOH method. Moreover, a key point is that NH_4OH solutions, after undergoing adequate processing (oxidation and acidification) allow also precise MTE measurements by using standard ICP-MS methods. Such MTE measurements appear much more reliable than those performed on acid condensates.

Pre-evacuated ammonia bottles appear therefore as an optimum tool to collect volcanic gases and to obtain their complete chemical composition.

1. INTRODUCTION

Volcanic gases are complex mixtures of H, C, O, S, minor acid gases (HCl, HF, HBr), trace gases (He, Ne, ...) and metallic trace elements (named MTE in this work : Pb, Se, Cd, Bi …). A very reliable method for sampling such mixtures was proposed by Giggenbach (1975). It uses NaOH as a reactant in empty bottles, and is now by far the most widely used method for the detection of all the above-mentioned species except MTE (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). These last elements are commonly sampled by collecting the so-called "acid condensates", in spite of evident sampling bias already evidenced (Bichler and Sortino, 1995; Toutain et al., 2000).

However, the availability of high precision data for MTE concentrations in magmatic fluids is highly needed to constrain the dynamics of cooling (Symonds et al., 1987; Quisefit et al., 1988) and elemental flux calculations. Moreover, MTE have been shown to potentially mark fluctuations of magmatic activity (Quisefit et al., 1988; Toutain et al., 1995; Goff et al., 1998; Schevenell and Goff, 2000), making them potential tracers for monitoring of volcanic activity.

Herein, we propose another simple and accurate method similar to that of Giggenbach (1975) but using NH_4OH reactant in place of NaOH. By using such a method, the complete and quantitative analysis of all species (acid gases, CO_2, incondensable gases, MTE) is easily performed. In this paper, we will validate the method by 1) establishing the good reproducibility of each measurement on NH_4OH bottles and 2) comparing chemical compositions obtained on NaOH, water condensates and NH_4OH bottles collected simultaneously. We believe that this method is reliable for routine measurements in most observatory conditions as it uses classical and widespread analytical techniques (High Pressure Liquid Chromatography, Gas Chromatography, titrimetry, ICP-MS). Volcanic fluids used for this comparison are from Vulcano (Aeolian Islands, Italy) and Merapi (Java, Indonesia).

2. PREVIOUS METHODS: SODA BOTTLE AND ACID CONDENSATES

Acid condensates: an open system.

Most of geochemists dealing with MTE in fumarolic gases have used acid condensates. The usual technique to obtain such samples is either the naturally cooling of the high temperature gas phase in a collecting bottle (Gemmell, 1987) or the forced cooling of the gas mixture in a Pyrex device using a refrigerant such as ether or acetone to force the condensation of the mixture (Quisefit et al., 1989). These two methods can be considered as "open systems" because non-condensable species (CO_2, O_2, N_2, Ar, He, H_2, …) have to be released to the atmosphere. Moreover, as the natural flow available at most high-temperature fumarolic vents is low, it has to be forced by using either manual

or electric pumping to allow a significant volume of fluid to be collected. The solution therefore obtained is supposed to contain the water, acid gases (SO_2 as SO_4^{--}+SO_3^-, HCl and HF as Cl^- and F^-) and MTE, which are thought to be dissolved in the solution. Such solutions display usually very low pH values (often close to 0) even if condensates of low temperature geothermal fluids may display near-neutral pH values. Such acid condensates have 2 main advantages: significant volumes are easily sampled, and their bulk chemistry supplies analytical matrix well adapted to the usual instrumental conditions for MTE analysis.

These solutions, however, have some characteristics that are not discussed in the literature (except Fischer et al., 1998):

- a white-to-pale yellow precipitate often appears within the solution quickly after collection. This is the result of S precipitation, which acts usually with a high kinetic. Recent results on acid condensates from Kudryavy volcano (Fischer et al., 1998) show that such precipitates are potentially MTE-rich (up to 33, 8 and 5 ppm for Pb, Bi and Rh, respectively). S precipitation may also remove trace elements showing high chemical affinity with S, such as Se, Te, As (not analysed in Fischer et al., 1998), in accord with the chemical composition of solid sulphur deposited around low temperature fumarolic vents (Greenland and Aruscavage, 1987; Toutain, 1987).
- these solid phases remain floating in solution, but are also adsorbed on the inner face of collecting flasks making S-budgets poorly constrained.
- during sampling, the collected solution may remain in the device at relatively high temperature (typically 30-50 °C, depending on gas temperature, input flow and capacity of the device) whereas the atmosphere above the solution is depressed as the result of pumping. This may lead to revolatilization of some MTE, the level of which likely increases with the volatility of the element. Moreover, incondensable gases (CO_2, He, N_2, CO ...) are not trapped by the system and may contribute also to MTE transport. Bichler et al. (1995) have shown that appreciable amounts of MTE were detected at the outlet of the condensate collector and concluded to their volatile transport from the solution as non-condensable species.

All these factors probably arise in the collection of solutions depleted in the most volatile MTE, which are also those of the highest volcanological interest (As, Se, Te, Tl, Pb, Bi, Hg, Cd, Zn, Sb). Acid condensates therefore display both a very high variability and possibly non-reliable MTE concentrations.

Soda bottles: a close system.

Giggenbach (1975) described a powerful method for sampling volcanic gases by using bottles under vacuum and partially filled with 4N NaOH. This procedure allows the dissolution of most of the compounds (H_2O, CO_2, SO_2, H_2S, HCl, HF, MTE), whereas non-condensable species (H_2, N2, Ar, O_2, He, CO) remain in the gas phase within the bottle. It enables considerable enrichment of the solution in trace species and operates in close system, without any leak to the atmosphere. Such soda solutions were recently experimented for MTE analyses in Vulcano and Kudryavy fumarolic fluids (Bichler, 1997; Fischer et al., 1998). They may appear as suitable for this objective, but due to the Na-bearing matrix, high dilution of the solutions (typically 1:250) and specific apparatus (high-sensitivity sector-field ICP-MS or INAA) where needed, that makes this procedure rather difficult for multi-elementary and routine measurements. Moreover, the use of soda solutions prohibits analysis of Na^+ ions in solution, which may be good indicators in hydrothermally derived fumarolic systems. There is therefore a need for a reliable sampling method and simple analytical procedures allowing both MTE and major gases routine precise measurements on a single sample.

Our objective was to setup a complete method allowing both the easy sampling and the routine multi-elementary analysis of major species, minor species and MTE on a single sample. Bichler and Sortino (1994, 1995, 1996, 1997, 1999) investigated the potentialities of various solutions such as Tris(hydroxymethyl)aminomethane**,** NaOH and NH_4OH for trapping and analysing MTE in fumarolic fluids. They concluded by using precise INAA measurements that NH_4OH was the best trapping solution owing to both its high level of purity and its applicability to a large range of elements (Bichler et al. 1999). However, because INAA needs both heavy installations and at least 2 months delay for radioactive decay of Na, it does not appear as a convenient and largely available method for routine analysis. Therefore, we selected ICP-MS for MTE measurements. To establish the reliability of this new method, volcanic gases trapped in NH_4OH solutions are compared for CO_2, acid gases, incondensable gases and MTE concentrations with samples collected simultaneously by using NaOH bottles or gas condensates.

3. SAMPLING

3.1 Sampling sites

Merapi (Indonesia) and Vulcano (Iatly) were chosen for their easy access to fumarolic fluids with a wide range of outlet temperatures.

- *Merapi* in Central Java is an andesitic, very active dome-forming and explosive volcano. The activity of Merapi is characterised by repeated episodes of dome growth and collapses (Voight et

al., 2000). Merapi emits high temperature gases (up to 911 °C in 2000) that can be collected in 2 fumarolic fields, namely Gendol and Woro, the former being systematically hotter than the latter.
- *Vulcano* is the southernmost island of a volcanic arc named Aeolian Archipelago in Southern Italy. Its active cone (La Fossa) is 391 m a.s.l., and has erupted for the last time in 1888-1890 (Keller, 1980) with phreatomagmatic to magmatic episodes producing viscous trachytic to rhyolitic pyroclasts. Since this event, and apart constant and low temperature hydrothermal manifestations at sea bottom, the activity is limited to fumarolic manifestations at La Fossa crater with strong temporal fluctuations of flow rates and gas temperatures.

3.2 Gas collection

Table 1 displays the different samples together with collection parameters. Gas vents were selected at Merapi and Vulcano on the basis of their outlet temperature in order to cover a large range of temperatures. Quartz "Dewar" tubes 0.7 m long and 1 cm diameter were used for collecting gases. Ash particles transported by the gas flow were blocked for most of them into the tube by inner prominences.

NH_4OH bottles

They are made of fused quartz to reduce the level of contamination by impurities commonly contained in Pyrex and the adsorption on the inner walls of bottles and are equipped with a Teflon stopcock. To obtain low blank values, quartz flasks were successively washed with 30% ultra-pure HNO_3 and 4N ultra-pure NH_4OH. The bottles were filled with 100 cc of 4N Merck ultra-pure NH_4OH and putted under vacuum. By using 600 ml bottles, that is 2-3 times the volume of NaOH bottles used commonly, we collect typically 50 to 100 g of volcanic gas. The weights of solutions are measured prior and after collecting to determine H_2O contents. Solutions are stored in PP bottles cleaned with double distilled HNO_3.

NaOH bottles

250 cc Pyrex bottles equipped with a Teflon stopcock are partially filled with 50-70 ml of 4N NaOH for the second set of samples. They are analysed for condensable and non-condensable species following the classical and reliable method already described by Giggenbach (1975) and Sortino et al. (1991).

Acid condensates

The third set of samples is made of "acid condensates". They are obtained by using a field condensor refrigerated with ether (boiling point: 34 °C). Slow manual pumping allows a continuous flow of gases through the device. Solutions are stored in pre-washed PP bottles.

4. EXPERIMENTAL

Ultrapure water is obtained from MilliQ™ (Millipore). HF, H_2O_2 and NaOH are "Suprapur" grade (Merck). Ultrapure HNO_3 is obtained in the laboratory by double sub-boiling in a quartz apparatus. For acid condensates, fractions of solutions were filtered on 0.45 µm cellulose acetate filters (Millipore) prior to major element analyses whereas centrifugation in PP tubes, which induces very low MTE blanks was performed before MTE analyses of both acid condensates and NH_4OH samples. MTE were analysed with a Elan 6000 ICP-MS (Perkin-Elmer), HPLC was performed with a DX300 (Dionex) and gas chromatography with a Perkin-Elmer using a double detector (HWD, FID). The general analytical procedures are summarized in table 2.

4.1. SULFUR AND HALOGENS

Procedure

Cl^-, F^- and total sulphur as SO_4^{--} ions are measured by ion chromatography (Sortino et al., 1991). Acid condensates are filtered and analysed following adequate dilution. Both NH_4OH and NaOH trapping solutions follow a different processing due their complex matrix. The exact procedure is displayed in Table 2 and can be generalized as follows:

1) Dilution of the totality of the NaOH and NH_4OH solutions to fixed volumes (usually 250 cc) in ultra-pure H_2O

2) Oxydation of the diluted NaOH solution (20 cc) or of the bulk NH_4OH solution (20 cc) with 3 cc of 35% ultra-pure H_2O_2 for a 30 min duration to oxidize reduced sulphur to sulphate.

3) Warming (20 – 40 min) of oxidized solutions to remove excess H_20_2 and dilution up to 50 cc with ultra-pure H_2O

4) Neutralisation of 3 cc of the diluted solutions by ion (H^+) exchange resin (DOWEX 50WX4-50) until pH ~ 7 is reached.

5) Dilution of both solutions (with various dilution factors, depending on the respective concentrations of anions and the calibration ranges chosen).

The reproducibility of the method has been checked by performing 9 replicates (preparation +analysis) on a single sample (V3) and a high level of reproducibility was obtained for Cl, SO_4 and F in NH_4OH solutions (Tab. 3). These results are very similar to statistics performed by Sortino (1991) on NaOH efficiency for acid gases trapping.

St/Cl ratios

These ratios are key indicators of the origin of gases and of volcanic activity. Comparisons of these ratios measured in NH_4OH, NaOH and acid condensates are displayed on figure 1 (A, B, C). 6 samples allow the comparison of SO_4/Cl ratios (Fig. 1-A) between NaOH and NH_4OH samples. All are close to the slope of value 1, except sample M2, which shows a ratio about twice in the soda bottle with respect to ammonia bottle. This exception has been confirmed by repeated analysis, and is probably due to an artefact during sampling. Except M2 sample, the general good agreement shows that the oxidation of sulphur species to sulphate ions is complete in both solutions and that both the sampling method and the general chemical procedure using ammonia do not fractionate S/Cl ratios.

F/Cl ratios

Numerous samples collected from identical fumaroles during IAVCEI workshops (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001) often display significant fractionation of HCl and HF in samples collected in NaOH bottles. This was interpreted as the result of the high solubility of these compounds that are likely to be fractionated into a liquid phase resulting from possible vapour loss during sampling. Figure 1-B and C does not suggest such effects to occur, with F/Cl ratios being almost similar in soda, ammonia and acid condensates samples. One can remark that F/Cl are more scattered between soda and ammonia bottles, this is probably because these solutions have undergone high dilutions in order to avoid HPLC columns saturation to occur, the precision on the measurement of F contents is therefore seriously lowered with respect to other elements.

4.2. CO_2 DETERMINATIONS

The procedure for NaOH solutions (titration of the basic solution by HCl) is described by Giggenbach (1975). A specific procedure has to be used for NH_4OH bottles to avoid pH decrease during warming of solutions (the pH decrease is due to NH_3 or N_2 loss under warming and leads to CO_2 degassing): 3 cc of bulk NH_4OH are mixed with 0.5 cc H_2O_2 and 1 cc of NaOH to fix a pH of about 13. Solutions are therefore warmed for excess H_2O_2 loss. Both oxidized solutions (NaOH and

NH_4OH) are acidified down to pH = 8.1 by using 1N HCl and therefore down to pH = 4.2 by using 0.1N HCl.

The validity of the method is first established first by comparing the repeatability of the sample preparation and CO_2 analysis using both NaOH and NH_4OH flasks (Tab. 4, upper part). CO_2 concentrations measured in the initial solutions are displayed with mean values together with 1 σ standard deviation. As only carbonate species were measured, values are displayed in mg/l of CO_2 instead of μmol/mol. Low and similar relative standard deviation in the range 1-2 % for both methods evidence that processing ammonia solution does not affect the reliability of the measurement with respect to soda solution.

The second step to validate the method is to compare CO_2 concentrations in NaOH and NH_4OH flasks sampled the same day and at the same fumarole. This was done for two sets of samples, collected at the Fossa crater and at the beach, each set being constituted by 1 to 9 replicated samples (Tab. 4, lower part).

Results are in good agreement (discrepancy of 6.4 and 9 % between soda and ammonia bottles for V3 and V4 sample sets, respectively). This evidences that no CO_2 loss occurs in ammonia solution upon warming due to soda addition, and that carbon speciation in both solution is similar.

4.3. NON CONDENSIBLE GAS

Non condensable species (N_2, Ar, O_2, H_2, CO, He, CH_4) are classically analysed in the gas phase remaining over the solution in NaOH flasks (Giggenbach, 1975; Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). In this work, analyses are performed by gas chromatography (Perkin Elmer) with a double detector (HWD, FID) with precisions below 5%.

The reliability of NH_4OH solution with respect to these species has been checked by analysing 8 NH_4OH samples (V3 sample set) collected the same day at the same site (fumarole F0, 12/04/2002). Analytical results with mean values together with one sigma (1 σ) standard deviation are shown on Table 5 in mm/mol of total gas. Standard deviations are in the range 4 - 12 % from CO to CH_4. The highest standard deviation concern trace elements (He and CH_4) and are close to standard deviation measured in soda bottles. The reasonable level of standard deviation calculated for ammonia bottles show that they are suitable for incondensable gas analyses.

4.4. MTE ANALYSIS

As mentioned above, we selected ICP-MS for MTE measurements, for its low detection limit, wide linear dynamic range, multi-element capabilities and high sample throughput, with minor sample preparation, making it usable for routine measurements.

Sample preparation for ICP-MS analysis

Parts of the NH4OH and gas condensates samples were centrifuged in double distilled HNO_3 pre-washed PP tubes (30ml). This procedure (table 2) allows the separation of sulphur precipitates and ashes from the aqueous fraction with low blanks. Aliquots of NH_4OH samples were treated with 0.5ml of ultrapure H_2O_2 to oxidize sulphur species in solution, which might precipitate as solid S during acidification. Samples were then diluted and acidified with double-distilled HNO_3 down to total dissolved solids (TDS) < 1 g/l. Maximum NH_4OH concentrations obtained in the analysed solutions was 0.3N whereas HNO_3 concentration was kept constant at 0.6N. Acid condensates were diluted with double-distilled HNO_3 2% down to total dissolved solids (TDS) < 1 g/l. An internal standard (In-Re) was added in all analysed solutions to correct for temporal drift. All preparations and analyses were replicated twice. Accuracy and precision of the measurements were controlled by analysing SLRS-4 and SRM 1640 certified reference material. Analytical errors are in the range of 5-10%.

Calibration of NH_4OH matrix

Nitric matrix is usually considered as the most suitable for ICP-MS analysis, because H, N and O are already present in air entrained by the plasma. These elements contribute to the formation of a wide range of polyatomic ions, such as $^{40}Ar^{1}H$, $^{40}Ar^{14}N$, $^{40}Ar^{16}O$, $^{40}Ar^{16}O^{1}H$, the intensity of which is not increased significantly by the addition of an HNO_3 (2%) matrix (Jarvis et al., 1992). However, it was necessary to check the influence of diluted ammoniac matrix because of its higher N, H, O apportion (0.3N NH_4OH/O.6N HNO_3) as regard to classical HNO3 2% matrix. This apportion should not be a major cause of increased polyatomic interferences, but might lead to subsequent changes in the plasma equilibrium (matrix effect). In order to evaluate this effect, a comparison was established by analysing in similar conditions multi-elemental reference solutions, diluted both in 2% HNO_3 and in 0.3N NH_4OH + 0.6N HNO_3 matrix. The correlation coefficients (r^2) observed between matrix-matched calibrations curves are in the range 0.99-1 (figure 2) for all analysed isotopes. As a similar response is observed for both matrixes, the effect of diluted NH_4OH matrix can be neglected. As a consequence, matrix-matched standards are not required and a single multi-elemental standard (2% HNO_3 matrix) was used for both NH_4OH and acid condensates solutions

analysis. This evidences that NH_4OH matrix are suitable for ICP-MS calibration and measurement of numerous MTE.

Interferences due to S and Cl contents.

The presence of major elements at high concentrations (Na, S, Cl) in NaOH samples, (S, Cl) in NH_4OH samples and Cl in acid condensates samples might generate spectroscopic or non-spectroscopic interferences during ICP-MS measurements. Various methods such as dilution, precipitation, solvent extraction or online separation are proposed in literature in order to reduce or overcome these effects (Evans and Giglio, 1993; Vanhoe et al., 1994). A well-documented table of polyatomic interferences is also available (May and Wiedmayer, 1998). In the case of classical volcanic gases measurements, these interferences are not discussed except in Fischer et al., 1998. These authors used a very high dilution (1:250) in order to reduce the interferences during the analyses of NaOH samples by ICP-MS. Such a high dilution was required because of the high Total Dissolved Solids (TDS≈130g/l) obtained in samples, mainly due to the 5N NaOH matrix used. A consequence of this dilution is that most of the MTE are undetectable with conventional quadrupole based ICP-MS methods and a high sensitivity, high-resolution instrument has to be used. In the case of NH_4OH samples and acid condensates, the TDS are significantly lower (10 to 20 times) as they are mainly dependent on S and Cl contents in the samples. As a consequence, significantly lower dilutions (1:10 to 1:30) leading to a TDS<1g/l during the ICP-MS measurements, are required to minimize the effects of non-spectroscopic interferences during ICP-MS measurements. Therefore, numerous reliable MTE data are accessible without the need of high resolution and sensitivity instruments. However, a particular attention is required for some elements or isotopes, which might be affected by spectroscopic S and Cl interferences even at low concentrations. Following Vanhoe et al. (1994), the main elements concerned are V and As (affected by Cl spectral interferences) and Ti and Zn (affected by S spectral interferences). These interferences might affect both acid condensates and NH_4OH measurements. Acid condensates are more subject to Cl interferences (higher Cl content) whereas NH_4OH samples should be more affected by S interferences (higher S content). In order to check these interferences during our measurements, we used solutions of "Suprapur" grade H_2SO_4 and double distilled HCl, diluted with HNO_3 2% to get a range of standards with concentrations between 50 and 500 ppm for Cl or S. We measured the same isotopes as for the samples, and considered only the isotopes for which we got a linear correlation between interfered isotopes and interfering element (fig.3 A and B). It was then possible to correct the interferences in the samples, according to their respective S and Cl contents during the measurements.

The importance of the interference was calculated directly from the comparison between the apparent analyte concentration (induced from the known S or Cl concentrations in the sample), and the measured concentration. In order to obtain an acceptable precision on the corrected values, results were discarded if the interference was estimated higher than 10 % of the total intensity. In many cases, the ratio isotope/interference is high enough, so that the correction is not necessary.

MTE: Results.

Validating trace elements analysis methods generally needs the use of reference standards analysed together with samples in similar conditions. This procedure can't be applied to volcanic gas samples. The only way to display the efficiency of our method is to compare it with that commonly used by gas geochemists, that is the "water condensate" method and to search for systematic discrepancies that could be interpreted in terms of method respective efficiency.

Absolute MTE concentrations cannot be compared in both matrix because 1) the acid condensate does not sample gases such as H_2S and CO_2 whereas the ammonia solution does, and 2) dilution by ammonia occurs in NH_4OH bottles. Comparisons of MTE between the 2 methods therefore require to use MTE concentrations normalized to a common element that do not undergo any fractionation during sampling and processing of solutions. Only acid gases can be used for such a purpose. As total sulphur is not trapped in acid condensates and F sometimes displays both some fractionation and shows too low concentrations for accurate measurements, only Cl concentrations are usable.

Figure 4 displays the ratio of each element normalized to chlorine in ammonia with respect to the same ratio in acid condensate for samples V1, V2, M2, M4, M5, M6, M7 and M8. Such plots allow the comparison of the level of enrichment of a given element with respect to chlorine for a same fumarole, in both solutions. Elements are displayed according to their known behaviour in high temperature fumarolic environments: volatile elements are As, Cd, Zn, Sb, Pb, Tl, Bi whereas refractory elements are Mg, Si, Mn, Co, La, Ce, Pr, Nd, Th, U. Even if data are clearly scattered, some features can be outlined. Volatile elements appear quite systematically enriched in ammonia solution compared to acid condensates. Indeed, 50 normalized ratios were obtained for volatile elements and 40 of them indicate a higher or a similar enrichment in NH_4OH solutions with respect to the acid condensate. This enrichment is not T°-controlled and may be related to the fact that acid condensates sampling may lead to revolatilization of MTE or scavenging of elements in solid S, which does not occur by using the closed pre-evacuated ammonia flask. However, 10 normalised ratios indicate that NH_4OH solutions are depleted for some volatile elements (Pb, Bi, Tl, Cd) with respect to the acid condensate. Such depletions arise probably from an inefficient aspiration due to a vacuum problem. Such small aspiration certainly lead to the cooling of volcanic gas before its

entrance into the collecting flask and probably allows the formation of solid sublimates potentially Pb, Bi, Tl and Cd rich (Symonds et al., 1987) on the sampling tube walls.

The presence of refractory elements in volcanic gases arises mainly from wall rock reactions or particle contaminations (Symonds et al., 1987). Their patterns (figure 4) are mainly dependent of these variable factors but indicate that these elements are adequately trapped by NH_4OH solutions.

Elements classically used to describe and quantify degassing processes at active volcanoes are the volatile elements. These elements seem to be reliably sampled by using the ammonia bottle, which should avoid possible vapour loss of elements or undesirable scavenging during S precipitation that may occur by using the classical acid condensate method. With sufficient precaution on the vacuum quality within the collecting flask, ammonia bottles appear as the most suitable method to collect and analyse volatile MTE.

5. CONCLUSION

Ammonia solutions used in pre-evacuated quartz bottles are suitable for volcanic gas sampling and analysing. Various tests (reproducibility and comparison with known methods such as NaOH pre-evacuated bottles and acid condensates) have been performed to check for their efficiency. Standard methods (HPLC, GC, titrimetry, ICP-MS) have been shown to be adapted to analyze acid gases (St, HCl, HF), carbon dioxide, incondensable gases (He, Ar, ...) and MTE in such matrix.

CO_2 is analyzed with similar efficiency in NH_4OH and NaOH bottles. This probably results from the same reactions involving CO_2 and both alkaline solutions. As seen from the very similar S/Cl ratios in NH_4OH and NaOH bottles and the good concordance of F/Cl ratios between NH_4OH, NaOH and acid condensates samples, acid gases seem to be correctly analysed by the NH_4OH sampling method. Moreover, incondensable gases remaining over alkaline solutions are analysed with similar results in NaOH and NH_4OH bottles.

A key point is that NH_4OH solutions, after undergoing adequate processing (oxidation, acidification, dilution) allow precise MTE measurements without the need of matrix matched standards. This shows that NH_4OH solutions are suitable for standard ICP-MS analysis. Volatile MTE concentrations normalized to chlorine are generally depleted in acid condensates with respect to ammonia solutions. This is probably due to revolatilisation and adsorption effects during sampling with the acid condensate technique. However, sufficient precautions on the quality of

vacuum in NH_4OH flasks have to be taken in order to avoid undesirable sublimates condensation during sampling. These results indicate that MTE measurements performed in NH_4OH solutions appear much more reliable than those performed on acid condensates.

Complete chemical composition (major, minor and trace gases) of the gas phase is therefore easily obtained by using pre-evacuated NH_4OH bottles and standard analytical techniques. We believe this new method to be adapted to routine procedures in active volcanology, allowing new approaches on the coupled variability of MTE and major and minor gases in the gas phase.

Aknowlegements.
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References

Bichler, M., Poljankc, K., Sortino, F., 1995. Determination and speciation of minor and trace elements in volcanic exhalations by NAA. J. Radioanal. Nucl. Chem., 192 : 183-194.

Bichler M., Sortino F., (1995) ^{7}LiOH solution - A suitable reagent to collect volcanic gas samples for NAA. Journal of Radiochemical and nuclear Chemistry. Vol. 199, No. 5, 365-374.

Bichler M., Sortino F., (1996) "Application of Tris(hydroxymethyl)aminomethane and ^{7}LiOH solution for collecting volcanic gas samples for neutron activation analysis. J. Trace and Microprobe Techniques,14(1), 275-284.

Bichler M., Sortino F., (1997) Freeze dried samples gases – a new method for the deatermination of trace elements by NAA. Radiochimica Acta 78, 177-180.

Bichler M., Pelz C., Sortino F., (1999) A comparison of new tecniques for the determination of minor and trace elements in volcanic gases by NAA. Czechoslovak Journal of Physics, Vol. 49, suppl. S1.

Evans, E.H., and J.J. Giglio (1993), Interferences in Inductively Coupled Plasma Mass Spectrometry, J. Anal. At. Spectrom., 8, 1-18.

Fischer, T.P., Shuttleworth, S. and O'Day, P.A., 1998. Determination of trace and platinium-group elements in high ionic-stength volcanic fluids by sector-field inductively coupled plasma mass spectrometry (ICP-MS). Ar. J. Anal. Chem., 362 : 457-464.

Gemmel, B.J., 1987. Geochemistry of metallic trace elements in fumarolic condensates from nicaraguan and costa-rican volcanoes. J. Volcanol. Geoth. Res., 33 : 161-181.

Giggenbach, W., 1975. A simple method for the collection and analysis of volcanic gas samples. Bull. Volcanol., 39: 132-145.

Giggenbach, W.F., Matsuo, S., 1991. Evaluation of results from second and third IAVCEI field worshop on volcanic gases, Mt Usu, Japan, and White Island, New-Zealand. Applied. Geochem., 6 : 125-141.

Giggenbach, W.F., Tedesco, D., Sulistiyo, Y., Caprai, A., Cioni, R., Favara, R., Fischer, T.P., Hirabayashi, J.I., Korzhinsky, M., Martini, M., Menyailov, I., Shinohara, H., 2001. Evaluation of results from the fourth and fifth IAVCEI field worshop on volcanic gases, Vulcano Island, italy, and Java, Indonesia. J. Volcanol. Geoth. Res., 108 : 157-172.

Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T., and Johnson, L., 1998. Geochemical surveillance of magmatic volatiles at Popocatepetl volcano, Mexico. G. S. A. Bulletin, 110: 695-710.

Greenland, L.P., and Aruscavage, P., 1986. Volcanic emission of Se, Te, and As from Kilauea volcano, Hawaii. J. Volcanol. Geotherm. Res., 27: 195-201.

Jarvis, K.E., Gray, A.L., Houk, R.S., 1992. Inductively coupled plasma mass spectrometry. Blackie, New-York, 380 pp.

Keller, G., 1980. The island of Vulcano. In L. Villari (Ed.), The Aeolian Islands, an active volcanic arc in the Mediternean sea. Rend. Soc. It. Mineral. Petrol., 36 (1) : 369-414.

May, T.W., and R.H. Wiedmeyer (1998), A Table of Polyatomic Interferences in ICP-MS, At. Spectrosc., 19, 150-155.

Quisefit, J.P., Bergametti, G., Tedesco, D., Pinart, J., Colin, J.L., 1988. Origin of particulate potassium in Mt Etna emissions before and during the 1983 eruption. J. Volcanol. Geoth. Res., 35 : 111-119.

Quisefit, J.P., Toutain, J.P., Bergametti, G., Javoy, M., Cheynet, B., and Person, A., 1989. Evolution versus cooling of gaseous volcanic emissions from Momotombo volcano, Nicaragua : thermochemical model and observations. Geochim. Cosmochim. Acta, 53: 2591-2608.

Schevenell, L. and Goff, F., 2000. Temporal geochemical variations in volatile emissions from Mount St Helens, USA, 1980-1994. J. Volcanol. Geotherm. Res., 99: 123-138.

Sortino, F., Inguaggiato, S, Francofonte, S., 1991. Determination of HF, HCl, and total sulfur in fumarolic fluids by ion chromatography. Acta Vulcanologica, 1 : 89-91.

Symonds, R.B., Rose, W.I., Reed, M.H., Lichte, F.E. and Finnegan, D.L., 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi volcano, Indonesia. Geochim. Cosmochim. Acta, 51 : 2083-2101.

Toutain, J.P., 1987. Contribution à l'étude des sublimés volcaniques. Minéralogie, géochimie, thermodynamique. Exemples du Momotombo, du Piton de la Fournaise et du Poas. PhD Thesis, Paris, 191 pp.

Toutain J.P., Aloupogiannis, P., Person, A., Blanc, PH. et Robaye, G. (1990) Vapor deposition of trace elements from degassed basaltic lava, Piton de la Fournaise Volcano, Reunion Island. J. Volcanol. Geot. Res., 40, 257-268.

Toutain, J.P., Quisefit, J.P., Briole, P., Aloupogiannis, P., Robaye, G. and Blanc, P., 1995. Mineralogy and chemistry of solid aerosols emitted from Mount Etna. Geochem. J., 29: 163-173.

Toutain, J.P., Polvé, M., Priatna, P., Sulisto, Y., and Mourot, P., 2000. A methodology for gas monitoring at Merapi Volcano. . IAVCEI meeting, Bali (Indonésie) July, symposium "Volcanic Gases".

Vanhoe, H., J. Goossens, L. Moens, and R. Dams (1994), Spectral Interferences Encountered in the Analysis of Biological Materials by Inductively Coupled Plasma Mass Specctrometry, J. Anal. At. Spectrom., 9, 177-185.

Voight, B., Constantine, E.K., Siswowidjoyo, S., Torley, R., 2000. Historical eruptions of Merapi Volcano, Central Java, Indonesia, 1768-1998. J. Volcanol. Geoth. Res., 100 : 69-138.

Figure captions

Fig. 1: A: comparison of SO_4/Cl ratios in NH_4OH and NaOH solutions. **B**: comparison of F/Cl ratios in NH_4OH and NaOH solutions. **C**: comparison of F/Cl ratios in NH_4OH and acid condensates solutions. Empty circles are samples from Vulcano. Grey circles are samples from Merapi.

Fig. 2: Examples of calibration curves obtained with multi-elemental reference solution diluted in 2% HNO_3 matrix (empty circle) and 0.3N NH_4OH/O.6N HNO_3 matrix (full diamonds) for ^{51}V, ^{75}As and ^{238}U. Rhenium was used as internal standard for peak normalisation. Correlation coefficients (r^2) observed between matrix-matched calibrations curves are ranging from 0.99 to 1 for all analysed isotopes.

Fig. 3: Examples of linear correlations for Cl (**A**) and S (**B**) standards used for interferences calibrations. Apparent analyte concentrations induced by the interfering element are shown for **A:** ^{51}V (round plot): $^{35}Cl^{16}O$, $^{37}Cl^{14}N$; ^{75}As (triangle plot): $^{40}Ar^{35}Cl$ and **B:** ^{49}Ti (square plot): $^{32}S^{16}O^{1}H$, $^{33}S^{16}O$; ^{66}Zn (diamond plot): $^{34}S^{16}O^{16}O$, $^{33}S^{16}O^{16}O^{1}H$, $^{32}S^{16}O^{18}O$.

Fig. 4: Comparison of X/Cl ratios in NH_4OH bottles with respect to the same ratio in acid condensate for volatile elements (empty circles) and refractory elements (full diamond).

Tab. 1. Collecting conditions of the 3 sets of samples at Vulcano and Merapi.F0 and FA (V1, V2, V3) are fumaroles on the rim of Fossa Crater. V4 sample was collected at Baia di Levante beach. Woro and Gendol are the 2 main fumarolic fields at Merapi.

Sample name	site	fumarole	Collected samples	date	outlet T (°C)
V1	Vulcano	F0	Cond., NH_4OH, NaOH	22/02/01	358
V2	Vulcano	FA	Cond., NH_4OH, NaOH	23/02/01	363
V3	Vulcano	F0	NH_4OH, NaOH	12/04/02	250
V4	Vulcano	beach	NH_4OH, NaOH	14/08/02	100
M1	Merapi	Gendol	NH_4OH, NaOH	28/09/01	660
M2	Merapi	Woro	Cond., NH_4OH, NaOH	21/09/01	590
M3	Merapi	Woro	NH_4OH, NaOH	21/09/01	497
M4	Merapi	Woro	Cond., NH_4OH, NaOH	21/09/01	407
M5	Merapi	Woro	Cond., NH_4OH	21/09/01	311
M6	Merapi	Woro	Cond., NH_4OH	03/03/02	574
M7	Merapi	Woro	Cond., NH_4OH	03/03/02	456
M8	Merapi	Woro	Cond., NH_4OH	13/06/02	297

Tab 2. General description of the respective procedures used for sampling and analysing CO_2 and acid gases.

- 1 : filtration of the solution on 0.45 mm cellulose acetate filters (Millipore)
- 2: centrifugation of the solution in PP tubes
- 3 : dilution with ultra-pure H_2O
- 4 : oxydation with 30% ultra-pure Oxygen Peroxyde.
- 5 : warming of the oxidised solution for elimination of excess H_20_2 (20 – 40 min)
- 6 : neutralisation of the alkaline solution by a ion (H+) exchange resin (DIOWEX 50WX4-50)
- 7: acidification with double distilled HNO_3
- 8 : 4N sodium hydroxide addition
    - external repeatability

type of sample	**compounds**	**sample processing**	**analytical technique**	**measured species**	**instrumental precision (%)***
acid condensates	HCl, HF	1,3	HPLC	Cl^-, F^-	5
	MTE	2,7	ICP-MS	MTE	1-10
NaOH bottles	S_t, HCl, HF	3,4,5,6,3	HPLC	SO_4^{--}, Cl^-, F^-	5
	CO_2	3,4,5	titrimetry	HCO_3^-	2
	Inc. gases		GC	N_2, CO, Ar ...	< 5%
NH_4OH bottles	S_t, HCl, HF	3,4,5,6,3	HPLC	SO_4^{--} , Cl^-, F^-	5
	CO_2	4,8,5	titrimetry	HCO_3^-	2
	Inc. gases		GC	N_2, CO, Ar ...	< 5%
	MTE	2,4,5,7	ICP-MS	MTE	1-10

Tab. 3. Reproducibility for sampling preparation and analysis of acid gases performed on 9 replicates of V3 sample (Vulcan) using the NH_4OH bottle.

	Type	n	Cl (mg/l)	F (mg/l)	SO_4 (mg/l)
V3	NH_4OH	**9**	60,34 ± 1,19	1,80 ± 0,17	193,99 ± 2,41

Tab. 4. Upper part of the table : repeatability for sampling preparation and analysis of acid gases performed on n replicates of n samples in both NaOH and NH_4OH matrix at Vulcano (sample V3) and Merapi (sample M3). Lower part of the table : comparison of CO_2 concentrations in NaOH and NH_4OH bottles at 2 different sites at Vulcano (F0 fumarole from Fossa crater and beach fumaroles from Baia di Levante). n is the number of samples and n' is the number of replicates on a single sample. One standard deviation (1s) has been calculated for the V3 sample. Absolute values are displayed for other samples.

sample set	Type	T °C	n	n'	CO_2 (mg/l)	CO_2 (µM/M)
V3	NH_4OH	250	1	9	60,34 ± 1,19	
M3	NaOH	497	1	9	427 ± 5,21	
V3	NH_4OH	250	9	1		48350 ± 1706
V3	NaOH	250	1	1		43999
V4	NH4OH	100	2	1		64183 - 63346
V4	NaOH	100	3	1		57371 - 57928 - 63797

Tab. 5. Variabilty (n = 8) of non-condensable gas measurements in NH_4OH. Mean values and one sigma standard deviation in mm/mole of total gas Analyses by gas chromatography.

	Type	T°C	n	He	H_2	CO	CH4
V3	NH_4OH	250	8	0,102	9,63	0,071	0,0022
1 sigma				0,013	0,56	0,003	0,0003

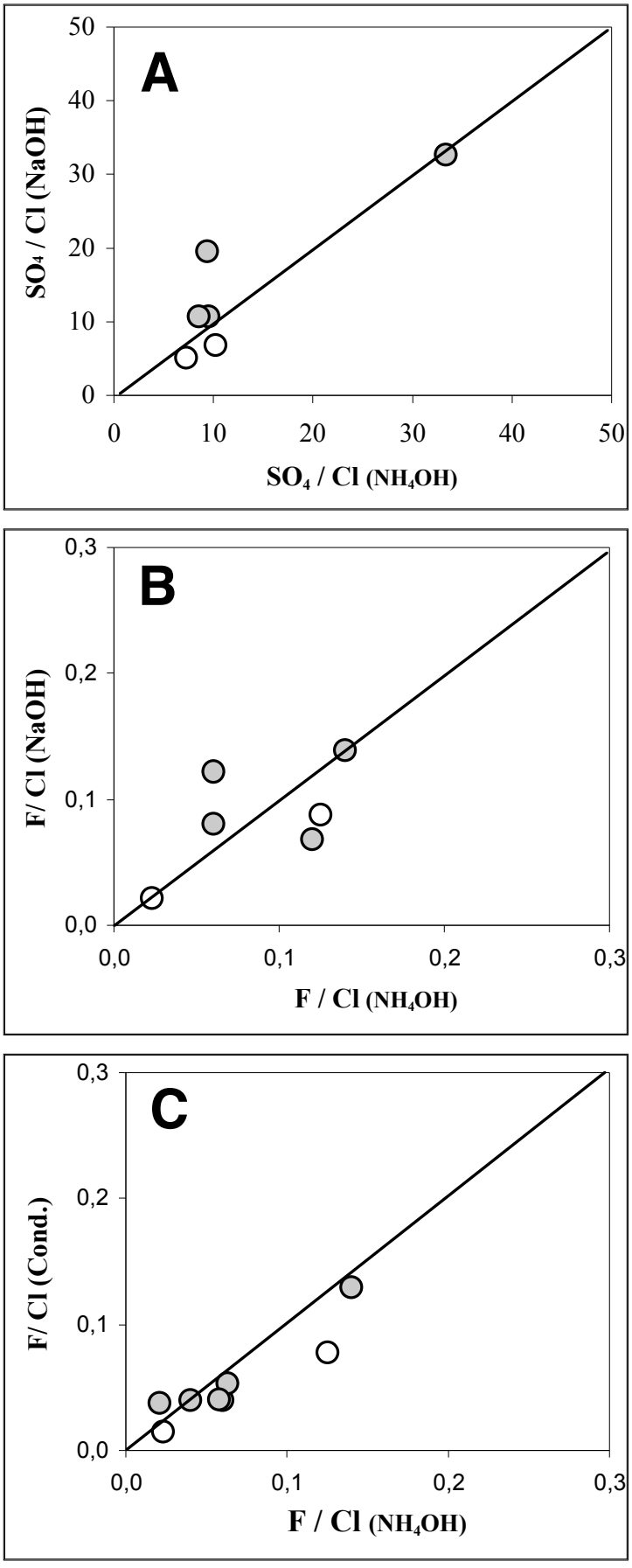


Fig.1.

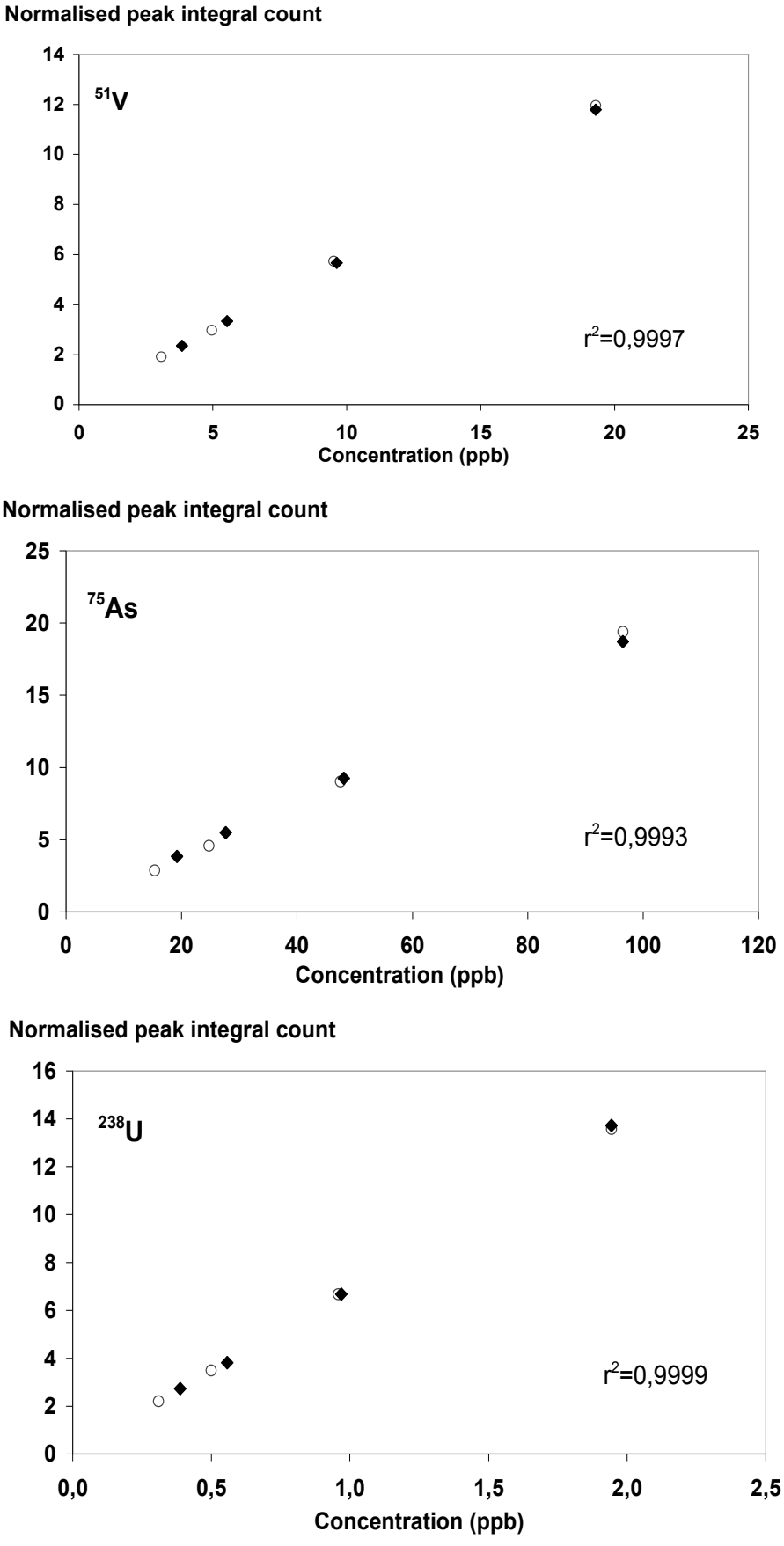
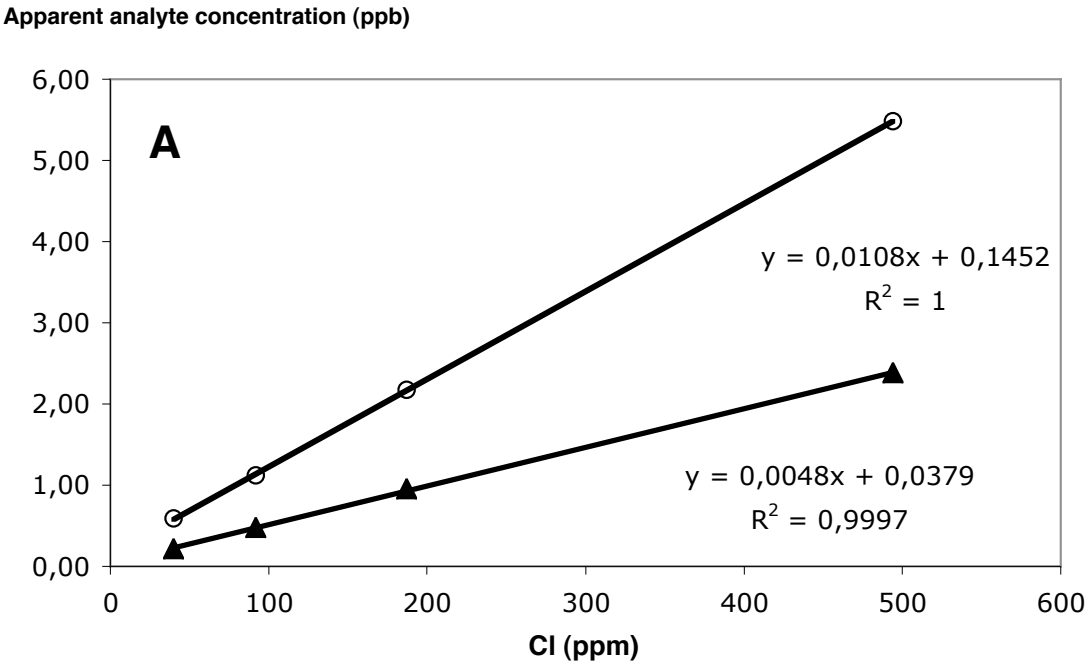


Fig.2.



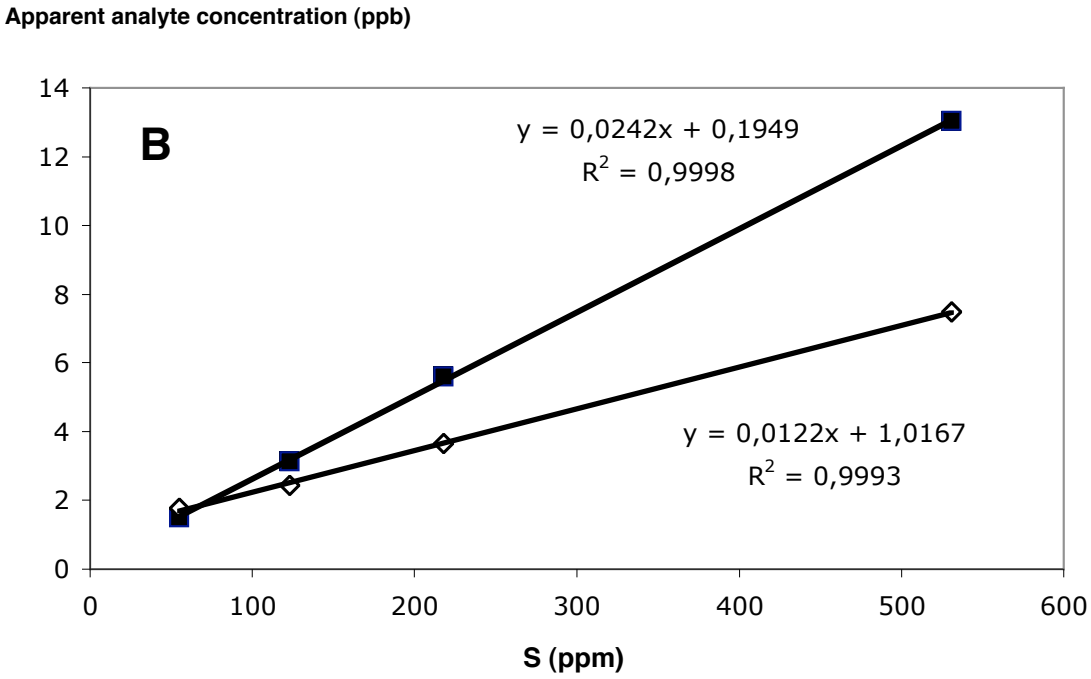


Fig 3

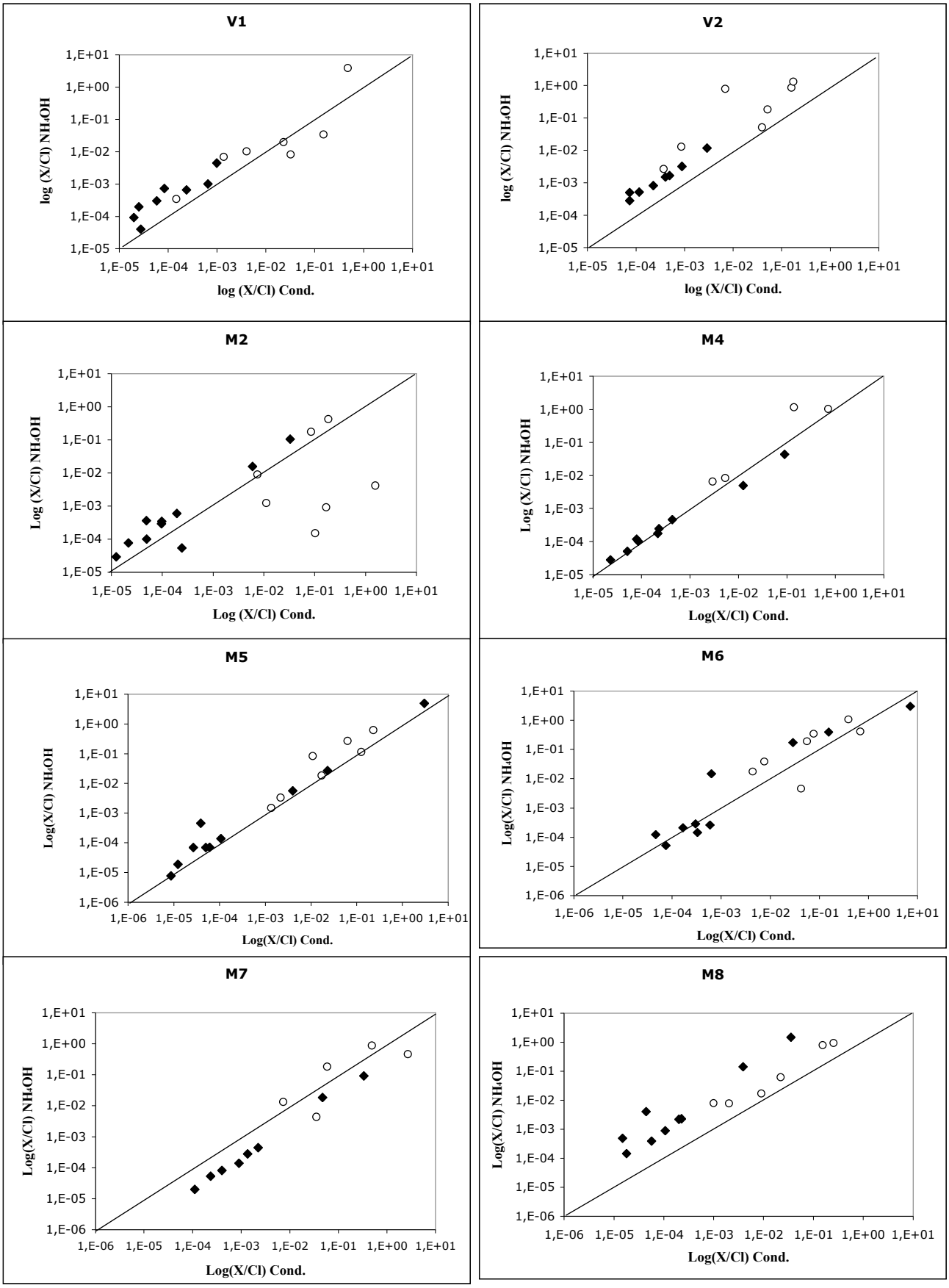


Fig.4.

Chapitre 3 :
Première étude isotopique couplée Sr/Pb des gaz volcaniques et des eaux thermales de Vulcano (Italie)

III-1 VERSION ABREGEE DE L'ARTICLE EN FRANÇAIS

Rappel : Le Sr et le Pb n'étant pas soumis à des fractionnements isotopiques significatifs par comparaison aux variations issues des désintégrations radioactives, le problème de l'échantillonnage des gaz volcaniques ne se pose pas dans cette étude car il n'est pas à même de modifier significativement la composition isotopique Sr/Pb des échantillons de gaz étudiés.

III-1-1 Introduction

Les systèmes hydrovolcaniques actifs sont des sites d'interactions complexes entre les gaz magmatiques émis en profondeur, la roche encaissante et des aquifères plus où moins profonds alimentés par des infiltrations d'eau météoriques ou d'eau de mer. Ces interactions sont généralement étudiées à l'aide de paramètres classiques comme la température, les compositions en éléments majeurs et trace, ou encore les compositions isotopiques δD, $^{3}He/^{4}He$, $\delta^{13}C$, $\delta^{18}O$, et plus récemment $\delta^{11}B$ et $\delta^{34}S$ des différents constituants [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 1999; *Chiodini et al.*, 1993; *Cortecci et al.*, 2001; *Harris and Maciejewski*, 2000; *Leeman et al.*, 2005; *Pennisi et al.*, 2000; *Quisefit et al.*, 1989; *Symonds et al.*, 1996; *Symonds et al.*, 1987; *Taran et al.*, 1995; *Tedesco*, 1997; *Tedesco et al.*, 1995]. L'ensemble de ces études ont conduit à des avancées significatives dans la compréhension des processus d'altération et des phénomènes de mélange entre fluides qui, dans certains cas, ont pu êtres associés aux évolutions de l'activité volcanique.

Cependant, le potentiel des isotopes radiogéniques Sr/Pb, largement utilisé dans la littérature pour l'étude des interactions eaux/roches ou pour l'identification des sources, n'a jamais été pleinement exploité en contexte volcanique ou hydrovolcanique, principalement en raison de l'absence quasi totale de données sur la phase gazeuse volcanique.

L'objectif de ce travail est de présenter la première étude élémentaire et isotopique couplée Sr/Pb des différents constituants du système hydrovolcanique actif de Vulcano (gaz volcanique, eaux thermales, roches, eau météorique et eau de mer). Cette étude a été effectuée dans le but de documenter la variabilité isotopique des différents constituants, d'identifier les sources de ces éléments et les processus contrôlant leur transfert dans ce système complexe.

L'ensemble des échantillons d'eaux thermales et de gaz (condensats acides) présentés dans ce travail ont été prélevés entre 1999 et 2001 (Fig 1, page 103).

III-1-2 Résultats :

. *Eaux thermales :*

Les compositions en éléments majeurs des eaux thermales sont présentées dans la Table 1, page 99. Les résultats obtenus dans ce travail sont en accord avec les données de la littérature et confirment la présence de 4 groupes principaux d'eaux souterraines classifiées en fonction de leurs concentrations en SO_4, Cl et HCO_3 (Figure 2, page 103).

Les concentrations Sr, Pb, mesurées dans les eaux thermales par ICP-MS quadrupolaire, sont présentées dans la Table 2, page 100. La modélisation thermodynamique de ces eaux (Table 3, page 101), réalisée avec le logiciel CHESS 3.0 indique que les teneurs en Sr et en Pb peuvent êtres contrôlés par la précipitation de carbonates ou de sulfures en fonction du caractère oxydant ou réducteur des eaux, les processus d'adsorption ou de co-précipitation sur les phases minérales majeures ou sur les argiles pouvant aussi influencer ces teneurs.

Les compositions isotopiques Sr/Pb des eaux ont été mesurées par TIMS et sont présentées dans la table 2, page 100 et les figures 3 et 4, page 104.

Les compositions élémentaires et isotopiques Sr indiquent que les teneurs Sr ne sont pas influencées par des infiltrations directes d'eau de mer à l'exception d'un site côtier, mais résultent principalement d'interactions eaux météoriques/roches modulées par les apports de gaz acides dans les aquifères superficiels.

Les compostions isotopiques Pb, mesurées dans 2 échantillons, indiquent une origine anthropique de cet élément pour au moins un des groupes d'eaux classifiées.

. *Gaz Fumeroliens :*

Les concentrations et compositions isotopiques Sr/Pb mesurées dans les condensats de gaz fumeroliens sont présentés dans la Table 4, page 102, avec les facteurs d'enrichissement respectifs de ces éléments calculés par rapport à l'aluminium. Les concentrations et les facteurs d'enrichissement du Sr sont nettement inférieurs à ceux du Pb, ce qui est en accord avec les comportements respectivement réfractaires et volatils de ces éléments dans les gaz volcaniques.

La majorité des compositions isotopiques Sr/Pb suggèrent que le Pb est principalement issu du dégazage magmatique alors que le Sr semble provenir du lessivage de la roche ou de contaminations particulaires pendant l'ascension du gaz. Cependant, deux échantillons de gaz (G3 et G7) fournissent des résultats très différents, avec des teneurs Sr et Pb faibles associées

à des signatures isotopiques Sr/Pb proche des pôles anthropiques/météoriques (Fig.3 et 4, page 104). Il est de plus clairement établi que ces résultats ne peuvent résulter d'un artefact analytique ou d'échantillonnage (répliques des séparations chimiques et des analyses TIMS, échantillonnage effectué par beau temps). Par conséquent, ces deux échantillons mettent en évidence des fluctuations épisodiques des signatures isotopiques des gaz fumeroliens entre les pôles magma/roche et météorique/anthropique. Les échelles de temps entre les fluctuations observées étant relativement faibles (1 année au maximum), il semble peu probable qu'un processus profond, comme un apport sédimentaire dans la circulation des fluides, puisse être responsable de ces variations. Du fait du comportement réfractaire du Sr dans les gaz volcaniques et des faibles teneurs en Pb dans l'eau de mer, une contribution marine ne peut être envisagée. Cependant, plusieurs études montrent que des variations dans la structure de l'édifice volcanique, dues à des évènements sismiques, ou a des phénomènes de scellement des conduits fumeroliens, sont susceptibles de modifier les flux d'émission, et la localisation des évents fumeroliens. Ce type de phénomène peut engendrer des interactions variables entre les gaz volcaniques et des eaux météoriques récemment infiltrées dans l'édifice volcanique. Le recyclage de ces eaux par les gaz ascendants expliquerait les compositions élémentaires et isotopiques observées dans les échantillons G3 et G7.

III-1-3 Conclusion :

Ces nouvelles données élémentaires et isotopiques suggèrent que les teneurs en éléments en trace métalliques des fumerolles et des eaux thermales de Vulcano sont influencées par les sources naturelles et atmosphériques/anthropiques. La majorité des échantillons de gaz indiquent une origine principalement naturelle du Sr et du Pb (dégasage magmatique et lessivage de la roche). Cependant, deux échantillons indiquent que les interactions gaz/eaux météoriques anthropisées dans une édifice volcanique à perméabilité variable peuvent modifier épisodiquement les teneurs et les signatures isotopiques des éléments en trace métalliques émis par les fumerolles. Une caractérisation plus précise de la source météorique permettrait de quantifier précisément l'influence de chacune des sources.

III-2 FIRST COUPLED Sr AND Pb ISOTOPIC MEASUREMENTS IN VOLCANIC GAS CONDENSATES AND GROUDWATERS OF VULCANO ISLAND (ITALY)

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First coupled Sr and Pb isotopic measurements in volcanic gas condensates and groundwaters of Vulcano island (Italy)

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Abstract

For the first time, coupled Sr-Pb concentrations and isotopic compositions have been measured on four crater fumaroles and six groundwaters sampled between 1999 and 2001 at Vulcano Island, Southern Italy. Sr concentrations and isotopic compositions of groundwaters show that the Sr budget results mainly from the leaching of volcanic rock by groundwaters. Leaching intensity is controlled by the variable dissolution of volcanic gases into shallow aquifers. The data do not reveal any influence of seawater except at one coastal site. Low Pb concentrations together with calculated saturation indexes with respect to mineral phases indicate that Pb content in groundwaters is strongly influenced by adsorption and/or precipitation processes. Pb isotopic ratios of two steam-heated waters display a clear anthropized meteoric water signature, suggesting gas dissolution or wall rock alteration to be a negligible process for this element in this particular context. Low (≈0.5) and high (10^2-10^3) enrichment factors were calculated for Sr and Pb, respectively indicating their refractory and volatile behaviour in volcanic gases. Most of gas samples display Sr and Pb isotopic ratios similar to parent rocks. These data suggest that Sr is mainly derived from wall rock or particle contamination during gas ascent whereas Pb results mainly from magma degassing. However, two gas condensates collected from two different fumarolic vents and at different periods show a dramatic Pb and Sr isotopic shift with a clear atmospheric/anthropogenic signature. Episodic permeability variations of the volcanic structure, probably arising from microseismicity swarms, changes of local stress field and migration of self-sealing processes, lead to changing interactions between freshly infiltrated meteoric water and volcanic gases that temporarily modify the trace metal signature of the fumarolic gas.

Index terms : hydrothermal systems, radiogenic isotopes geochemistry, volcanic gases

Keywords: strontium isotopes, lead isotopes, fumaroles, groundwaters, metallic trace elements

1. Introduction

Active hydro-volcanic systems are sites of complex interactions between magmatic gases, wall rock and aquifers fed by meteoric water and/or seawater. These interactions are usually investigated by using classical parameters such as temperature, major and trace compounds chemistry, oxygen fugacity, and δD, $^{3}He/^{4}He$, $\delta^{13}C$ or $\delta^{18}O$ isotopic compositions applied to fumarolic gases and shallow groundwaters [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 1999; *Chiodini et al.*, 1993; *Harris and Maciejewski*, 2000; *Quisefit et al.*, 1989; *Symonds et al.*, 1996; *Symonds et al.*, 1987; *Taran et al.*, 1995; *Tedesco*, 1997; *Tedesco et al.*, 1995]. More recently, boron and sulfur isotope compositions were also used to constrain these interactions [*Cortecci et al.*, 2001; *Leeman et al.*, 2005; *Pennisi et al.*, 2000]. Using these parameters provide insights on source effects, mixing and alteration processes, possibly interpreted in terms of volcanic/magmatic processes.

Volcanic exhalations are also a source of heavy metals to the atmosphere [*Dongarra and Varrica*, 1998; *Ferrara et al.*, 1995; *Piccardi et al.*, 1979; *Quisefit et al.*, 1989; *Symonds et al.*, 1987; *Taran et al.*, 1995; *Toutain et al.*, 2003; *Vallelonga and Mather*, 2003]. Gases emitted through occasional eruptions or quiescent degassing are mainly composed of H_2O and CO_2 steam with minor amounts of H_2S, SO_2, HCl, HF and trace gases. Gases contain also metallic trace elements (MTE), that are more or less enriched with respect to the magma [*Symonds et al.*, 1987; *Taran et al.*, 1995; *Toutain et al.*, 2003] as evidenced by highly contrasted Enrichment Factors (EF) defined as follows:

$$EF_X = \left[(X/X_R)_g / (X/X_R)_r \right]$$

for an element X, g and r being the gas condensate sample and the rock, respectively, X_R corresponding to an element displaying a refractory behaviour with respect to volcanic fluids. [*Quisefit et al.*, 1989]. High EF elements (Se, Re, Bi, Te, As, Cd, Pb, Tl, among others) are volatile elements mainly produced by selective distillation at the magma chamber level. Low

EF elements (Sr, Al, Fe, Mg, Mn among others) are refractory elements mainly present in the gas phase through wall rock and or ash alteration processes in highly acidic context. By coupling the study of both a refractory and a volatile element, one should make available a powerful tool to discriminate processes that contribute to MTE transport in the volcanic pile.

As Sr and Pb isotopes do not fractionate measurably in nature [*Barbieri and Morotti*, 2003; *Bollhöfer and Rosman*, 2001], their variations are controlled by radioactive processes only and Sr and Pb isotopic compositions are powerful geochemical tracers to identify natural, anthropogenic or atmospheric sources [*Bollhöfer and Rosman*, 2001; *Freydier and Viers*, 2003; *Monna et al.*, 1999; *Monna et al.*, 1997], to study water rock interactions [*Barbieri and Morotti*, 2003; *Goff et al.*, 1991; *Möller et al.*, 2004; *Pennisi et al.*, 2000] or to describe magmatic evolution [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997; *De Astis et al.*, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003]. However, probably as the result of sampling or analytical difficulties, and because most of the metals (including Pb) are strongly partitioned in the particulate phase of volcanic plumes [*Hinkley*, 1991], Sr and Pb isotopic data on volcanic gases totally lack. Only few Pb isotopic data have been recently published on volcanic aerosols [*Monna et al.*, 1999; *Vallelonga and Mather*, 2003] and secondary solid phases [*Ferrara et al.*, 1995]. On the contrary, in thermal waters, Sr and Pb isotopes are common tools for sources identifications and characterisation of water-rock interactions [*Barbieri and Morotti*, 2003; *Goff et al.*, 1991; *Möller et al.*, 2004; *Pennisi et al.*, 2000].

In this work, we propose the first coupled isotopic study of Sr and Pb in fumarolic gases and thermal waters from Vulcano Island. Data are processed together with rock data [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997; *De Astis et al.*, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003] and local anthropogenic/atmospheric signatures [*Monna et al.*, 1999]. The aim of this work is to

document the isotopic variability in the hydro-volcanic environment, to identify sources of elements and to constrain processes that control Sr and Pb transfers.

2. Geological setting and hydrovolcanic context

Vulcano is the southernmost island of the Aeolian volcanic Archipelago, southern Tyrrhenian Sea (Fig.1). Its magmatic activity began in the upper Pleistocene with leucitic tephrites to highly potassic trachytes, followed in historic time by alkali-rhyolitic obsidian [*Keller*, 1980]. Since the last eruption in 1888-1890, the volcanic activity is restricted to: 1) a wide fumarolic field located on the rim and the internal wall of the « La Fossa » crater (391m a.s.l.), 2) low temperature fumaroles (close to 100°C) located on the « Porto di Levante » beach, 3) CO_2-dominated soil gas emissions in the Vulcano porto area and around the « La Fossa » crater edifice and 4) thermomineral waters related to an active hydrothermal system and accessible from shallow water wells. During the last century, the fumarolic field of « La Fossa » crater has displayed wide variations in outlet temperature (from 200°C to 700°C) and gas composition [*Barbieri et al.*, 1991; *Harris and Maciejewski*, 2000]. Fluctuations of the size and location of fumarolic vents have also been reported [*Harris and Maciejewski*, 2000] and interpreted in terms of variable magma degassing generating permeability modifications of the volcanic edifice by fracturation processes and self-sealing of the fumarolic conducts.

Previous studies display chemical and light stable isotope evidences that shallow waters and fumarolic gases compositions result from multiple interactions between magmatic, hydrothermal, meteoric and seawater components [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 2001; *Capasso et al.*, 1991; *Capasso et al.*, 1992; *Capasso et al.*, 1999; *Cortecci et al.*, 2001; *Dongarra et al.*, 1988; *Leeman et al.*, 2005; *Martini*, 1980; *Panichi and Noto*, 1992]. Seismic events, leading to variable fracture permeability, are supposed to modulate mixing processes between geothermal waters, shallow thermal waters and ascending magmatic vapour [*Bolognesi and D'Amore*, 1993]. The involvement of

seawater in the hydrothermal system of Vulcano Island remains a controversial question [*Bolognesi*, 1996; *Chiodini et al.*, 1995; *Cortecci et al.*, 2001; *Leeman et al.*, 2005]. Seawater signature modified by wall-rock interactions seems obvious in crater-rim fumaroles [*Leeman et al.*, 2005; *Panichi and Noto*, 1992] whereas the contribution of seawater to the shallow aquifers appears unlikely except for selected samples close to sea-side [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Cortecci et al.*, 2001].

3. Sampling techniques

Four crater fumaroles and waters from six wells were sampled between 1999-2001 (Fig.1). Fumarolic gases were channelled through a silica tube to an acetone-cooled condensor [*Chevrier and Le Guern*, 1982] allowing the fast condensation of water, acid gases and associated trace elements. In order to ensure a continuous flow of gas, a weak and constant aspiration was applied with a hand-pump. Gas condensates were sampled from F11 (G1, G2, G3 samples), FA (G4, G5 samples), F0 (G6, G7, G8 samples) and FR2 (G9 sample) fumarolic vents.

Water samples were filtered in the field through 0.2µm Millipore filters, stored in suprapur HBr pre-washed teflon bottles and acidified with suprapur HNO_3 to avoid Sr and Pb adsorption on bottles walls. A sampling and filtration blank was made with ultra-pure water. Waters were sampled from the following wells: Istmo (W1 sample), Piscio (W2 sample), Vasca (W3 sample), Rifici (W4 sample), C.Sicilia (W5, W6 samples) and Centro (W7, W8 samples).

4. Analytical methods

Temperature, pH and redox potential (Eh) were measured directly in the field. Alkalinity was obtained by titration with 0.01N HCl. SO_4^{2-} and Cl^- concentrations were measured by High Pressure Liquid Chromatography (DX 300, Dionex). Na, K, Ca and Mg

concentrations were determined by Atomic Adsorption (5100 ZL, Perkin Elmer SCIEX). Sr and Pb abundances were measured using a quadrupole-based ICP-MS (Elan 6000, Perkin-Elmer SCIEX). Accuracy and precision of the measurements were controlled by analysing SLRS-4 certified reference material. Analytical errors are in the range of 5-10%.

The amount of gas condensate and water samples needed for Sr and Pb isotopic measurements was calculated from Sr and Pb concentrations and evaporated. The solid deposits were submitted to acid digestion (HF + HNO_3), oxidation (H_2O_2) and dried at 50°C. The final deposits were then dissolved with 0.5 ml of suprapur 2N HNO_3 and centrifuged before chemical extraction. Each dissolution was performed using ultrasonic agitation. The Sr and Pb chemical separation was on polypropylen columns containing 150 µl of Sr-spec resin, following the protocol described by *Deniel and Pin* [2001]. Blank contributions with respect to the total amount of sample analysed were generally < 0.25%. Higher blank contributions are discussed later.

Sr and Pb isotopic compositions were measured using a Thermal-Ionisation Mass Spectrometer (Finnigan MAT 261). Pb was loaded on a double Re filament using the silica gel/phosphoric acid loading technique. Sr was loaded on a single W filament together with "Ta-activator". Regular measurement of NBS-981 Pb standard allowed the correction of the Pb isotopic data for mass fractionation (1.30 ± 0.05‰ per amu) using a linear law [*Doucelance and Manhès*, 2001]. For Sr, regular measurement of NBS-987 Sr standard was used to monitor accuracy. Sr isotopic ratios were normalized to $^{88}Sr/^{86}Sr = 0.1194$. Duplicates of four waters (W2, W4, W5, W8) and one fumarole (G3) show good reproducibility and confirm the significance of analytical data.

Blank contributions

The blank of the bulk procedure (dissolution + chemical extraction) was measured by ICP-MS for each set of eight samples. The mean values obtained were 0.45ng and 0.92ng for Sr and Pb, respectively. For some samples, Sr or Pb blank contribution appears to be potentially significant (i.e. from 0.25% to 5.9%) with respect to the total amount of element analysed. This is due to the limited quantities of sample available and to the low Sr and/or Pb concentrations observed in some cases. In order to evaluate the impact of the blanks on our isotopic data, binary mixtures calculations were performed based on the assumption that the total amount of the element analysed was a combination of blank and sample contribution. Sr-Spec procedural blanks were analysed by TIMS for their Sr isotopic composition by *Dessert* [2002] at the LMTG, Toulouse. As our analyses were performed in nearly similar conditions (laboratory, reagents, material), the $^{87}Sr/^{86}Sr$ blank value = 0.72108±0.00008 determined by *Dessert* [2002] appears to be suitable for our blank impact calculations. No isotopic compositions of Sr-spec procedural blanks were available for Pb. Moreover, Pb blanks display a high variability between the different chemical extractions (from 0.2ng to 1.9ng). This phenomenon was ascribed to variable atmospheric contamination during the chemical procedure and Pb blank was then supposed to result mainly from this source. As a consequence, the Pb isotopic composition of Toulouse airborne ($^{206}Pb/^{207}Pb$=1.1042±0.0001; $^{208}Pb/^{206}Pb$=2.1563±0.0004, station 6, ORAMIP) analysed by *Monna et al.* [1997] was used for the calculation and all isotopic data associated with blank contribution > 0.25% were corrected by this method. The maximum Sr blank contribution (5.9%) was observed for sample G7 whereas the maximum Pb blank contribution (3.6%) was observed in W2 and W3 samples. Maximum corrections applied correspond to 0.1% for $^{87}Sr/^{86}Sr$ ratio of G7 sample, and to 0.16% and 0.085% of W3 $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios, respectively. The minimum corrections applied correspond to 0.006% of the G3 $^{87}Sr/^{86}Sr$ isotopic ratio and to

0.15% to 0.08% of G4 $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios, respectively. Such corrections have no significant implication on our interpretations of Sr and Pb isotopic compositions.

5. Results and discussion

5.1. Thermomineral waters

5.1.1. Major element geochemistry

Sampling temperatures, pH and Eh vary between 21.2 to 81°C, 1.15 to 7.62 and -361 to 194mV, respectively (Table 1). The major elements geochemistry of Vulcano groundwaters is extensively described in literature [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 2001; *Cortecci et al.*, 2001]. Our major elements data presented are in agreement with previous studies. Therefore, in order to avoid redundancy, only general points will be presented. Sampled waters observed in classical anionic triangular plot (Fig.2) are far from the "mature water" field defined by *Giggenbach* [1988]. This indicates that Vulcano groundwaters are far from equilibrium with their host rocks. Following *Aiuppa et al.* [2000], Vulcano groundwaters can be classified in four groups:

W1 water, sampled at the sea-side (Fig.1) can be classified as a chloride-rich water. W1 displays the highest Total Dissolved Solids (TDS = 35862 mg/kg) and lowest Eh (-361mV) as the result of seawater contribution and bubbling of reducing gases (CH_4, H_2S).

W2, W3 and W4 waters were sampled between the coastal area and the volcanic edifice (Fig.1). Their anion contents (Fig.2) correspond to the steam-heated water group. These waters are supposed to result from the interaction of shallow groundwaters of meteoric origin and H_2S-rich geothermal steam released from a deep (≈200m) boiling geothermal aquifer fed by ascending volcanic gases. This hypothesis is actually supported by geothermal explorative drillings as reported by *Sommaruga* [1984]. An intense interaction of geothermal

steam with W3 aquifer, leading to the oxidation of H_2S to H_2SO_4, is likely to be responsible of the low pH, low Eh, high sulphate and high TDS value of this sample.

W5 and W6 waters were sampled close to the volcanic edifice (Fig.1) and fall in the compositional field of volcanic waters (Fig.2), also named chloride-sulfate groundwaters or magmatic waters [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993]. As described in these studies, these groundwaters result from a mixing between meteoric water and HCl/H_2SO_4 condensates of volcanic origin and subsequent water-rock interaction.

W7 and W8 were sampled far from the volcanic edifice, close to the "Porto di Ponente area" (Fig.1). These waters can be classified as shallow groundwaters because of their low TDS samples ascribed to the meteoric recharge.

When plotted in the classical *Giggenbach* [1988] Na, K, Mg triangular diagram, most of thermal waters fall in the field of immature waters along a line characteristic of the isochemical rock dissolution [*Bolognesi and D'Amore*, 1993; *Capasso et al.*, 2001; *Cortecci et al.*, 2001]. This confirms the observation previously made with the anionic triangular diagram (Fig.2) which evidence that waters are far from thermodynamical equilibrium with the host rocks.

5.1.2. Sr and Pb concentrations and aqueous speciation.

As shown in Table 2, Sr content ranges from 4.4 to 9731.8 µg/kg, whereas Pb is considerably less abundant with concentrations from 0.15 to 89.6 µg/kg. These values are similar to previous studies [*Aiuppa et al.*, 2000; *Cellini Legittimo et al.*, 1980]. Thermodynamical modelling of our samples was performed with the CHESS 3.0 software program [*Van der Lee and De Windt*, 2000] with T°C, pH, Eh, major element and Sr, Pb concentrations as inputs. This software was used for the determination of the aqueous elemental speciation and for the calculation of saturation indexes (SI) with respect to solid phases with the aim to determine

the influence of mineral precipitation to the Sr, Pb content in groundwaters. The results are reported in Table 3, and show that Sr aqueous chemistry in groundwaters is dominated by Sr^{2+} free ion and sulphate complexes, whereas the most abundant Pb species are respectively $PbCO_3$ and Pb^{2+} free ion. However, in the case of high Cl concentrations and/or reducing environment (i.e., W1 and W3 samples), chloride complexes become significant for Sr ($SrCl^+$) and Pb ($PbCl_2$, $PbCl^+$, $PbCl_3^-$) and even dominant for lead in W1 sample which presents the highest Cl concentration and the lowest Eh. Saturation indexes (SI) with respect to mineral phases show that Sr contents in Vulcano groundwaters can be controlled by carbonate mineral precipitation in oxidizing environment. Indeed, $SrCO_3$ was found to be supersaturated in W5 sample and close to equilibrium values for W2 and W4 samples. In reducing and/or low pH environment (i.e., W1 and W3 samples) sulphide mineral precipitations are possible for Pb.

Major mineral phases (silica, carbonates, sulphates and fluorides minerals) are close to equilibrium or supersaturated. We did not calculate the saturation indexes for clay minerals because of the poor quality of the relevant thermodynamic data, but it is clear that they dominate the alteration facies at least for the more acidic fluids. In any case, this short thermodynamic analysis indicates that adsorption on and/or coprecipitation with these minerals have also to be considered as partially influencing the trace metals abundances in Vulcano groundwaters and might be responsible of the low Pb contents measured in our samples.

5.1.3 Sr and Pb isotopic compositions

Sr concentrations and isotopic compositions of Vulcano groundwaters are displayed in Table 2. In Fig 3., $^{87}Sr/^{86}Sr$ ratios are plotted versus Sr concentrations, together with the seawater (SW) value (Sr = 8100 μg/g; $^{87}Sr/^{86}Sr$ = 0.70918) derived from the study of Etna

groundwaters by *Pennisi et al.* [2000]. In meteoric waters (MW), Sr concentrations and isotopic compositions fluctuate accordingly to the variable aerosol sources (sea-salt, soil dust, biological or anthropogenic emissions). *Pennisi et al.* [2000] assigned a 10µg/kg concentration and the typical $^{87}Sr/^{86}Sr$ isotopic ratios of seawater to their hypothetical meteoric water end-member. However, *Negrel and Roy* [1998] obtained Sr contents as low as 0.35 µg/kg in Massif Central rainwaters. North African aerosols might also influence the Vulcano's rain water budget [Monna et al., 1999]. Saharan dust [*Krom et al.*, 1999] displays $^{87}Sr/^{86}Sr$ isotopic ratios ranging from 0.7160 to 0.7192. Concerning southern Europe, *Grousset et al.* [1998] have measured $^{87}Sr/^{86}Sr$ isotopic ratios in Corsican aerosols and obtained values ranging from 0.71925 to 0.72451. This shows that direct measurements of Vulcano rainwater are required to characterise more precisely the Sr concentrations and isotopic compositions of MW in this area. As a consequence, MW water possible values are represented as a range in Fig.3, with Sr concentrations ranging from 0.35 to 10 µg/kg and a minimum $^{87}Sr/^{86}Sr$ ratio corresponding to the SW value from *Pennisi et al.* [2000]. The rock values, selected from literature data [Clocchiatti et al., 1994; De Astis et al., 1997; De Astis et al., 2000; Del Moro et al., 1998; Ellam et al., 1989; Esperança et al., 1992; Gioncada et al., 2003] are also presented in Fig.3. The lower rock isotopic value corresponds to sample VL229/1a+b from De Astis et al. [1997] displaying a $^{87}Sr/^{86}Sr = 0.70412$ whereas the higher value corresponds to sample VL90/3La from De Astis et al. [2000] with a $^{87}Sr/^{86}Sr = 0.70588$.

In Fig.3, W1 sample display a higher Sr content than SW and a $^{87}Sr/^{86}Sr$ ratio between the higher Vulcano rock signature and the SW value. This confirms the seawater main contribution for this sample already suggested by major elements chemistry. All other waters display significantly lower Sr concentrations, and most of them have $^{87}Sr/^{86}Sr$ ratios in the range of rock values. Steam-heated and volcanic waters both display low $^{87}Sr/^{86}Sr$ ratios and high Sr concentrations with respect to shallow groundwaters, likely as the result of enhanced

rock leaching due to a higher input of geothermal and/or magmatic fluids. Together with major elements geochemistry, these observations suggest that the Sr budget of steam-heated and volcanic waters results mainly from a balance between two end-members (meteoric water and parent rock) modulated by acid gases influx. Indeed, variable dissolution of rising gases into shallow aquifers modifies the physico-chemical parameters of groundwaters and therefore controls the intensity of rock leaching. W7 and W8 samples display the lowest Sr concentrations and $^{87}Sr/^{86}Sr$ signatures between the Vulcano rock and the MW range. This suggests a strong influence of MW for these samples together with a lower efficiency of rock leaching which is in agreement with major elements geochemistry.

Due to the low Pb contents, only two Pb isotopic data are available for water samples (see Table 2). In Fig 4., W2 and W3 samples plot far from the Vulcano rocks isotopic compositions and in the field of recent anthropogenic signatures [*Monna et al.*, 1999]. For these steam-heated waters, these results suggest a strong influence of anthropogenic Pb either via meteoric water infiltrations or contamination of the relative aquifers by geothermal drillings performed in the 50's [*Sommaruga*, 1984]. Natural Pb influence due to wall rock interactions, magmatic gas dissolution or re-entrainment of volcanogenic aerosols in MW during rainfall appears negligible for these samples. Any marine contribution can also be ruled out due to the very low Pb content (about 10^{-12}g/g) in sea water [*Yuan-Hui*, 1991].

5.2. Fumarolic gas condensates

Sampling temperature, Sr and Pb concentrations and isotopic compositions of gas condensates from La Fossa crater fumarolic field are reported in Table 4. Sr and Pb enrichment factors (EF) with respect to Al are also shown in Table 4. Al is chosen because of its refractory behaviour in volcanic fluids. Ti or Zr may also be chosen with little effect for

global results. EF were calculated using the mean of Vulcano rocks analyses from *Clocchiatti et al.* [1994].

The outlet temperatures of fumarolic vents, sampled during the 1999-2001 period, range from 104°C (G9) to 446°C (G3). Sr concentrations are ranging from 1.4 µg/kg (G3) to 151.7 µg/kg (G5) whereas Pb is much more abundant with concentrations ranging from 90.3 µg/kg (G7) to 7968.5 µg/kg (G8). $^{87}Sr/^{86}Sr$ ratios vary from 0.70487±0.00002 (G8) to 0.71009±0.00002 (G3). $^{206}Pb/^{207}Pb$ ratios range from 1.1780±0.0001 (G3) to 1.2396±0.0001 (G5) and $^{208}Pb/^{206}Pb$ ratios vary from 2.0314±0.0003 (G7) to 2.0756±0.0002 (G3). No clear correlations were observed between the outlet temperature of the fumarolic vents and Sr and Pb concentrations or isotopic compositions.

Pb and Sr display respectively high (10^2-10^3) and low (≈0.5) EF in volcanic fluids (Table 4), as the result of their respective volatile and refractory behaviours. This accounts for the very contrasted elemental and isotopic compositions for Sr and Pb in Vulcano condensates.

In Fig 3, most of gas samples (G1, G2, G5, G6, G8) display low Sr isotope ratios, within the bulk rock range, suggesting both Sr content in volcanic gases to be mainly derived from wall rock or particle leaching during gas ascent and Sr contamination from meteoric water infiltrations to have a negligible impact on the $^{87}Sr/^{86}Sr$ isotopic ratios. However, two samples (G3, G7) display a definitely contrasted isotopic signature, close to, or inside the meteoric water range. These samples also display the lowest Sr concentrations observed in gas condensates.

In the $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ diagram (Fig 4.), G1, G4, G5, G6, G8 and G9 samples plot in the field of parent rocks. This observation is in accord with previous studies performed in plume aerosols from Masaya [*Vallelonga and Mather*, 2003] and in lead sulphosalts sublimates of Vulcano [*Ferrara et al.*, 1995] displaying lead isotopic ratios of volcanic

exhalations similar to respective parent rock. Some Pb may originate, as Sr, from acid fluid-rock interactions. However, due to high EF (10^2-10^3) in gas condensates, the Pb budget is likely to be dominated by magma degassing. Because isotopic mass fractionation during Pb degassing does not induce measurable effects, gases and rocks should display similar Pb isotopic compositions. Therefore, it is not possible to discriminate if small Pb isotopic variations between samples G1, G4, G5, G6, G8 and G9 are due to interactions with isotopically different pathways during gas ascent or to limited magmatic signature variations.

G3 and G7 samples display large differences in both Sr and Pb isotopic ratios with signatures close to the meteoric/anthropogenic values. These samples display the lowest Sr and Pb concentrations measured in gas condensates and one may suggest a possible contamination. However, an artefact due to a rainfall-induced contamination is unlikely because sampling was performed during sunny days and the percentage of contamination should be almost total due to the low concentrations generally observed in meteoric water. Contamination of samples by solid particles can be also ruled out, as it would induce higher Sr and Pb contents. Therefore, episodic variations of both Sr and Pb isotope ratios between magmatic/rock signatures and atmospheric/anthropogenic signatures are obvious for F11 (G1, G2, G3 samples) and F0 (G6, G7, G8 samples) fumaroles. As the time scale is quite short between the different sampling campaigns (from 1999 to 2001), a deep process, such as the involvement of Calabrian meta-sediment [*Caggianalli et al.*, 1991] in deep fluid circulation can be ruled out as already concluded by *Ferrara et al.* [1995]. Moreover, a marine contribution by deep infiltration within the volcanic pile is unlikely to affect Sr and Pb isotopic compositions of the crater fumaroles because 1) Sr has a refractory behaviour in volcanic gas and large amounts of this element could not be transported in fumarolic fluids from deep levels to the volcano/atmosphere interface, 2) Pb content in sea water is very low [*Yuan-Hui*, 1991] and can be considered as a negligible source of Pb in fumaroles. As

suggested by several studies [*Ferrara et al.*, 1995; *Harris and Maciejewski*, 2000], local fluctuations of the volcanic structure permeability are likely to occur due to both seismic events and self-sealing processes that continuously change the circulation pathways and local fluxes of fumarolic fluids. Such changes may lead ascending volcanic gases to undergo variable interactions with meteoric water, which has recently filtered into the shallow volcanic edifice, therefore accounting for the meteoric/anthropogenic isotopic signature of samples G3 and G7. As discussed above, MW measurements are required to define more precisely the MW range in the Vulcano island area because Sr concentrations and isotopic compositions of rainwater are dependent on aerosols sources.

6. Conclusion

These new coupled Sr-Pb concentrations and isotopic measurements clearly indicate that the Metallic Trace Elements (MTE) budget of fumarolic gases and shallow waters of Vulcano Island is influenced by both natural and atmospheric/anthropogenic sources. The Sr budget in groundwaters appears to result mainly from water/rock interaction modulated by volcanic gas input into shallow aquifers. The Pb isotope ratios measured in two steam-heated waters reveal the dominant anthropogenic origin of this element at least in these shallow waters. In most gas samples, the data indicate that Pb is originated from magma degassing whereas Sr results mainly from wall-rock or particle contamination during gas ascent. Two gas samples were found to display clear anthropogenic/atmospheric Sr and Pb isotopic signatures. This might indicate that variable permeability of the volcanic edifice allows the recycling of fresh meteoric water by ascending volcanic fluids. Because of the short time-scale of variations of the isotopic signatures for a single fumarole (one year period), modifications of the fluid migration network within the volcanic pile appears as a fast-operating process. The 3-D permeability distribution appears as highly dependent on local

stress field changes, micro-fracturation due to small volcanic earthquakes and migrating self-sealing processes. These interpretations, performed on the first set of Sr and Pb isotopic ratios in Vulcano gases and groundwaters, have to be confirmed by future Sr and Pb isotopic measurements, coupled with multi-parameters data (fluid geochemistry, seismicity, deformations). This will allow a considerable improvement of the comprehension of interactions between ascending gases, shallow aquifers, infiltered meteoric water and wall rock in a continuously permeability changing structure.

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References

Aiuppa, A., G. Dongarra, G. Capasso, and P. Allard (2000), Trace elements in the thermal groundwaters of Vulcano Island (Sicily), *J. Volcanol. Geotherm. Res.*, *98*, 189-207.

Barbieri, F., G. Neri, M. Valenza, and L. Villari (1991), 1987-1990 unrest at Vulcano, *Acta Vulcanol.*, *1*, 95-106.

Barbieri, M., and M. Morotti (2003), Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture Volcano, Italy, *Appl. Geochem.*, *18*, 117-125.

Bollhöfer, A., and K.J.R. Rosman (2001), Isotopic source signature for atmospheric lead: The Northern Hemisphere, *Geochim. et Cosmochim. Acta*, *65* (11), 1727-1740.

Bolognesi, L. (1996), Comment on "Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance" by G. Chiodini, R. Cioni, L. Marini, and C. Panichi, *Bull. Volocanol.*, *58*, 319-320.

Bolognesi, L., and F. D'Amore (1993), Isotopic variation of the hydrothermal system on Vulcano Island, Italy, *Geochim. et Cosmochim. Acta*, *57*, 2069-2082.

Caggianalli, A., A. Del Moro, A. Paglionico, G. Piccarreta, L. Pinarelli, and A. Rottura (1991), Lower crustal granite genesis connected with chemical fractionation in the continental crust of Calabria (Southern Italy), *Eur. J. Mineral.*, *3*, 159-180.

Capasso, G., W. D'Alessandro, R. Favara, S. Inguaggiato, and F. Parello (2001), Interactions between the deep fluids and the shallow groundwaters on Vulcano Island (Italy), *J. Volcanol. Geotherm. Res.*, *108*, 187-198.

Capasso, G., G. Dongarra, R. Favara, S. Hauser, and M. Valenza (1991), Chemical changes in waters from Vulcano Island: an update, *Acta Vulcanol.*, *1*, 199-209.

Capasso, G., G. Dongarra, R. Favara, S. Hauser, and M. Valenza (1992), Isotope composition of rain water, well water and fumarole steam on the Island of Vulcano, and their implications for volcanic surveillance, *J. Volcanol. Geotherm. Res.*, *49*, 147-155.

Capasso, G., R. Favara, S. Francofonte, and S. Inguaggiato (1999), Chemical and isotopic variations in fumarolic discharge and thermal waters at Vulcano Island (Aeolian Islands, Italy) during 1996: evidence of resumed volcanic activity., *J. Volcanol. Geotherm. Res.*, *88*, 167-175.

Cellini Legittimo, P., M. Martini, and G. Piccardi (1980), Il contenuto di metalli pesanti nelle acque freatiche di Vulcano e l'influenza di fluidi idrotermali, *Rend. Soc. It. Min. Petrol.*, *36*, 253-260.

Chevrier, R.M., and F. Le Guern (1982), Prélèvement et analyses des condensats de fumerolles sur volcans actifs: Soufrière de la Guadeloupe (1976-1977) et Pouzzoles et Vulcano (Italie) (1978), *Bull. Volocanol.*, *45*, 173-178.

Chiodini, G., R. Cioni, and L. Marini (1993), Reactions governing the chemistry of crater fumaroles from Vulcano Island, and implications for volcanic surveillance, *Appl. Geochem.*, *8*, 357-371.

Chiodini, G., R. Cioni, L. Marini, and C. Panichi (1995), Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance, *Bull. Volocanol.*, *57*, 99-110.

Clocchiatti, R., A. Del Moro, A. Gioncada, J.L. Joron, M. Mosbah, L. Pinarelli, and A. Sbrana (1994), Assessment of shallow magmatic system : the 1888-90 eruption, Vulcano Island, Italy, *Bull. Volocanol.*, *56*, 466-486.

Cortecci, G., E. Dinelli, L. Bolognesi, T. Boschetti, and G. Ferrara (2001), Chemical and isotopic compositions of water and dissolved sulfate from shallow wells on Vulcano Island, Aeolian Archipelago, Italy, *Geothermics*, *30*, 69-91.

De Astis, G., L. La Volpe, A. Pecerrillo, and L. Civetta (1997), Volcanological and petrological evolution of Vulcano island (Aeolian Arc, southern Tyrrhenian Sea), *J. Geophys. Res.*, *102* (B4), 8021-8050.

De Astis, G., A. Peccerillo, P.D. Kempton, L. La Volpe, and T.W. Wu (2000), Transition from calc-alkaline to potassium-rich magmatism in subduction environments: geochemical and Sr, Nd, Pb isotopic constraints from the island of Vulcano (Aeolian arc), *Contrib. Mineral. Petrol.*, *139*, 684-703.

Del Moro, A., A. Gioncada, L. Pinarelli, A. Sbrana, and J.L. Joron (1998), Sr, Nd, and Pb isotope evidence for open system evolution at Vulcano, Aeolian Arc, Italy, *Lithos*, *43*, 81-106.

Deniel, C., and C. Pin (2001), Single stage method for the simultaneous isolation of lead and strontium from silicate materials for isotopic measurements, *Anal. Chim. Acta*, *426*, 95-103.

Dessert, C. (2002), Ph.D. Thesis, Impact du Volcanisme sur le climat et sur les cycles géochimiques globaux, Université Paul Sabatier, Toulouse, France

Dongarra, G., S. Hauser, G. Capasso, and R. Favara (1988), Characteristics of variations in water chemistry of some wells from Vulcano island, *Rend. Soc. It. Min. Petrol.*, *43*, 1123-1131.

Dongarra, G., and D. Varrica (1998), The presence of heavy metals in air particulate at Vulcano island, *Sci. Total Environ.*, *212*, 1-9.

Doucelance, R., and G. Manhès (2001), Reevalution of precise lead isotope measurements by thermal ionisation mass spectrometry: comparison with determinations by plasma source mass spectrometry., *Chem. Geol.*, *176*, 361-377.

Ellam, R.M., C.J. Hawkesworth, M.A. Menzies, and N.W. Rogers (1989), The Volcanism of Southern Italy: Role of Subduction and the Relationship Between Potassic and Sodic Alkaline Magmatism, *J. Geophys. Res.*, *94* (B4), 4589-4601.

Esperança, S., G.M. Crisci, R. de Rosa, and R. Mazzuoli (1992), The role of crust in the magmatic evolution of the island of Lipari (Aeolian Islands, Italy), *Contrib. Mineral. Petrol.* (112), 450-462.

Ferrara, G., A. Garavelli, L. Pinarelli, and F. Vurro (1995), Lead isotope composition of the sublimates from the fumaroles of Vulcano (Aeolian Islands, Italy): inferences on the deep fluid circulation, *Bull. Volocanol.*, *56*, 621-625.

Freydier, R., and J. Viers (2003), Isotopic study of lead transfer at the interface soil-plants-atmosphere, *Geophys. Res. Lett.*, *30* (5), 1227.

Giggenbach, W.F. (1988), Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators, *Geochim. et Cosmochim. Acta*, *52*, 2749-2765.

Gioncada, A., R. Mazzuoli, M. Bisson, and M.T. Pareschi (2003), Petrology of volcanic products younger than 42ka on the Lipari-Vulcano complex (Aeolian Island, Italy): an example of volcanism controlled by tectonics, *J. Volcanol. Geotherm. Res.*, *122*, 191-220.

Goff, F., H.A. Wollenberg, D.C. Brookins, and R.W. Kistler (1991), A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California, *J. Volcanol. Geotherm. Res.*, *48*, 265-281.

Grousset, F.E., M. Parra, A. Bory, P. Martinez, P. Bertrand, G. Shimmield, and R.M. Ellam (1998), Saharan wind regimes traced by the Sr-Nd isotopic composition of subtropical atlantic sediments: late glacial maximum vs today, *Quat. Sci. Rev.*, *17*, 395-409.

Harris, A.J.L., and A.J.H. Maciejewski (2000), Thermal surveys of the Vulcano Fossa fumarole field 1994-1999: evidence of migration and sealing., *J. Volcanol. Geotherm. Res.*, *102*, 119-147.

Hinkley, T.K. (1991), Distribution of metals between particulate and gaseous forms in a volcanic plume, *Bull. Volocanol.*, *53*, 395-400.

Keller, J., (1980)The Island of Vulcano, in *The Aeolian Islands-An active Volcanic Arc in the Mediterranean Sea.*, edited by L. Villari, pp. 369-414, Rendiconti della Società Italiana di Mineralogia e Petrologia.

Krom, M.D., R.A. Cliff, L.M. Eijsink, B. Herut, and R. Chester (1999), The characterisation of saharan dusts and Nile particulate matter in surface sediments from the Levantine basin using Sr isotopes., *Mar. Geol.*, *155*, 319-330.

Leeman, W.P., S. Tornarini, M. Penissi, and G. Ferrara (2005), Boron isotopic variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: Implications for evelution of volcanic fluids, *Geochim. et Cosmochim. Acta*, *69* (1), 143-163.

Martini, M. (1980), Geochemical Survey on the Phreatic Waters of Vulcano (Aeolian Islands, Italy), *Bull. Volocanol.*, *43* (1), 265-274.

Möller, P., P. Dulski, Y. Savascin, and M. Conrad (2004), Rare earth elements, yttrium and Pb isotope ratios in thermal spring and well waters of West Anatolia, Turkey: a hydrochemical study of their origin, *Chem. Geol.*, *206*, 97-118.

Monna, F., A. Aiuppa, D. Varrica, and G. Dongarra (1999), Pb Isotope Composition in Lichens and Aerosols from Eastern Sicily : Insight into the Regional Impact of Volcanoes on the Environment, *Environ. Sci. Technol.*, *33*, 2517-2523.

Monna, F., J. Lancelot, I.W. Croudace, A.B. Cundy, and J.T. Lewis (1997), Pb Isotopic Composition of Airborne Particulate Material from France and Southern United Kingdom : Implications for Pb Pollution Sources in Urban Areas, *Environ. Sci. Technol.*, *31* (8), 2277-2286.

Negrel, P., and S. Roy (1998), Chemistry of rain water in the Massif Central (France): a strontium isotope and major element study, *Appl. Geochem.*, *13* (8), 941-952.

Panichi, C., and P. Noto (1992), Isotopic and chemical composition of water, steam and gas samples of the natural manifestations of the island of Vulcano (Aeolian Arc, Italy), *Acta Vulcanol.*, *2*, 297-312.

Pennisi, M., W.P. Leeman, S. Tonarini, A. Penissi, and P. Nabelek (2000), Boron, Sr, O and H isotope geochemistry of grounwaters from Mt. Etna (Sicily) - Hydrologic implications, *Geochim. et Cosmochim. Acta*, *64* (6), 961-974.

Piccardi, G., M. Martini, and P. Cellini Legittimo (1979), On the presence of Cu, Zn, Cd, Sb, Bi and Pb in the fumarolic gases of Vulcano (Aeolian island), *Rend. Soc. It. Min. Petrol.*, *35* (2), 627-632.

Quisefit, J.P., J.P. Toutain, G. Bergametti, M. Javoy, B. Cheynet, and A. Person (1989), Evolution versus cooling of gaseous volcanic emmissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations, *Geochim. et Cosmochim. Acta*, *53*

Sommaruga, C. (1984), Le ricerche geotermiche svolte a Vulcano negli anni '50, *Rend. Soc. It. Min. Petrol.*, *39*, 355-366.

Symonds, R.B., Y. Mizutani, and P.H. Briggs (1996), Long term geochemical surveillance of fumaroles at Showa-Shinzan dome, Uzu volcano, Japan, *J. Volcanol. Geotherm. Res.*, *73*, 177-211.

Symonds, R.B., W.I. Rose, M.H. Reed, F.E. Lichte, and D.L. Finnegan (1987), Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia., *Geochim. et Cosmochim. Acta*, *51*, 2083-2101.

Taran, Y.A., J.W. Hedenquist, M.A. Korzhinsky, S.I. Tkachenko, and K.I. Shmulovich (1995), Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands, *Geochim. et Cosmochim. Acta*, *59* (9), 1749-1761.

Tedesco, D. (1997), Systematic variations in the $^{3}He/^{4}He$ ratio and carbon of fumarolic fluids from active volcanic areas in Italy: Evidence for radiogenic ^{4}He and crustal carbon addition by the subducting African plate?, *Earth Planet. Sci. Lett.*, *151*, 255-269.

Tedesco, D., G. Miele, Y. Sano, and J.P. Toutain (1995), Helium isotopic ratio in Vulcano island fumaroles: temporal variations in shallow level mixing and deep magmatic supply, *J. Volcanol. Geotherm. Res.*, 117-128.

Toutain, J.P., F. Sortino, B. Reynier, B. Dupre, M. Munoz, A. Nonell, M. Polve, and S. Chancha Do Vale (2003), A new collector for sampling volcanic aerosols, *J. Volcanol. Geotherm. Res.*, *123* (1-2), 95-103.

Vallelonga, P., and T.A. Mather (2003), Lead (Pb) fluxes and Pb isotopic compositions from Masaya Volcano, Nicaragua, *Atmos. Envir.*, *37*, 4453-4460.

Van der Lee, J., and L. De Windt,(2000), *CHESS Tutorial and Cookbook. Updated for version 3.0. User Manual Nr. LHM/RD/02/13. Ecole des Mines de Paris, Fontainebleau, France.,*

Yuan-Hui, L. (1991), Distribution patterns of the elements in the ocean: A synthesis, *Geochim. et Cosmochim. Acta*, *55*, 3223-3240.

Figure captions

Fig .1. Geographic location of Vulcano Island and sampling sites, modified from *Bolognesi and D'Amore* [1993]. Groudwaters (square plot) and fumaroles (triangle plot) sampling sites are shown.

Fig .2. Ternary plot (Cl, SO_4, HCO_3) for thermomineral waters of Vulcano Island.

Fig .3. $^{87}Sr/^{86}Sr$ ratios vs. Sr (µg/kg) in acid condensates (triangle plot) and thermomineral waters (square plot) from Vulcano Island. The seawater value (round plot) is taken from the study of *Pennisi et al.* [2000]. The clear shaded area corresponds to the MW range whereas the dark shaded area corresponds to the rock values from literature (see text for details). Vulcano rocks extreme isotopic values are from *De Astis et al.* [1997] and *De Astis et al.* [2000]. The Sr concentrations and isotopic compositions of fluid samples are related both to the intensity of rock leaching (horizontal arrow) and to the influence of SW and MW (vertical arrows).

Fig .4. $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ in acid condensates (triangle plot) and thermomineral waters (square plot) from Vulcano Island. In this type of diagram, any linear trend can be interpreted in terms of mixing between two end-members. The shaded area includes Vulcano rock data [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997; *De Astis et al.*, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003]. The range of town and industrial airborne in the Sicily area (arrow) is also plotted for comparative purposes [*Monna et al.*, 1999].

Table.1 Major elements composition (mg/kg), T(°C), pH, Eh(mV) and Total Dissolved Solids (TDS (mg/kg)) in Vulcano island groundwaters. n.d. stands for non determined. Sampling dates are also shown.

Water well	No.	Date	T	pH	Eh	SO4	Cl	F	Alk	Na	K	Ca	Mg	TDS
Chloride-rich waters														
Istmo	W1	24.02.2001	61.0	5.7	-361	2863	19834	2	694	11214	655	600	1341	35862
Steam-heated waters														
Piscio	W2	24.02.2001	27.3	7.1	194	1713	287	4	357	383	152	438	61	3333
Vasca	W3	24.02.2001	81.0	1.1	-47	8210	1511	7	0	1071	379	255	180	11433
Rifici	W4	24.02.2001	31.0	6.7	186	1787	430	3	409	314	161	602	89	3705
Volcanic groundwaters														
C.Sicilia	W5	24.02.2001	49.5	7.6	161	1704	2084	9	411	1656	627	140	88	6631
C.Sicilia	W6	18.05.1999	56.4	7.5	n.d.	1962	1788	8	390	1469	463	95	71	6176
Shallow groundwaters														
Centro	W7	24.02.2001	21.2	6.9	33	328	411	14	405	348	90	88	32	1685
Centro	W8	20.05.1999	22.0	6.7	n.d.	418	366	13	210	352	80	88	33	1527

Table.2 Sr and Pb concentrations (µg/kg) and isotopic compositions of Vulcano island groundwaters. (*) Results corrected for blank contribution (see text).

No.	Sr	Pb	$^{87}Sr/^{86}Sr$	2 S.D	$^{206}Pb/^{207}Pb$	2 S.D	$^{208}Pb/^{206}Pb$	2 S.D	$^{206}Pb/^{204}Pb$	2 S.D
W1	9731.8	0.78	0.70799	0.00001						
W2	635.9	5.4	0.70474	0.00001	1.1437*	0.0009*	2.1184*	0.0013*	17.750*	0.026*
duplicate			0.70473	0.00001						
W3	3710.2	89.6	0.70516	0.00001	1.1576*	0.0004*	2.1056*	0.0016*	18.017*	0.018*
W4	1106.7	3.0	0.70466	0.00001						
duplicate			0.70466	0.00001						
W5	3608.2	0.84	0.70462	0.00001						
duplicate			0.70461	0.00001						
W6	2154.2	1.3	0.70463	0.00001						
W7	6.7	0.15	0.70619*	0.00001*						
W8	4.4	0.18	0.70601*	0.00001*						
duplicate			0.70616	0.00001						

Table.3 Main Sr and Pb chemical species in 2001 Vulcano Island groundwaters. Calculated saturation indexes with respect to Sr and Pb mineral phases (log(SI)>-5) are also shown.

	W1	W2	W3	W4	W5	W7
Aqueous species (µg/kg)						
Sr^{2+}	8521	424	3650	761	2654	5.7
$SrCl^{+}$	1698	1.2	84	3.3	61	*<0.1*
$SrSO_4$	*<0.1*	439	*<0.1*	717	1868	1.9
Pb^{2+}	*<0.1*	1	52	1.2	0.05	0.03
$PbCl_2$	0.46	*<0.1*	6	*<0.1*	*<0.01*	*<0.01*
$PbCl^{+}$	0.3	0.1	38	0.2	0.04	*<0.01*
$PbCl_3^{-}$	0.14	*<0.1*	*<0.1*	*<0.1*	*<0.01*	*<0.01*
$PbCO_3$	*<0.1*	5.4	*<0.1*	2	0.9	0.14
Mineral phases saturation indexes (log(SI))						
Strontium minerals						
SrF_2	-4.5	-4.7	*<-5*	-4.7	-3.3	*<-5*
Strontianite ($SrCO_3$)	*<-5*	-0.59	*<-5*	-0.84	0.78	-2.56
Celestite ($SrSO_4$)	*<-5*	-2.25	*<-5*	-2	-1.46	-4.6
Lead minerals						
Cerussite ($PbCO_3$)	*<-5*	-0.74	*<-5*	-1.19	-1.65	-2.3
Galena (PbS)	6.3	*<-5*	0.27	*<-5*	*<-5*	*<-5*
Pb	-2.8	*<-5*	*<-5*	*<-5*	*<-5*	*<-5*
Alamosite ($PbSiO_3$)	*<-5*	-2.7	*<-5*	-3.4	-2.9	-4.9
Anglesite ($PbSO_4$)	*<-5*	-3	*<-5*	-3	-4.5	-5
Paralauriaunite (PbCl(OH))	*<-5*	-4	*<-5*	-4.1	-4	*<-5*
Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$)	*<-5*	-4.1	*<-5*	*<-5*	*<-5*	*<-5*
Lanarkite ($Pb_2(SO_4)O$)	*<-5*	-4.8	*<-5*	*<-5*	*<-5*	*<-5*

Table 4. Sr and Pb concentrations (µg/kg) and isotopic compositions in Vulcano fumarolic gases. (*) Results corrected for blank contribution (see text). Sr and Pb enrichment factors (EF) with respect to Al are also shown (see text). The vent temperature T(°C) and the collection date are also listed. F0, F11, FA and FR2 refer to the classical denomination of fumaroles used at Vulcano (See text).

Fumarolic vent	No.	Date	T	Sr	Pb	EF_{Sr}	EF_{Pb}	$^{87}Sr/^{86}Sr$	2 S.D	$^{206}Pb/^{207}Pb$	2 S.D	$^{208}Pb/^{206}Pb$	2 S.D	$^{206}Pb/^{204}Pb$	2 S.D
F11	G1	23.02.2001	365	17.6	1392.8	0.5	$8x10^2$	0.70520*	0.00001*	1.2349	0.0010	2.0397	0.0013	19.531	0.131
F11	G2	28.05.2000	410	46.8	828.3			0.70530*	0.00005*						
F11	G3	19.05.1999	446	1.4	127.6					1.1780	0.0001	2.0756	0.0002	18.407	0.036
duplicate								0.71009*	0.00002*	1.1782	0.0007	2.0754	0.0026	18.413	0.023
duplicate								0.71008*	0.00003*	1.1789	0.0007	2.0727	0.0025	18.386	0.026
FA	G4	23.02.2001	363	6.4	692.5	0.5	$1.2x10^3$			1.2379*	0.0004*	2.0319*	0.0013*	19.445*	0.011*
FA	G5	28.05.2000	404	151.7	7470.3			0.70507	0.00001	1.2396	0.0001	2.0352	0.0003	19.448	0.003
F0	G6	23.02.2001	307	34.8	1289.6	0.4	$3x10^2$	0.70502*	0.00001*	1.2355	0.0003	2.0365	0.0013	19.457	0.010
F0	G7	27.05.2000	313	8.4	90.3			0.70848*	0.00004*	1.1859	0.0001	2.0717	0.0002	18.539	0.003
F0	G8	20.05.1999	343	41.9	7968.5			0.70487*	0.00002*	1.2352	0.0001	2.0314	0.0003	19.388	0.003
FR2	G9	21.05.1999	104	3.7	335.9					1.2320	0.0004	2.0346	0.0004	19.344	0.005

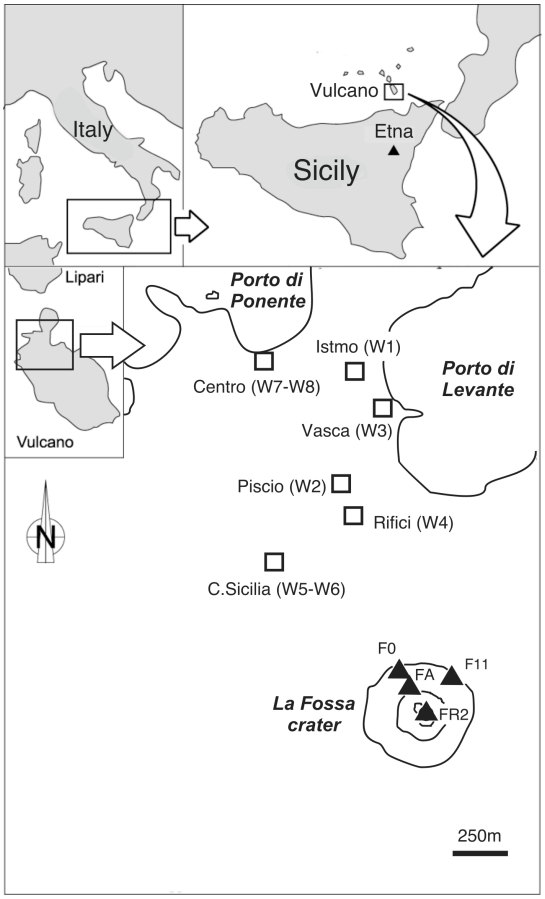

FIG. 1

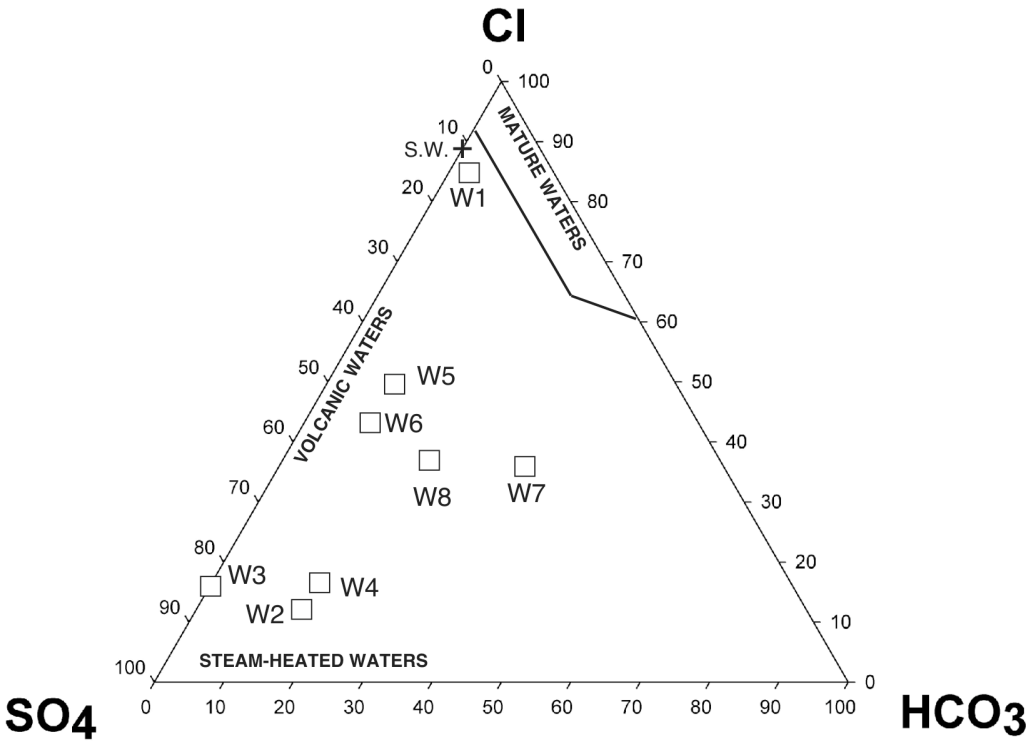

FIG. 2

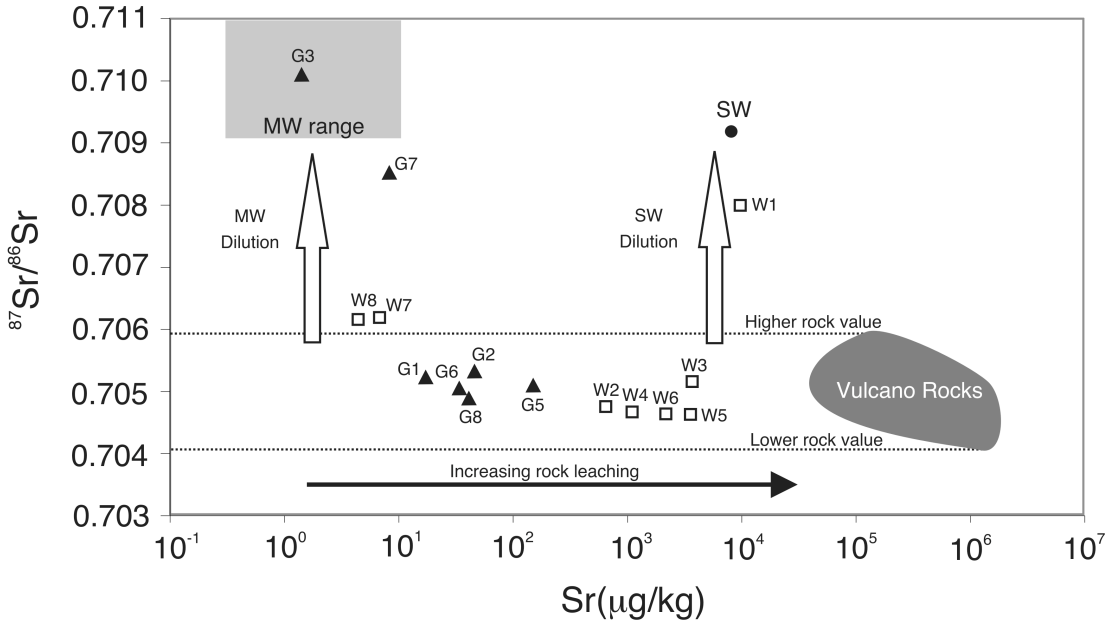

FIG.3

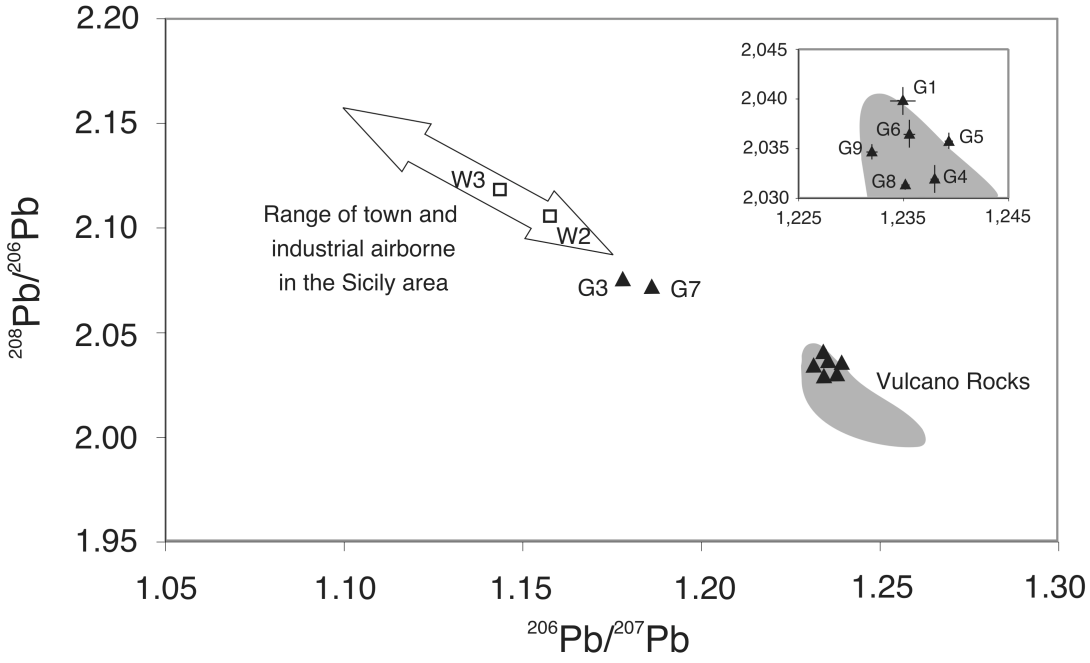

FIG.4

Chapitre 4:
Variations isotopiques du Zn dans les gaz volcaniques, les sublimés et les roches du Merapi (Indonésie)

IV-1 VERSION ABREGEE DE L'ARTICLE EN FRANÇAIS

Rappel : Le Zinc étant susceptible de fractionner lors du prélèvement des gaz fumeroliens, plusieurs techniques d'échantillonnage (condensat acide, ampoules NH_4OH) ont été utilisées dans cette étude afin d'évaluer l'impact du mode de prélèvement sur les compositions isotopiques mesurées.

Remarque : Il est très difficile d'analyser précisément les concentrations du Zn dans les ampoules NH_4OH par ICP-MS quadrupolaire. En effet, l'ensemble de ses isotopes sont interférés par le soufre présent en quantité dans ces solutions. La connaissance précise de ces concentrations est cependant nécessaire pour l'obtention de données isotopiques fiables (contribution des blancs, rendements d'élution…). Grâce à la procédure de correction d'interférences présentée dans le chapitre 2, les concentrations en Zn ont pu être déterminées précisément sur 3 échantillons NH_4OH qui sont utilisés dans ce travail.

IV-1-1 Introduction

L'apparition récente des spectromètres de masse à source plasma induit et multi-collecteurs (MC-ICP-MS) a rendu possible l'étude des variations des isotopes stables des éléments de masse moyenne et lourds. Des travaux récents montrent que l'étude de ces variations fournit des informations premières importances dans plusieurs domaines scientifiques comme la géochimie, la cosmochimie, la biochimie ou encore la médecine [*Galy et al.*, 2001; *Marechal et al.*, 1999; *Pichat et al.*, 2003; *Poitrasson et al.*, 2004; *Rehkämper et al.*, 2004; *Rouxel et al.*, 2004; *Viers et al.*, 2004; *Weiss et al.*, 2005]. Cependant, les bases de données concernant ces nouveaux isotopes stables sont encore très incomplètes. De même, la compréhension des processus responsables de ces variations reste limitée.

Les volcans actifs sont des sites potentiellement privilégiés pour l'étude de ces variations en contexte naturel. En effet, les processus complexes rencontrés dans ce type de sites, comme les changements de phase ou les mélanges entre fluides d'origines variées, sont susceptibles d'engendrer d'importantes variations dans la composition isotopique de ces nouveaux isotopes stables.

Dans ce cadre, nous avons effectué les premières mesures des compositions isotopiques de Zn dans les gaz volcaniques, les roches et les sublimés (phases minérales condensées lors du refroidissement des gaz volcaniques). Nous avons choisi d'étudier le Zn car celui-ci est présent en quantités significatives dans l'ensemble de ces échantillons. De plus, cet élément est peu sensible aux changements des conditions d'oxydoréduction (le degré d'oxydation +2 étant très largement dominant dans la nature) ce qui nous permet de restreindre les causes possibles des variations isotopiques observées.

L'objectif de ce travail, réalisé sur des échantillons prélevés au Merapi entre 2001 et 2002, est de documenter les bases de données sur la variabilité isotopique naturelle de cet élément et d'identifier les causes possibles (fractionnement isotopique, effets de source) des variations observées.

IV-1-2 Résultats

Les résultats présentés dans ce travail ont été obtenus par ICP-MS quadrupolaire et INAA pour la détermination des concentrations de Zn dans les échantillons, et par MC-ICP-MS (Plasma 54 et Neptune) pour la détermination des compositions isotopiques Zn.

. *Variations isotopiques Zn :*

D'importantes variations isotopiques Zn ont été observées entre les différents échantillons analysés (0.82‰ par unité de masse atomique). L'ensemble des résultats obtenus est présenté dans la Table 4., page 135. Dans les échantillons de gaz, les compositions isotopiques (exprimées en notation classique $\delta^{66/64}$Zn) varient de 0.05 à 0.85‰. Dans les sublimés, les signatures isotopiques observées sont sensiblement plus élevées avec des valeurs comprises entre 1.48 et 1.68‰. Les échantillons de roches présentent quant à eux des signatures très homogènes, avec une valeur moyenne de 0.24‰.

.*Origine des variations observées :*

Deux couples condensat acide/ampoules NH_4OH (311°C et 590°C) fournissent des compositions isotopiques équivalentes alors que le troisième (574°C) présente une variation isotopique plus significative entre les 2 techniques d'échantillonnage (≈0,3‰). Même si ces résultats ne semblent pas pouvoir modifier significativement nos interprétations, il est nécessaire à ce stade d'entreprendre des systématiques de comparaison sur un plus grand

nombre d'échantillons afin de quantifier précisément l'impact du mode de prélèvement sur les compositions isotopiques mesurées.

Les résultats obtenus dans les gaz (prélevés pendant la saison sèche) et les sublimés indiquent une claire dépendance de la composition isotopique Zn en fonction de la température (Fig 4, page 138). Les gaz volcaniques s'appauvrissent en isotope lourd lors de la décroissance de température, tandis qu'un effet opposé est observé pour les sublimés. Ces résultats semblent en accord avec un processus de fractionnement isotopique à l'équilibre (Fig 5, page 138) lors de la formation des sublimés.

Les données suggèrent aussi que la phase gazeuse de haute température s'enrichit en isotope lourd par rapport au magma lors du dégazage magmatique. Cet effet a déjà été observé pour les isotopes légers H, B, C, et peut être expliqué par une diminution de la coordinance du Zn entre le liquide silicaté (coordinance 8 ou 4) et la phase gazeuse (coordinance 2).

IV-1-3 Conclusion

Des variations significatives des compositions isotopiques Zn ont été mesurées entre les roches, les gaz fumeroliens et les sublimés échantillonnés sur le Merapi entre 2001 et 2002. Ces variations semblent induites par des fractionnements isotopiques lors des processus de changement de phase. Dans le contexte de ce travail, les effets de source ou d'échantillonnage ne semblent pas êtres susceptibles de modifier significativement ces interprétations. Les compositions isotopiques des sublimés sont significativement différentes par rapport aux données de la littérature obtenues sur divers gisements métallifères. De plus elles semblent dépendre de leurs températures de condensation. Si cette dépendance en température est confirmée, il est possible d'envisager l'utilisation des isotopes du Zn comme géothermomètres. Ce type d'application peut fournir de précieux renseignements sur les conditions de formations des gîtes minéraux et sur le comportement des éléments métalliques dans les fluides magmatiques de haute température.

IV-2 EVIDENCE FOR ZN ISOTOPIC VARIATIONS AT MERAPI ACTIVE VOLCANIC SYSTEM

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Evidence for Zn isotopic variations at Merapi active volcanic system.

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Abstract

Fumarolic gases, rocks and sublimates samples from Merapi volcano (Indonesia) have been analysed by multiple collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) for their Zn isotopic compositions. The variation observed, expressed as $\delta^{66}Zn$ ($\delta^{66}Zn=[(^{66}Zn/^{64}Zn)_{sample}/(^{66}Zn/^{64}Zn)_{JMC\ 3\text{-}049L}-1]\times10^3$) are ranging from 0.05 to 1.68‰. The overall reproducibility was found to be better than 0.09‰. The $\delta^{66}Zn$ of andesitic rock samples are homogeneous with a mean value of 0.24‰, which is comparable to previously reported basalt data. $\delta^{66}Zn$ are ranging from 0.05 to 0.85‰ and 1.48 to 1.68‰ in fumarolic gases and sublimates, respectively. The gas phase is depleted in the heavy Zn isotopes upon gas cooling whereas increasing values of $\delta^{66}Zn$ in sublimates phases were found to be associated with their decreasing temperature of formation. We infer that the variations observed between magma, gas and sublimates samples result mainly from mass dependent isotopic fractionation processes occurring during magma degassing and gas-particule condensation.

1. Introduction

Investigations on non-traditional stable isotopes [*Reviews in Mineralogy*, 2004] are now possible due to the recent development of multiple-collector inductively coupled mass spectrometry (MC-ICP-MS) which combines the high ionisation efficiency of the ICP sources to the flat top peaks produced by magnetic-sector mass spectrometers. This innovative technology enables high precision measurements (<0.1‰) of these isotopic variations whereas reproducibility better than 1‰ are difficult to achieve with earlier analytical techniques such as thermal ionisation mass spectrometry or ion microprobe. Recent studies in geochemistry, cosmochemistry, biochemistry or marine chemistry, display suitable analytical procedures and initiated the exploration of "non-traditional" isotopic sytems. Up to date, results concern Mg [*Galy et al.*, 2001; *Galy et al.*, 2000], Ti [*Zhu et al.*, 2002b], Ca [*Halicz et al.*, 1999], Fe [*Anbar*, 2004; *Poitrasson et al.*, 2004; *Poitrasson et al.*, 2005; *Rouxel et al.*, 2003a; *Zhu et al.*, 2001; *Zhu et al.*, 2002a], Se [*Rouxel et al.*, 2004; *Rouxel et al.*, 2002], Mo [*Barling et al.*, 2001], Tl [*Nielsen et al.*, 2004; *Rehkämper et al.*, 2004; *Rehkämper et al.*, 2002; *Rehkämper and Halliday*, 1999], Te [*Fehr et al.*, 2004], Cd [*Wombacher et al.*, 2004; *Wombacher et al.*, 2003], Sb [*Rouxel et al.*, 2003b], Ge [*Hirata*, 1997] or Cu and Zn [*Archer and Vance*, 2004; *Bermin et al.*, 2004; *Büchl et al.*, 2004; *Cloquet*, 2005; *Luck et al.*, 1999; *Luck et al.*, 2003; *Marechal*, 1998; *Marechal et al.*, 2000; *Marechal et al.*, 1999; *Mason et al.*, 2004a; *Mason et al.*, 2004b; *Pichat et al.*, 2003; *Viers et al.*, 2004; *Weiss et al.*, 2005; *Zhu et al.*, 2002a; *Zhu et al.*, 2000]. Significant isotope variations, induced by various processes such as sources effects or mass dependent isotopic fractionation, were observed in almost all cases. However, the databases concerning these stable isotopic systems are incomplete. In addition, progresses have to be made on the description of the processes responsible of the isotopic variations observed.

Active volcanoes should be privileged sites to study such natural isotopic variations. Indeed, volcanic gases are emitted during magma degassing as the result of supersaturation of species in the magma. En route to the surface, volcanic fluids are submitted to steep physical and chemical gradients (T, fO_2) and are involved in complex processes such as wall rock leaching or mixing with other fluids such as meteoric water or sea water [*Nonell et al.*, 2005]. During gas migration, mineral deposits (sublimates, incrustations) are partitioned from the gas phase as the result of gas cooling and condensation [*Bernard*, 1985; *Quisefit et al.*, 1989; *Symonds et al.*, 1987]. Such complex interactions and phase changing processes might induce

significant isotopic variations between the different components (magma-gas-minerals). A "non traditional" stable elements study of these components should therefore provide important insights for a better understanding of the origin of the natural isotopic variations of these elements.

In this work, we performed Zn isotopic measurements in fumarolic gas, sublimates and andesitic rocks samples from Merapi volcano (Indonesia). Zn was chosen because of its significant concentrations in magma, fumarolic gases, aerosols, sublimates and incrustations of many active volcanoes [*Symonds et al.*, 1987; *Taran et al.*, 2001; *Taran et al.*, 1995; *Toutain et al.*, 2003]. In addition, Zn is weakly redox sensitive due to its dominant oxidation state (+2), which helps to restrict the possible causes of isotopic variations [*Albarède*, 2004]. Zinc has five stable isotopes with masses 64, 66, 67, 68 and 70 and average abundances 48.63%, 27.90%, 4.10%, 18.75% and 0.62%, respectively [*Rosman and Taylor*, 1998]. Among the non-traditional stable isotopes [*Reviews in Mineralogy*, 2004], Zn displays little but significant isotopic variations (0.84‰ per amu, including analytical precision) in terrestrial samples [*Weiss et al.*, 2005]. [*Marechal*, 1998; *Marechal et al.*, 1999] described reliable chemical separation and mass spectrometry procedures to investigate Cu and Zn isotopic variations and published the first precise Cu and Zn isotopic compositions in various natural samples, including ores, biological samples and marine particles. Several following studies of Zn isotopic compositions in terrestrial samples are summarized in Fig.1. However, the Zn isotopic database is clearly incomplete and very little is known about the origin of Zn isotopic variations [*Albarède*, 2004]. The aim of this work is to document Zn isotopic variations upon volcanic degassing processes in order to complete the description of Zn isotopic variations in earth material and to identify the possible mass dependent isotopic fractionation and/or source effects responsible for these variations.

2. Magmatic gases and sublimates at Merapi

Merapi (2965 m a.s.l) is an andesitic stratovolcano located in central Java (Fig 2.). High temperature gases (up to 900°C) are continuously emitted from the two main fumarolic fields: Gendol, and Woro [*Le Guern and Bernard*, 1982; *Symonds et al.*, 1987]. Historical eruptions, hazard evaluation and volcanic processes are rewiewed in [*Voight et al.*, 2000a]. Recent eruptive activity is characterized by successive formation and collapse of an andesitic dome [*Ratdomopurbo and Poupinet*, 2000; *Voight et al.*, 2000b] generating lava and pyroclastic

flows. Early data on high temperature gases and sublimates phases are available [*Bernard*, 1985; *Le Guern and Bernard*, 1982; *Symonds*, 1993; *Symonds et al.*, 1987]. The gas phase is mainly composed of H_2O and CO_2 with minor amounts of H_2S, SO_2, HCl, HF, trace gases and metal species originated mainly from shallow magma degassing at 915°C [*Symonds et al.*, 1987]. Thermodynamic calculations indicate that metals (including Zn) are mainly transported as chloride species in the gas phase. Silica tubes sublimates, which are more representative of naturally condensing species in the ground than incrustations sampled at the vents were also collected at Merapi [*Bernard*, 1985; *Le Guern and Bernard*, 1982; *Symonds*, 1993; *Symonds et al.*, 1987]. A summary of the mineral phases identified is presented in Table.1. In these solid deposits, Zn was detected as an enriched minor element in hercinite, K-Ca sulfate, acmite, aphtitalite and Na-K-Fe sulfate. A specific Zn compound ($ZnS_{(S)}$) was identified at temperature around 300-600°C, which is in accord with thermodynamic modelling [*Symonds et al.*, 1987]. A Zn sulphate mineral ($Zn_3(SO_4)(Cl,OH)_4$) was also identified at lower T°C in the 1984 silica tube, probably as the result of more oxidizing conditions due to atmospheric contamination.

3. Sample collection

3.1.Gas samples

Eight gas condensates were collected at Woro fumarolic field in 2001-2002. Fumarolic gases were channelled through a silica tube to a condensor constituted by a reception balloon coupled with an acetone-cooler [*Chevrier and Le Guern*, 1982]. In order to insure a continuous flow of gas, a weak and constant depression was applied with a hand-pump allowing the fast condensation of water, acid gases and associated trace elements. Three fumaroles were also sampled during the same periods by using NH_4OH bottles. These are 600ml quartz flasks pre-washed with double distilled HNO_3 and 4N ultra-pure NH_4OH partially filled with 100cc of Merck ultra-pure NH_4OH and then putted under vacuum. This new sampling technique derived from [*Giggenbach*, 1975] allows the complete collection of gas in closed system [*Sortino et al.*, submitted]. Gas condensates and NH_4OH samples were stored in double distilled HNO_3 pre-washed PP bottles before laboratory treatment.

3.2.Silica tube sublimates and rock samples

In 2001, a silica tube (0.7m long and 3cm of inner diameter) was inserted during three days in a 495°C fumarole of Woro fumarolic field selected with respect to the stability of the gas flux and outlet temperature. The temperature range inside the tube was 495-275°C. In the

laboratory, the silica tube was cut in different sections. No sublimates were observed in the high temperature section W0 (0-16 cm). A thin grey/black deposit was observed in the W1 (16-27cm) section, but amounts were too low to allow the complete analyses of solids. In the following sections W2 (27-38 cm), W3 (38-46 cm), W4 (46-57cm) and W5 (57-70 cm), black solid deposits were observed together with yellow/orange deposits, the latter becoming dominant towards the low temperature sections (W4 and W5). We analysed also four rock samples from the 1883 (R1), 1940 (R2), 1954 (R3) and 1994 (R4) lava flows.

4. Analytical procedures

4.1. Solid samples preparation

Sublimates were collected from the inner wall of the tube by using a teflon spatula and crushed in a MilliQ pre-washed agate mortar. Parts of the powdered samples were washed with MilliQ water and carefully dried at 50°C to collect the non-soluble fraction. Bulk and non-soluble fractions were analysed by X-ray diffraction. Bulk fractions were also analysed by Instrumental Neutron Activation Analysis (INAA) for the determination of Zn concentrations. In order to check the homogeneity of the powdered samples, up to four INAA duplicate analyses were performed for each sections. The overall reproducibility of INAA measurements is in the range 5-10% (2σ). Rock samples were crushed in an agate mortar as described above.

4.2. Gas samples preparation

Gas samples (condensates and NH_4OH solutions) were centrifuged in double distilled HCl pre-washed PP tubes in order to remove ashes and solid S. Zn contamination associated with the centrifugation procedure was estimated to ≈ 0.2ng/ml of sample, corresponding to a blank contribution <0.2% with respect to the total amount of Zn in gas samples. Centrifuged gas condensates were diluted in double distilled 2% HNO_3 and analysed by ICP-MS (Elan 6000, Perkin-Elmer SCIEX) for Zn concentrations. NH_4OH samples were oxidized by using suprapur H_2O_2 and diluted with double distilled HNO_3 prior to ICP-MS measurements performed following the procedure described in [*Sortino et al.*, submitted]. The amount of solutions required for MC-ICP-MS measurements was carefully dried at 80°C before Zn isolation procedure.

4.3. Sample treatment for Zn analyses

Powdered residues (sublimates + rocks) and dried gas samples were submitted to hydrogen peroxide (H_2O_2) and acid digestions (HF + HNO_3 and HCl + HNO_3) allowing a total dissolution of samples and were then dried. Each sample was subsequently dissolved in 1ml of double distilled 7N HCl prior to chemical separation. Zn was isolated from the bulk sample following the purification procedure of [*Marechal et al.*, 1999] on AGMP-1 anion exchange resin (Biorad, USA). An overall procedural blank (dissolution + chemical separation) was measured by ICP-MS for each batch of 8 samples. Zn blanks were found to be less than 10ng, corresponding to a blank contribution < 1% with respect to the total amount of Zn analysed. Because isotopic fractionation may occur during the elemental separation on the ion-exchange resin [*Marechal and Albarède*, 2002], yields of the dissolution and chemical separation procedure were controlled by ICP-MS and were found to be close to 100%, taking into account ICP-MS measurements uncertainties (≈ 5%).

4.4. Mass spectrometry

Zn isotopic measurements were performed in Lyon (Ecole Normale Supérieure) on a Plasma 54 MC-ICP-MS (Fisons Instruments) and in Toulouse on a Thermo-Finnigan Neptune MC-ICP-MS. The Plasma 54 instrumental settings used in this study are extensively described in [*Marechal et al.*, 1999] and therefore, will not be detailed in this paper.

4.4.1. Neptune instrumental settings

The Neptune introduction system used in this study consists of a tandem quartz glass spray chamber (cyclone + standard Scott double pass) coupled with a low flow PFA nebulizer (50 to 70 µl/min.). Ar gas flows of 15 l/min., 1.2 l/min. and 0.6 l/min were used for coolant, nebulizer and auxiliary, respectively. For ICP operation, an RF generator power of 1300 W was used. The beams were collected on a multi-collector module with eight movable and one fixed Faraday cups, displaying a maximum relative mass range of 17% [*Weyer and Schwieters*, 2003]. The collector configuration used for Zn isotopic measurements is similar on both Plasma 54 and Neptune MC-ICP-MS (Table 2.). This cup configuration allowed to collect simultaneously the four Zn masses (64, 66, 67, 68), ^{63}Cu and ^{65}Cu for mass bias correction and mass 62 to check for eventual Ni interferences [*Marechal*, 1998]. After a minimum of four hours of instrument warm up and setting, analytical sequences were run automatically using a Cetac ASX-100 autosampler. Between each sample and standard, the machine was rinsed with 0.05N HNO_3 from two different vials for 1 minute each. Blank

measurements consist of 1 block of 10 cycles (8s) and sample and standard measurements consist of 2 blocks of 20 cycles of 8s each. For a single measurement (40 cycles), internal precision was found to be in the range 5-10ppm (2σerr.) for both $^{66}Zn/^{64}Zn$ and $^{65}Cu/^{63}Cu$ ratios.

4.4.2. Measurements

Instrumental mass fractionation was corrected by using the method described by [*Marechal et al.*, 1999] on both Plasma 54 and Neptune instruments. A Cu standard (NIST 976) was added to the purified Zn fractions and a Cu (NIST 976) + Zn (JMC 3-0749L) standard mixture was run as a bracketing standard. Cu-Zn concentrations were adjusted to 300ppb in a 0.05N HNO_3 matrix for both samples and standards. This was done to obtain matched Cu/Zn ratios (close to 1) preventing differences in the relative mass bias behaviour of solutions [*Archer and Vance*, 2004]. The ^{62}Ni signal was measured to evaluate the isobaric interference of ^{64}Ni on the ^{64}Zn signal and no significant interferences were found in our samples. As already observed by [*Marechal et al.*, 1999] on the Plasma 54 MC-ICP-MS , the ratio of Cu and Zn fractionation factors (i.e. f_{Cu}/f_{Zn}) was constant over a single analytical session (i.e. one day of measurement) for both Plasma 54 and Neptune instruments. However, this f_{Cu}/f_{Zn} does not remain constant from one day to another. The results are given by using the standard delta per mil notation.

$$\delta^{66}Zn_{JMC} = \left(\frac{\left({}^{66}Zn/{}^{64}Zn \right)_{SAMPLE}}{\left({}^{66}Zn/{}^{64}Zn \right)_{JMC}} - 1 \right) \times 10^3$$

$\delta^{67}Zn$ and $\delta^{68}Zn$ were used to verify the quality of our measurements. Fig 3 shows a plot of $\delta^{68}Zn$ *versus* $\delta^{66}Zn$ and $\delta^{67}Zn$ *versus* $\delta^{66}Zn$, where our results fall on the predicted mass dependent fractionation lines, as the regression slopes are proportional to the mass differences: ≈2.0 and ≈1.5, respectively. Replicates analyses of samples (dissolution + chemical separation + mass spectrometry) display an overall reproducibility in the range 0.01-0.09 ‰, showing that sample heterogeneity is not significant. Zn (JMC 3-0749L) standard was also processed several times through ion exchange chemistry. The column treated Zn (JMC 3-0749L) fractions were analysed on both Plasma 54 and Neptune instruments. We obtained a $\delta^{66}Zn$= 0.04 ± 0.04 ‰ (n = 7; 2σ err.) in accord with the 0‰ expected value. In addition, we obtained a $\delta^{66}Zn$= 0.26 ± 0.02 ‰ (n=5; 2σ err.) for replicated analyses (dissolution + chemical extraction + mass spectrometry) of BCR-1 basalt standard (from

USGS, USA), in good agreement with $\delta^{66}Zn$= 0.20 ± 0.09 ‰ reported by [*Archer and Vance*, 2004].

5. Results

5.1.Sublimates mineralogical description

X-Ray diffraction results are reported in Table 3. The temperature gradient in the 2001 silica tube (≈200°C) is significantly lower than in previously reported data on silica tubes from Merapi (800°C and 350°C, see Table.1). Sulphur was clearly identified in W2, W3, W4 and W5 sections whereas Pb-NH_4 Chloride was identified in all sections except the coldest one (W5). NH_4Cl was identified in W2 section. Sulphur minerals (PbS and FeS_2) were found in W2 and W4 sections. Andesite-low was also identified in W4 section probably due to rock particles contamination. ZnS was found as possible phase in W2, W3, W4, W5, but its presence has not been clearly confirmed due to the complexity of XRD spectra obtained.

5.1.Zn concentrations and isotopic compositions

Zn concentrations and isotopic compositions measured in gas, sublimates and rocks samples are displayed in Table 4. Zn concentrations are in the range 100-1250 ppb, 343-540 ppm and 70-87 ppm in gas, sublimates and rocks samples, respectively. Both gas and sublimates samples show significant $\delta^{66}Zn$ variations, from 0.05-0.85 ‰ and 1.48-1.68 ‰, respectively. Such isotopic range is large with respect to the previously reported Zn isotopic variations in terrestrial samples (0.84‰ per amu, including analytical precision) and it is noteworthy that sublimates from Merapi display the higher $\delta^{66}Zn$ reported in earth materials (Fig.1.). As shown in Fig. 4, both sublimates and gas Zn isotopic signatures display clear temperature dependences. The gas phase becomes depleted in the heavy isotope upon decreasing vent temperature whereas mineral phases become enriched in heavy Zn isotopes upon decrease of the estimated condensation temperature. The temperature dependence of the gas condensates and NH_4OH samples seem to be slightly different probably as the result of a sampling or source effect (discussed below). For all gas samples, Zn concentrations generally decrease with vent temperature and $\delta^{66}Zn$ whereas no clear trend is observed for sublimates phases (Table 4.). Merapi rocks display homogeneous Zn isotopic signature with a mean value of $\delta^{66}Zn$=0.24‰, similar to previous basalts data reported in literature [*Archer and Vance*, 2004; *Marechal*, 1998].

6. Discussion

6.1. Gas condensates versus NH_4OH samples

The reliability of gas condensates sampling for trace metal analysis has recently been contested because some metals may be lost through pumping or scavenged in solid sulphur which is often precipitated in these samples [*Fischer et al.*, 1998; *Sortino et al.*, submitted]. Two couples gas condensates/NH_4OH solutions collected at 311°C and 590°C display nearly similar Zn isotopic compositions whereas one couple collected at 574°C displays a more significant variation (≈0.3‰). However, considering only 3 couples gas condensates/NH_4OH solutions is not sufficient to assess the behaviour of Zn in the respective open and closed sampling systems and further systematic comparison have to be performed in a wide range of temperature. In any cases both gas condensates and NH_4OH solutions suggests a similar trend, with a gas phase being depleted in the heavy isotope upon gas cooling.

6.2. Sources effects versus mass fractionation processes

Both source effects and mass fractionation processes may account for the Zn isotopic variations reported. Considering sources effects, one can assume that the main sources able to affect Zn isotopic composition of gas and sublimates samples are the magma/rock and the meteoric/atmospheric end-members. The δ^{66}Zn of the distinct Merapi rock samples (R1, R2, R3, R4) are identical within error (Table 4.), with a mean value of 0.24‰. Therefore, it can be assumed that the Zn isotopic signatures of the rocks from fumarolic conducts are homogeneous. Enrichment Factors (EF) of Zn in the gas phase with respect to the rock were calculated as follows:

$$EF_X = \left[(X/X_R)_g / (X/X_R)_r \right]$$

for an element X, g and r being the gas sample and the rock, respectively, X_R corresponding to an element displaying a refractory behaviour with respect to volcanic fluids. In this study, Mg was chosen because of its refractory behaviour but Ti or Zr may also be used with little effect on the global results. The EF values obtained for the gas samples are ranging from 0.4×10^2 to 8.5×10^2 (Table 4.). Such high values indicate that Zn behaves as a volatile element in volcanic gas, suggesting fumarolic Zn to be originated mainly from magma degassing. Rock leaching during gas ascent is thus not considered as a major process responsible of the Zn isotopic variations observed. The fumarolic gas composition can also be affected by episodic meteoric water infiltrations within the volcanic pile [*Nonell et al.*, 2005; *Richter et al.*, 2004]. Zn isotopic compositions were measured in French rain waters by [*Luck et al.*, 1999] and vary

from -0.2 to +0.2‰. It is also well known that dissolved components in rain waters might be derived from sea salt aerosols, terrestrial aerosols (soil dust, biological emissions) and anthropogenic sources [*Negrel and Roy*, 1998]. The above cited materials were characterised for their Zn isotopic compositions [*Bermin et al.*, 2004; *Cloquet*, 2005; *Luck et al.*, 1999; *Viers et al.*, 2004] and display variations ranging from –0.91‰ to 0.8‰ (Fig 1.), but no data are available for Java. As most of the samples (gas and sublimates) were collected during the dry season, where rainfalls are rare [*Richter et al.*, 2004; *Zimmer and Erzinger*, 2003], the meteoric water/volcanic gas interactions should be minimized. Therefore, both fumarolic and sublimate Zn are assumed to be originated mainly from magma degassing and only samples from 574°C and 456°C fumaroles (collected during the rainy season) might have been influenced by meteoric infiltration. Then, the observed isotopic variations in all the other gas and sublimates samples are likely to be the result of isotopic mass fractionation processes rather than of sources effects.

6.3. Mass dependent isotopic fractionation during phase changing processes

Mass dependent isotopic fractionation between species or phases can be induced by both kinetic and equilibrium processes. Kinetic fractionation results from motions whereas equilibrium processes are pure quantum phenomenon [*Young et al.*, 2002]. These theoretical concepts, applied to non traditional stable isotopes can be found in [*Schauble*, 2004]. As mass dependent fractionation laws are different for kinetic and equilibrium processes, a theoretical approach might be helpful to distinguish between the most probable processes responsible of the Zn isotopic fractionation observed in our samples.

Two main phase changing processes might explain the Zn isotopic variations observed 1) In the silica tubes, where Zn isotopes undergoes gas-sublimate condensation 2) at the magma/gas interface, where Zn is degassed from the silicate melt. Hereafter, we will confront the Zn isotopic data obtained in rock, gas and sublimates samples with the different mass fractionation theories in order to propose the most suitable model for the description of Zn isotopic fractionation during the above-cited processes.

6.3.1. Gas-sublimate condensation

Previous studies on sublimates and metal speciation in gas conducted at Merapi [*Bernard*, 1985; *Le Guern and Bernard*, 1982; *Symonds et al.*, 1987] clearly indicate that $ZnCl_{2(g)}$ is dominant in the volcanic gas phase with respect to the other potential species

($Zn_{(g)}$, $ZnF_{2(g)}$, $ZnS_{(g)}$, $ZnBr_{2(g)}$). This feature is commonly observed at all kinds of active volcanoes [*Symonds*, 1990]. In addition, thermodynamic calculations indicate that the dominant Zn compound present in Merapi silica tubes should be $ZnS_{(s)}$ [*Symonds et al.*, 1987]. Therefore, the main reaction involving Zn during gas-sublimate condensation is assumed to be:

$$ZnCl_{2(g)} + H_2S_{(g)} \Leftrightarrow ZnS_{(s)} + 2HCl_{(g)}$$

As seen from Fig.4, Zn in sublimates becomes enriched in the heavy isotope with decreasing temperature. At the opposite, δ^{66}Zn decrease with fumarolic vent temperature. In order to describe this phenomenon, fractionation factors $\alpha_{s/v}$ (*solid versus vapour*) were calculated between the solid and the gaseous phase at the estimated temperatures of the sublimates formation following:

$$\alpha_{S/V} = \frac{1000 + \delta^{66}Zn_s}{1000 + \delta^{66}Zn_v}$$

s and *v* being the solid and the vapour phase, respectively. For these calculations, the δ^{66}Zn of the gas phase corresponding to the sublimate temperature were evaluated by using the linear regression derived from the gas data collected during the dry season (Fig. 4.), for which sources effects should be minimized. The results of these calculations are displayed in Fig.5. The clear $1/T^2$ dependence of the $\alpha_{s/v}$ is a typical characteristic of an equilibrium mass dependent fractionation process [*Schauble*, 2004]. By extrapolating the regression lines calculated for sublimates and gas samples shown in Fig.4, this mass fractionation phenomenon seems to become insignificant for T>650°C which corresponds to a gas isotopic composition close to 1‰. This observation is in accord with the equilibrium mass fractionation theory, indicating that fractionation becomes very low at high T°C due to the quantum mechanic $1/T^2$ dependence of the fractionation factor $\alpha_{s/v}$. As $ZnCl_{2(g)}$ is supposed to be the dominant Zn specie in the gaseous phase for T>650°C [*Symonds et al.*, 1987] and because no mass fractionation processes are expected between 650°C and the magma-degassing temperature (≈900°C), we will assume that the fluid degassed at the magma chamber level has a δ^{66}Zn close to 1‰ . This value will be used in for the following interpretation of the magma-gas fractionation processes.

6.3.2. Magma-gas interface

Mass dependent isotopic fractionation during magma degassing has already been described in literature for light elements such as B, C and H [*Jiang and Palmer*, 1998; *Taylor*,

1986]. In this high temperature context, isotopic fractionation is generally modelled by using two approaches: closed or open system degassing (Rayleigh fractionation). The closed system-degassing model supposes that the vapour phase remains in equilibrium with the magma during the degassing process. In this case, the following approximation can be used:

$$\delta_f = \delta_i - (1-F)10^3 \ln\alpha_{v/m}$$

where δi and δf are the initial and final isotopic composition of the magma, respectively, F is the mol fraction of the element remaining in the melt and $\alpha_{v/m}$ is vapour-melt fractionation factor. In the case of an open degassing system, the vapour phase is removed from the melt after its formation preventing a continuous equilibrium between the vapour phase and the magma. This process can be described with the following equation:

$$\delta_f = (\delta_i + 1000)(F^{\alpha_{v/m}-1}) - 1000$$

Both theoretical approaches are based on the evolution of the mol fraction F of the element remaining in the melt upon degassing and the isotopic variations observed between the original "undegassed" melt and the final degassed material [*Jiang and Palmer*, 1998]. As no variations are observed in rock samples and because the evaporated fractions of Zn are difficult to estimate, we were not able to conduct extensive calculations. However, the emanation coefficients of Zn were estimated at Mt. Etna by [*Gauthier and Le Cloarec*, 1998] and were close to 0,13%(ε_{Zn}). As the emanation coefficients are defined by:

$$\varepsilon_{Zn} = (N_{Zn})_v / (N_{Zn})_0$$

where $(N_{Zn})_v$ is the number of atoms in the vapour phase and $(N_{Zn})_0$ is the number of atoms in the magma before degassing, they can be assimilated to the fraction of Zn degassed by the melt. No data are available concerning ε_{Zn} at Merapi volcano. However, the lava viscosity at Merapi is higher than at Etna. This should induce for Merapi lower ε_{Zn} because the andesitic magma would restrain the escape of gaseous components [*Nho et al.*, 1996]. Therefore, we have conducted calculations with decreasing iterations of the Zn emanation coefficient (ε_{Zn}=0,13%, 0,01%, 0,001%, 0,0001%) in order to check if such a range of Zn degassing is in accord with the non-variability of δ^{66}Zn observed in the rock samples. Calculations were performed for both open and closed system approaches by using a fractionation factor $\alpha_{v/m}$=1,0007 (*vapour versus melt*) derived from the δ^{66}Zn ≈1‰ assumed for the vapour emitted at the magma chamber level and the δ^{66}Zn =0,24‰ mean value of rock samples, assumed to be representative of the melt value. As expected, such low emanation coefficients lead to very small variations of the Zn isotopic signature between the degassed and

undegassed magma. With both open and closed system calculation, a maximum variation of 0.001‰ was calculated for a ε_{Zn}=0,13%. Then, the amplitude of variations was found to decrease with the decreasing ε_{Zn}. These calculations clearly indicate that magma degassing cannot induce a significant Zn isotopic variation in the residual melt, which is compatible with the uniformity of δ^{66}Zn observed in the rock samples.

On the other hand, our data clearly indicate that the gas phase is enriched in the heavy Zn isotope with respect to the magma during the degassing process. Similar observations were made by [*Jiang and Palmer*, 1998; *Taylor*, 1986] for B, C and H isotopes, and interpreted as resulting from the variable speciation of these elements between the silicate melt and the volatile fluid. The heavy isotope was found to be enriched in the low-coordinated volatile material and impoverished in the residual highly coordinated silicate melt species. This interpretation might also be suitable for Zn isotopes as Zn is found to be octa or tetra coordinated in silicate glasses [*Galoisy et al.*, 2001; *Le Grand et al.*, 2000] whereas the coordination number (CN) of Zn in the $ZnCl_{2(g)}$ gaseous phase is 2.

Conclusion

Significant Zn isotopic variations (0.82‰ per amu) were measured between fumarolic gases, rocks and sublimates samples from Merapi volcano. These variations are considerable with respect to previously reported data on earth materials (0.84‰ per amu) and are proposed to result mainly from mass dependent isotopic fractionation during phase changing processes. Gas sampling artefacts and/or meteoric water/gas interactions (sources effects), were found to induce possible shifts on the Zn isotopic compositions of the gas phase. Even if such variations observed do not modify significantly our interpretations, further analyses are required to quantify precisely these effects. During magma degassing, heavy Zn isotopes are preferentially partitioned into the vapour phase probably as the result of variable Zn coordination between the silicate melt (CN= 4 or 8) and the vapour phase (CN=2). Both open and closed system degassing calculations indicate that the degassing process does not significantly affect the Zn isotopic composition of the residual magma, which might partly explain the homogeneity of previously reported Zn isotopic signatures of basalts [*Archer and Vance*, 2004; *Marechal*, 1998]. During gas-sublimates condensation, our results show that heavy Zn isotopes are enriched in solid deposits. Gas and sublimates data are consistent with an equilibrium mass dependent isotopic fractionation during the gas-sublimate condensation.

As the sublimates phases display high $\delta^{66}Zn$ (1.48 to 1.68‰) compared to previously reported data on Zn ores from various locations (-0.19 to 0.44‰, see [*Marechal et al.*, 1999]), and because a Zn isotopic signatures of gas and sublimates where found to be temperature dependent, it is possible to envision the use of Zn isotopes as geothermometers. This application might supply important insights for the characterisation of ore forming conditions and for the understanding of volatile behaviour in volcanic fluids. Such kind of approaches might also furnish number of data on the "natural" isotopic fractionation factors between phases, which can be used as references for the validation of future fractionation factors theoretical calculations on these non-traditional stable isotopic systems.

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References

Albarède, F., The Stable Isotope Geochemistry of Copper and Zinc, *Reviews in Mineralogy & Geochemistry*, *55*, 409-427, 2004.

Anbar, A.D., Iron stable Isotopes: beyond biosignatures, *Earth and Planetary Science Letters*, *217*, 223-236, 2004.

Archer, C., and D. Vance, Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes, *Journal of Analytical Atomic Spectrometry*, *19*, 656-665, 2004.

Barling, J., G.L. Arnold, and A.D. Anbar, Natural mass-dependent variations in the isotopic composition of molybdenum, *Earth and Planetary Science Letters*, *193*, 447-457, 2001.

Bermin, J., D. Vance, and P. Statham, A technique for the separation and isotopic analysis of Fe and Zn in seawater, Goldschmidt conference, Copenhagen, Denmark, 5-11 June, *Geochimica and Cosmochimica Acta*, *68* (11S), A346, 2004.

Bernard, A., Les mécanismes de condensation des gaz volcaniques., Ph.D. thesis thesis, University of Brusseles, Belgium, 1985.

Büchl, A., C. Archer, D.R. Brown, C.J. Hawkesworth, E. Leighton, K.V. Ragnarsdottir, and D. Vance, Combined high precision Cu, Zn and Fe isotopes in mice brains, Goldschmidt conference, Copenhagen, Denmark, 5-11 June, *Geochimica and Cosmochimica Acta*, *68* (11S), A528, 2004.

Chevrier, R.M., and F. Le Guern, Prélèvement et analyses des condensats de fumerolles sur volcans actifs: Soufrière de la Guadeloupe (1976-1977) et Pouzzoles et Vulcano (Italie) (1978), *Bulletin of Volcanology*, *45*, 173-178, 1982.

Cloquet, C., Ph.D. Thesis, Géochimie élémentaire et isotopique des métaux lours. Applications environnementales en tissus urbains et industriels., 2005.

Fehr, M.H., M. Rehkämper, and A.N. Halliday, Application of MC-ICP-MS to the precise determination of tellurium isotope compositions in chondrites, iron meteorites and sulfides, *International Journal of Mass Spectrometry*, *232*, 83-94, 2004.

Fischer, T.P., S. Shuttleworth, and P.A. O'Day, Determination of trace and platinum-group elements in high ionic strength volcanic fluids by sector-field inductively coupled plasma mass spectrometry (ICP-MS), *Journal of Analytical Chemistry*, *362*, 457-464, 1998.

Galoisy, L., L. Cormier, G. Calas, and V. Briois, Environment of Ni, Co and Zn in low alkali borate glasses: informations from EXAFS and XANES spectra, *Journal of Non-Cristalline Solids*, *293-295*, 105-111, 2001.

Galy, A., N.S. Belshaw, L. Halicz, and R.K. O'Nions, High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, *208*, 89-98, 2001.

Galy, A., E.D. Young, R.D. Ash, and R.K. O'Nions, The formation of chondrules at high gas pressures in the solar nebula, *Science*, *290*, 1751-1753, 2000.

Gauthier, P.J., and M.F. Le Cloarec, Variability of alkali and heavy metal fluxes released by Mt.Etna volcano, Sicily, between 1991 and 1995, *Journal of Volcanology and Geothermal Research*, *81*, 311-326, 1998.

Giggenbach, W.F., A simple method for the collection and analysis of volcanic gas samples., *Bulletin of Volcanology*, *39*, 132-145, 1975.

Halicz, L., A. Galy, N.S. Belshaw, and R.K. O'Nions, High-precision measurement of calcium isotopes in carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *Journal of Analytical Atomic Spectrometry*, *14*, 1835-1838, 1999.

Hirata, T., Isotopic variations of germanium in iron and stony iron meteorites, *Geochimica and Cosmochimica Acta*, *61* (20), 4439-4448, 1997.

Jiang, S.Y., and M.R. Palmer, Boron isotope systematics of tourmalines from granites and pegmatites: a synthesis, *European Journal of Mineralogy*, *10*, 1253-1265, 1998.

Le Grand, M., A.Y. Ramos, G. Calas, L. Galoisy, D. Ghaleb, and F. Pacaud, Zn environment in aluminoborosilicate glasses by Zn K-edge x-ray adsorption fine structure spectroscopy, *Journal of Material Research*, *15* (9), 2015-2019, 2000.

Le Guern, F., and A. Bernard, A new method for sampling and analysing volcanic sublimates - Application to Merapi volcano, Java, *Journal of Volcanology and Geothermal Research*, *12*, 133-146, 1982.

Luck, J.M., D. Ben Othman, F. Albarède, and P. Télouk, Pb, Zn and Cu isotopic variations in rain. In Armannsson (editor). Balkema, Rotterdam., *Geochemistr of the Eath Surface*, 199-202, 1999.

Luck, J.M., D. Ben Othman, J.A. Barrat, and F. Albarède, Coupled 63Cu and 16O excesses in chondrites, *Geochimica and Cosmochimica Acta*, *67* (1), 143-151, 2003.

Marechal, C.N., Géochimie des isotopes du cuivre et du zinc: méthode, variabilité naturelle et application océanographique, Ph.D. thesis, Ecole Normale Supérieure de Lyon et Université Claude Bernard - Lyon I, 1998.

Marechal, C.N., and F. Albarède, Ion-Exchange fractionation of copper and zinc isotopes, *Geochimica and Cosmochimica Acta*, *66* (9), 1499-1509, 2002.

Marechal, C.N., E. Nicolas, C. Douchet, and F. Albarède, Abundance of zinc isotopes as marine biochemical tracer, *Geochemistry Geophysics Geosystems*, *1*, 1999GC000029, 2000.

Marechal, C.N., P. Télouk, and F. Albarède, Precise analysis of copper and zinc isotopic compositons by plasma-source mass spectrometry, *Chemical Geology*, *156*, 251-273, 1999.

Mason, T.F.D., D.J. Weiss, M. Horstwood, R.R. Parrish, S.S. Russell, E. Mullane, and B.J. Coles, High-precision Cu and Zn isotope analysis by plasma source mass spectrometry Part 1. Spectral interferences and their correction, *Journal of Analytical Atomic Spectrometry*, *19*, 209-217, 2004a.

Mason, T.F.D., D.J. Weiss, M. Horstwood, R.R. Parrish, S.S. Russell, E. Mullane, and B.J. Coles, High-precision Cu and Zn isotope analysis by plasma source mass spectrometry Part 2. Correcting for mass discrimination effects, *Journal of Analytical Atomic Spectrometry*, *19*, 218-226, 2004b.

Negrel, P., and S. Roy, Chemistry of rain water in the Massif Central (France): a strontium isotope and major element study, *Applied Geochemistry*, *13* (8), 941-952, 1998.

Nho, E.Y., M.F. Le Cloarec, B. Ardouin, and W.S. Tjetjep, Source strength of volcanic trace elements emitted from the indonesian arc, *Journal of Volcanology and Geothermal Research*, *74*, 121-129, 1996.

Nielsen, S.G., M. Rehkämper, J. Baker, and A.N. Halliday, The precise and accurate determination of thallium isotope compositions and concentrations for water samples by MC-ICP-MS, *Chemical Geology*, *204*, 109-124, 2004.

Nonell, A., J.P. Toutain, M. Polve, M. Munoz, and G. Berger, First coupled Sr and Pb isotopic measurements in volcanic gas condensates and groudwaters of Vulcano island (Italy), *Geochemistry Geophysics Geosystems*, 2005GC000980, in press., 2005.

Pichat, S., C. Douchet, and F. Albarède, Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka, *Earth and Planetary Science Letters*, *210*, 167-178, 2003.

Poitrasson, F., A.N. Halliday, C.D. Lee, S. Levasseur, and N. Teutsch, Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms, *Earth and Planetary Science Letters*, *223*, 253-266, 2004.

Poitrasson, F., S. Levasseur, and N. Teutsch, Significance of iron isotope mineral fractionation in pallasites and iron meteorites for the core-mantle differentiation of terrestrial planets, *Earth and Planetary Science Letters*, *in press*, 2005.

Quisefit, J.P., J.P. Toutain, G. Bergametti, M. Javoy, B. Cheynet, and A. Person, Evolution versus cooling of gaseous volcanic emmissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations, *Geochimica and Cosmochimica Acta*, *53*, 1989.

Ratdomopurbo, A., and G. Poupinet, An overview of the seismicity of Merapi volcano (Java, Indonesia), 1983-1994, *Journal of Volcanology and Geothermal Research*, *100*, 193-214, 2000.

Rehkämper, M., M. Frank, J.R. Hein, and A.N. Halliday, Cenozoic marine geochemistry of thallium deduced from isotopic studies of ferromanganese crusts and pelagic sediments, *Earth and Planetary Science Letters*, *219*, 77-91, 2004.

Rehkämper, M., M. Frank, J.R. Hein, D. Porcelli, A.N. Halliday, J. Ingri, and V. Liebetrau, Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits, *Earth and Planetary Science Letters*, *197*, 65-81, 2002.

Rehkämper, M., and A.N. Halliday, The precise measurement of Tl isotopic compositions by MC-ICP-MS: Applications to the analysis of geological materials and meteorites, *Geochimica and Cosmochimica Acta*, *63* (6), 935-944, 1999.

Reviews in Mineralogy, V., Geochemistry of non traditional stable isotopes, in *Reviews in Mineralogy & geochemistry*, edited by C.M. Johnson, B.L. Beard, and F. Albarède, pp. 454, 2004.

Richter, G., J. Wassermann, M. Zimmer, and M. Ohrnberger, Correlation of seismic activity and fumarole temperature at the Mt.Merapi volcano (Indonesia) in 2000, *Journal of Volcanology and Geothermal Research*, *135*, 331-342, 2004.

Rosman, K.J.R., and P.D.P. Taylor, Isotopic composition of the elements 1997, *Journal of Analytical Atomic Spectrometry*, *13*, 45N-55N, 1998.

Rouxel, O., N. Dobbek, J. Ludden, and Y. Fouquet, Iron isotope fractionation during oceanic crust alteration, *Chemical Geology*, *202*, 155-182, 2003a.

Rouxel, O., Y. Fouquet, and J. Ludden, Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: Evidence from sulfur, selenium, and iron isotopes, *Geochimica and Cosmochimica Acta*, *68* (10), 2295-2311, 2004.

Rouxel, O., J. Ludden, J. Carignan, L. Marin, and Y. Fouquet, Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry, *Geochimica and Cosmochimica Acta*, *66* (18), 3191-3199, 2002.

Rouxel, O., J. Ludden, and Y. Fouquet, Antimony isotope variations in natural systems and implications for their use as geochemical tracers, *Chemical Geology*, *200*, 25-40, 2003b.

Schauble, E.A., Applying Stable Isotope Fractionation Theory to New Systems, *Reviews in Mineralogy & Geochemistry*, *55*, 65-111, 2004.

Sortino, F., A. Nonell, J.P. Toutain, M. Munoz, M. Valladon, and G. Volpicelli, Giggencach's 1975 revisited: using ammoniac to sample volcanic gases, *Journal of Volcanology and Geothermal Research*, submitted.

Symonds, R.B., Ph.D. Thesis, Application of multicomponent chemical equilibria to volcanic gases at Augustine volcano, volcanic halogen emissions, and volcanological studies of gaz-phase transport, Michigan Technological University, 1990.

Symonds, R.B., Scanning electron microprobe observations of sublimates from Merapi volcano, Indonesia, *Geochemical Journal*, *26*, 337-350, 1993.

Symonds, R.B., W.I. Rose, M.H. Reed, F.E. Lichte, and D.L. Finnegan, Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia., *Geochimica and Cosmochimica Acta*, *51*, 2083-2101, 1987.

Taran, Y., A. Bernard, J.C. Gavilanes, E. Lunezheva, A. Cortés, and M.A. Armienta, Chemistry and mineralogy of high temperature gas discharges from Colima volcano, Mexico. Implications for magmatic gas-atmosphere interaction, *Journal of Volcanology and Geothermal Research*, *108*, 245-264, 2001.

Taran, Y.A., J.W. Hedenquist, M.A. Korzhinsky, S.I. Tkachenko, and K.I. Shmulovich, Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands, *Geochimica and Cosmochimica Acta*, *59* (9), 1749-1761, 1995.

Taylor, B.E., Magmatic volatiles: isotopic variations of C,H and S, in *Stable isotopes in high temperature geological processes*, edited by H.P.T.J.R.O.N.e. J.W. Walley, pp. 185-226, Rev.Mineral., 1986.

Toutain, J.P., F. Sortino, B. Reynier, B. Dupre, M. Munoz, A. Nonell, M. Polve, and S. Chancha Do Vale, A new collector for sampling volcanic aerosols, *Journal of Volcanology and Geothermal Research*, *123* (1-2), 95-103, 2003.

Viers, J., P. Oliva, R. Freydier, and B. Dupre, The use of Zinc isotopes to constrain the biogeochemical cycling of metals in watersheds, Goldschmidt conference, Copenhagen, Denmark, 5-11 June, *Geochimica and Cosmochimica Acta*, *68* (11S), A413, 2004.

Voight, B., E.K. Constantine, S. Siswowidjoyo, and R. Torley, Historical eruptions of Merapi volcano, Central Java, Indonesia, 1768-1998, *Journal of Volcanology and Geothermal Research*, *100*, 69-138, 2000a.

Voight, B., R. Sukhyar, and A.D. Wirakusumah, Introduction to the special issue on Marapi Volcano, *Journal of Volcanology and Geothermal Research*, *100*, 1-8, 2000b.

Weiss, D.J., T.F.D. Mason, F.J. Zhao, G.J.D. Kirk, B.J. Coles, and M. Horstwood, Isotopic discrimination of zinc in higher plants, *New Phytologist*, *in press*, 2005.

Weyer, S., and J.B. Schwieters, High precision Fe isotope measurements with high mass resolution MC-ICPMS, *International Journal of Mass Spectrometry*, *226*, 355-368, 2003.

Wombacher, F., M. Rehkämper, and K. Mezger, Determination of mass-dependence of cadmium isotope fractionation during evaporation, *Geochimica and Cosmochimica Acta*, *68* (10), 2349-2537, 2004.

Wombacher, F., M. Rehkämper, K. Mezger, and C. Münker, Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS, *Geochimica and Cosmochimica Acta*, *67* (23), 4639-4654, 2003.

Young, E.D., A. Galy, and H. Naghara, Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, *Geochimica and Cosmochimica Acta*, *66* (6), 1095-1104, 2002.

Zhu, X.K., Y. Guo, R.K. O'Nions, E.D. Young, and R.D. Ash, Isotopic homogeneity of iron in the early solar nebula, *Nature*, *412*, 311-312, 2001.

Zhu, X.K., Y. Guo, R.J.P. Williams, R.K. O'Nions, A. Matthews, N.S. Belshaw, G.W. Canters, E.C. de Waal, U. Weser, B.K. Burgess, and B. Salvato, Mass fractionation

processes of transition metal isotopes, *Earth and Planetary Science Letters*, *200*, 47-62, 2002a.

Zhu, X.K., A. Makishima, Y. Guo, N.S. Belshaw, and R.K. O'Nions, High precision measurement of titanium isotope ratios by plasma source mass spectrometry, *International Journal of Mass Spectrometry*, *220*, 21-29, 2002b.

Zhu, X.K., R.K. O'Nions, Y. Guo, N.S. Belshaw, and D. Rickard, Determination of natural Cu-isotope variation by plasma-source mass spectrometry: implications for use as geochemical tracers, *Chemical Geology*, *163*, 139-149, 2000.

Zimmer, M., and J. Erzinger, Continuous H_20, CO_2, ^{222}Rn and temperature measurements on Merapi Volcano, Indonesia., *Journal of Volcanology and Geothermal Research*, *125*, 25-38, 2003.

Figure captions

Fig .1. Summary of $\delta^{66}Zn$ in terrestrial samples. Black ranges correspond to literature data [*Archer and Vance*, 2004; *Bermin et al.*, 2004; *Büchl et al.*, 2004; *Cloquet*, 2005; *Luck et al.*, 1999; *Marechal*, 1998; *Marechal et al.*, 2000; *Marechal et al.*, 1999; *Pichat et al.*, 2003; *Viers et al.*, 2004; *Weiss et al.*, 2005].

Fig .2. Geographic location of Merapi volcano.

Fig .3. Plot of $\delta^{68}Zn$ *versus* $\delta^{66}Zn$ and $\delta^{67}Zn$ *versus* $\delta^{66}Zn$ for our samples. The regression slopes calculated for our samples are proportional to the mass differences: 2.0 and 1.5, respectively, indicating mass dependent fractionation.

Fig .4. $\delta^{66}Zn$ in sublimates (empty square plot), gas condensates (round plot) and NH4OH bottles samples (triangle plot) *versus* T°C. For all gas samples empty plots corresponds to wet season samples whereas full plots corresponds to dry season samples. The $\delta^{66}Zn$ range in Merapi rocks (shaded area) is also shown for comparative purpose. The regression lines calculated for sublimates and dry season gas samples are also shown. Their extrapolation to high temperature suggests that gas-sublimate fractionation becomes negligible at T°C > 650°C (see text for details). Error bars corresponding to the 2σ err. (Table 4) are also shown. For some gas samples, this data was not available and the mean 2σ err. (0.07‰) calculated from other gas values was applied.

Fig .5. Traditional $10^3 \ln\alpha_{s/v}$ *versus* $10^6/T^2$ diagram. $\alpha_{s/v}$ were calculated between the supposed dominant solid ($ZnS_{(S)}$) and vapour ($ZnCl2_{(g)}$) phases at the estimate temperature of the sublimates formation (see text for details). The $1/T^2$ dependence suggests an equilibrium mass-dependent fractionation of Zn isotopes during sublimates condensation.

Table 1. Summary of sublimates phases collected in silica tubes at Merapi volcano in 1978-1980[*Bernard*, 1985; *Le Guern and Bernard*, 1982] and in 1984 [*Symonds*, 1993; *Symonds et al.*, 1987]. Mineral phases are listed in the order observed in the silica tubes (from highest to lowest temperature)

Sampling Date	Mineral phase	Composition	Enriched Minor Elements	Temperature (°C)
1978-1980 Silica tubes				
	Magnetite	Fe_3O_4		900-600
	Hercynite	$FeAl_2O_4$	Mn,Zn	900-600
	Cristoballite	SiO_2		900-600
	Acmite	$NaFeSi_2O_6$		650-600
	Molybdenite	MoS_2	Re	650-550
	Wolframite	$(Fe,Mn)WO_4$		630-600
	Halite	NaCl		630-300
	Sylvite	KCl		630-300
	Pyrite	FeS_2		550-300
	Sphalerite	ZnS	Cd,Fe	550-300
	Galena	PbS	Bi,Sn	450-150
	Pb-Bi Sulfide	$PbBi_2S_4$(?)	Sn	450-150
	Pb-NH4 Chloride	$NH_4Pb_2Cl_5$	Br,Tl	300-150
	Salamoniac	NH_4Cl	Br	250-150
	Sulfur	S	As,I,Te,Se	150-100
1984 Silica tubes				
	Cristoballite	SiO_2		AROUND 800°C
	Magnetite	Fe_3O_4	Al,Ti	
	K-Ca Sulfate	$K_2Ca(SO_4)_2$	Cu,Zn,Cl	
	Acmite	$NaFeSi_2O_6$	Cl,K,Cu,Zn,Pb	
	Halite	NaCl		
	Sylvite	KCl		
	Pyrite	FeS_2		
	Wollastonite	$CaSiO_3$	Cl,Al	
	Sphalerite	ZnS	Cd,Fe	
	Aphtitalite	$(Na,K)_3Na.(SO4)_2$	Cu,Zn,Cl	
	Galena	PbS	Sn	
	Cs-K Sulfate	?		
	Pb-K chloride	$PbKCl_3$		
	Na-K-Fe Sulfate	$(Na,K)_2Fe(SO_4)(Cl)_2$	Cu,Zn	
	Chalcocyanite	$CuSO_4$		
	Zn Sulfate	$Zn_3(SO_4)(Cl,OH)_4$		
	K-Pb Sulfate	$K_2Pb(SO4)_2$		
	K-Zn Sulfate	$K_2Zn(SO_4)(Cl)_3$		AROUND 450°C

Table 2. Collector configuration used for Zn isotopic measurements on both Plasma 54 (ENS, Lyon) and Thermo-Finnigan Neptune (LMTG, Toulouse). Figures in brackets are the relative isotope abundances for each element [*Rosman and Taylor*, 1998].

Nominal mass	62	63	64	65	66	67	68
Measured element			Zn (48.63%)		Zn (27.90%)	Zn (4.10%)	Zn (18.75%)
Mass bias correcting element		Cu (69.17%)		Cu (30.83%)			
Interfering element	Ni (3.63%)		Ni (0.93%)				
Faraday cup used	L4	L2	L1	C	H1	H2	H3

Table 3. Summary of sublimates phases collected in silica tubes at Merapi volcano in 2001. Temperature ranges are estimated by considering a uniform gradient from the beginning to the end of the tubes.

Tube-Section	Mineral phase	Composition	Estimated Temperature (°C)
WORO 2001 tube			
W0	-	-	495-445
W1	Halite	NaCl	445-410
	Pb-NH_4 Chloride	$NH_4Pb_2Cl_5$	
W2	Sulfur	S	410-375
	Pb-NH_4 Chloride	$NH_4Pb_2Cl_5$	
	Salamoniac	NH_4Cl	
	Galena	PbS	
	Pyrite	FeS_2	
W3	Sulfur	S	375-345
	Pb-NH_4 Chloride	$NH_4Pb_2Cl_5$	
W4	Sulfur	S	345-310
	Pb-NH_4 Chloride	$NH_4Pb_2Cl_5$	
	Pyrite	FeS_2	
	Andesite-low		
W5	Sulfur	S	310-275

Table 4. Zn concentrations (ppb) and isotopic compositions in Merapi gas, sublimates and rock samples. Samples in italics were collected during the wet season. Enrichment factors with respect to Mg are also shown. For all gas samples, T°C is the vent temperature. For sublimates, T°C represent an estimated temperature considering a uniform gradient from the beginning to the end of the tube. The number of full replicates (dissolution + chemical separation + mass spectrometry): Nf are also shown. In all cases, the average values (Av.)of δ^{66}Zn are reported together with the 2σ error.

Sample	Date	T°C	Zn	EF_{Mg}	Nf	δ^{66}Zn Av.	2σ err.
GAS SAMPLES							
Gas condensates							
Cd W590	09.2001	590	848	6.8×10^2	1	0.72	
Cd W574	*03.2002*	*574*	*370*	*1.3×10^2*	*1*	*0.75*	
Cd W561	06.2002	561	194	3.5×10^2	2	0.81	0.08
Cd W456	*03.2002*	*456*	*289*	*0.5×10^2*	*1*	*0,34*	
Cd W437	06.2002	437	129	0.4×10^2	1	0.46	
Cd W407	09.2001	407	172	0.5×10^2	1	0.56	
Cd W311	09.2001	311	102	1.3×10^2	1	0.18	
Cd W297	06.2002	297	124	1.7×10^2	1	0.12	
NH_4OH solutions							
A W590	09.2001	590	1250	4.6×10^2	1	0.85	
A W574	*03.2002*	*574*	*770*	*2.4×10^2*	*2*	*0.46*	*0.03*
A W311	09.2001	311	632	8.5×10^2	2	0.05	0.09
SUBLIMATE PHASES							
Woro tube							
W2	09.2001	391	343000		2	1.48	0.03
W3	09.2001	360	540000		2	1.57	0.01
W4	09.2001	329	477000		2	1.58	0.01
W5	09.2001	293	432000		2	1.68	0.01
ROCKS							
R1		-	81000		2	0.25	0.01
R2		-	79000		2	0.25	0.02
R3		-	70000		2	0.24	0.02
R4		-	87000		2	0.23	0.01
BCR-1			130000		5	0.26	0.02

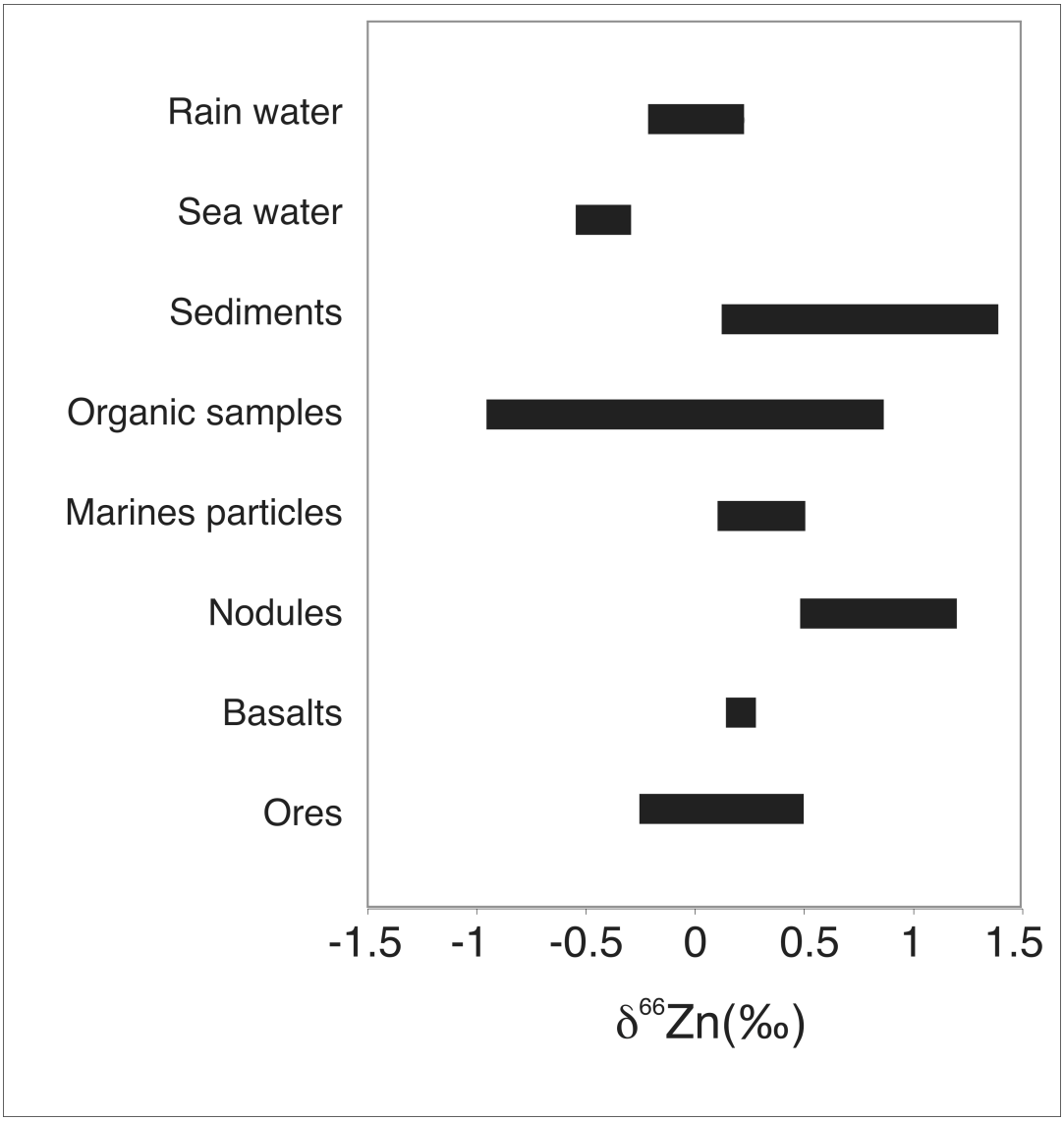


FIG.1

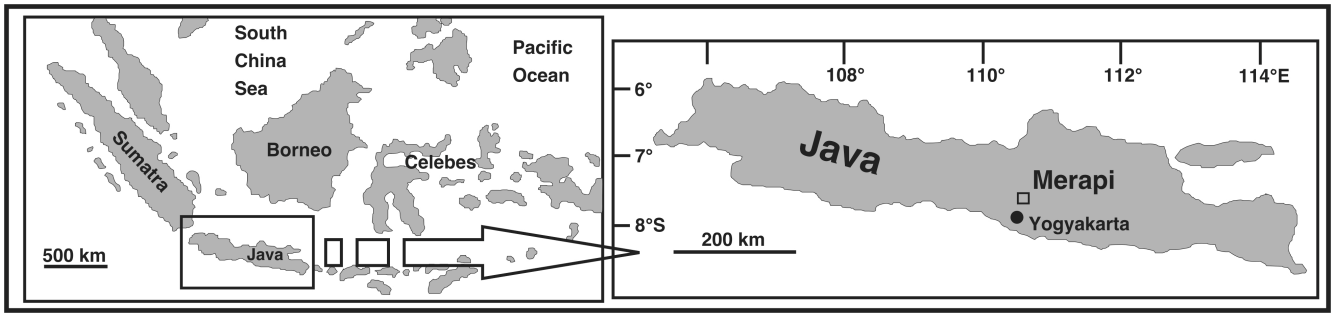
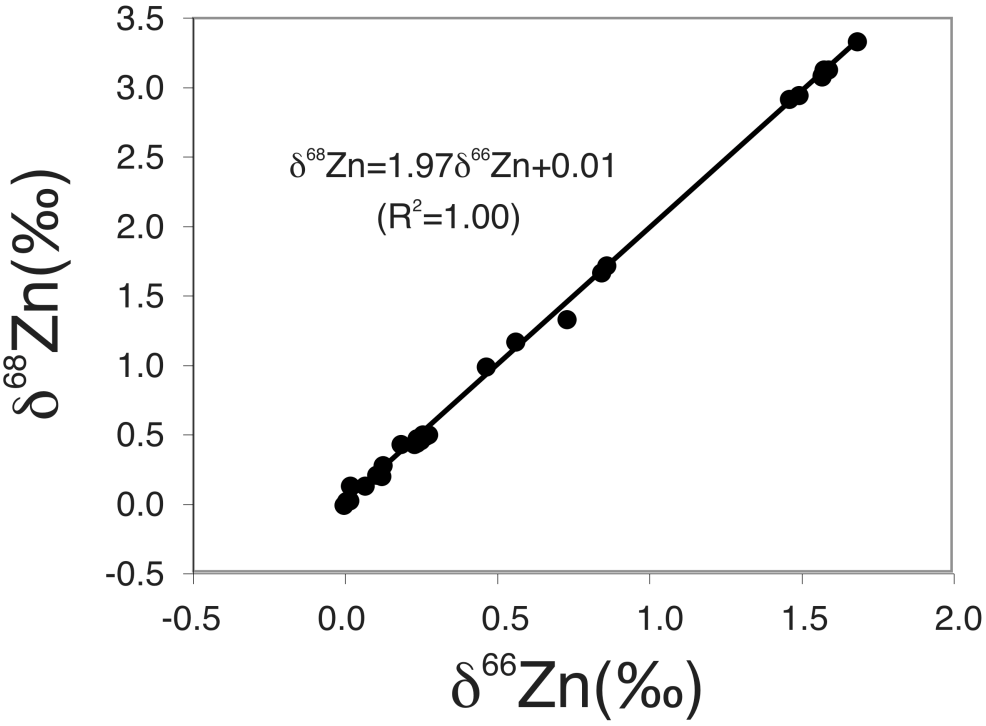


FIG.2



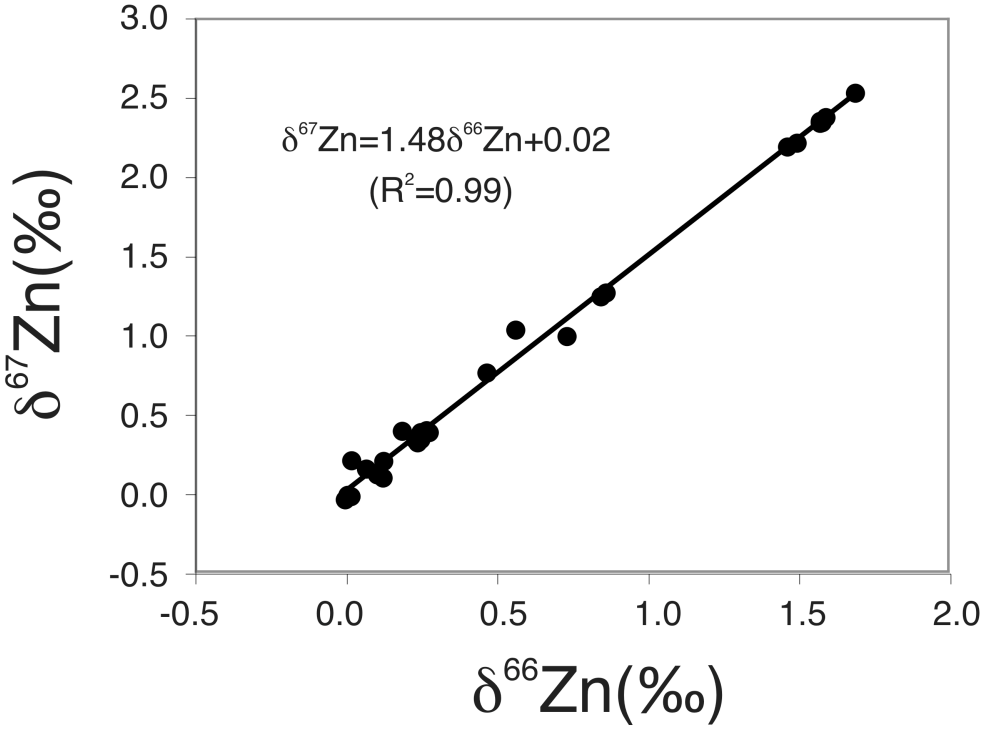


FIG.3

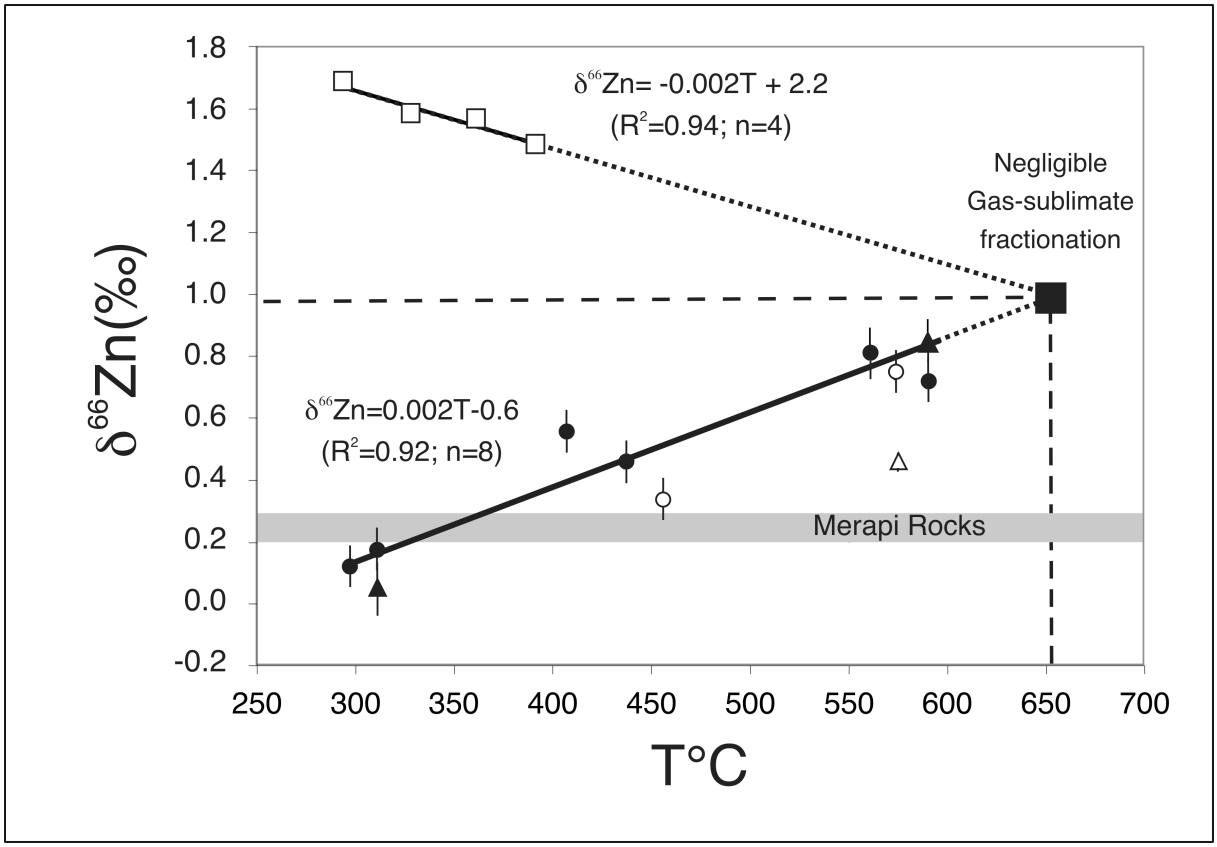


FIG.4

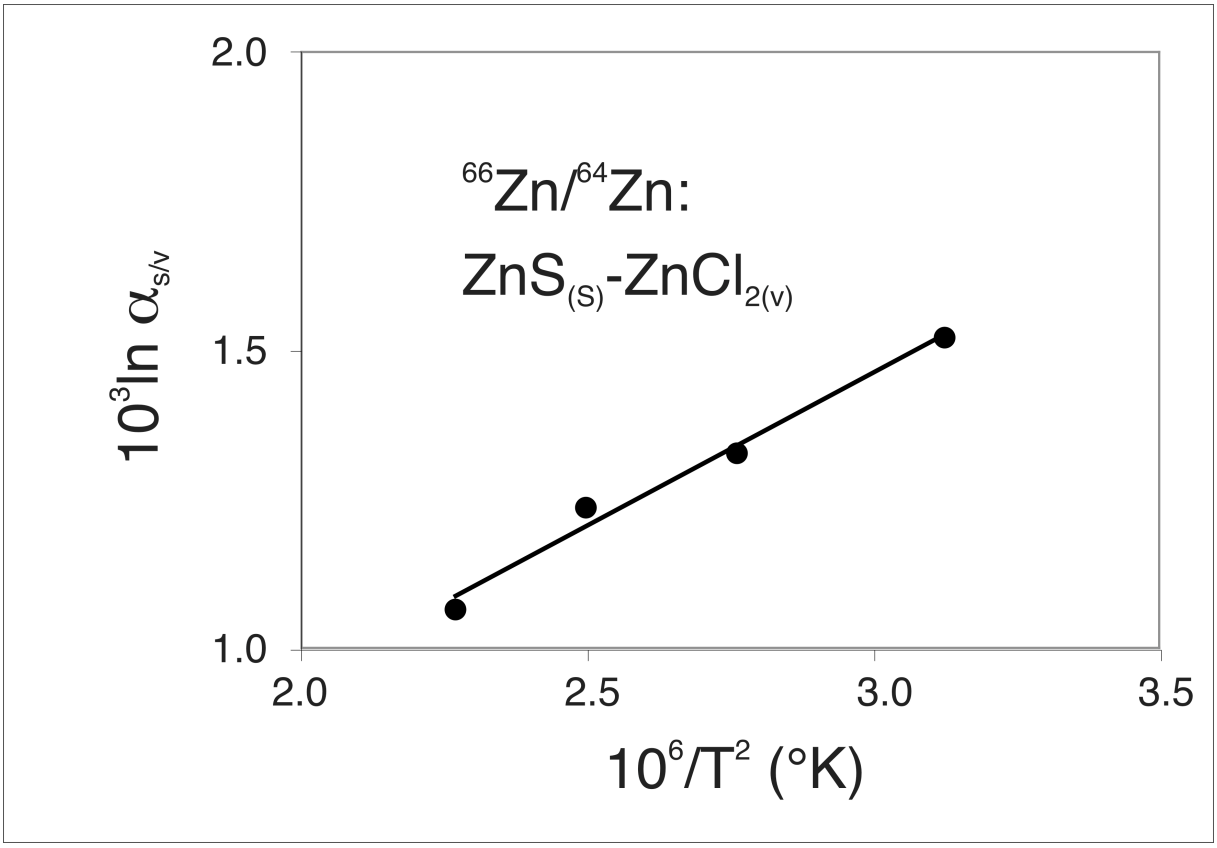


FIG.5

Conclusion générale

CONCLUSION GENERALE

Nouvelles méthodologies de prélèvements des gaz et des panaches volcaniques:

Un des objectifs de cette thèse visait à développer de nouvelles méthodologies d'échantillonnage et d'analyse des émanations volcaniques afin d'augmenter la représentativité des prélèvements et de faciliter l'obtention de données complètes sur la composition de ces émanations. Dans ce cadre, deux nouvelles techniques de prélèvement des gaz fumeroliens et des panaches volcaniques (basées sur l'utilisation de solutions d'ammoniac ultra-pur) ont été proposées. Les protocoles analytiques mis au point dans ce travail permettent l'analyse de ces solutions par des techniques analytiques largement répendues (HPLC, GC, titrage et ICP-MS).

Le premier dispositif, testé à Vulcano, a été développé pour l'échantillonnage des panaches volcaniques : le VES (Venturi Effect System). Cet appareil permet d'obtenir des données fiables sur les rapports Stotal/Cl/F et sur les facteurs d'enrichissement des éléments en trace métalliques dans les panaches volcaniques. La concordance des résultats obtenus par comparaison des échantillons de gaz aux échantillons de panache a permis la validation de cette procédure.

La seconde méthodologie, développée pour les prélèvements des gaz fumeroliens, est basée sur l'utilisation de solutions d'ammoniac purifiées dans des ampoules en quartz sous vide. Différents tests et comparaisons ont été effectués par rapport aux méthodes d'échantillonnage de référence comme les ampoules à soude sous vide et les condensats acides, sur des échantillons prélevés au Mérapi et à Vulcano. Les résultats obtenus dans les ampoules à ammoniac sont très similaires à ceux qui sont obtenus avec la méthode classique des ampoules à soude pour l'analyse des gaz acides et incondensables. En revanche, les résultats des analyses en éléments trace montrent que les prélèvements des gaz effectués à l'aide de cette nouvelle procédure offrent, dans la majorité des cas, une meilleure représentativité par rapport à la méthode classique des condensats acides, et ce pour la majorité des éléments volatils. Cependant, il a aussi été démontré que des précautions doivent être prises quant à la qualité du vide dans les ampoules à NH_4OH pour éviter les condensations indésirables de sublimés pendant l'échantillonnage.

. Apports et perspectives de ces études :

Ces nouvelles méthodologies d'échantillonnages des gaz fumeroliens et des panaches volcaniques se sont révélées être des outils simples et efficaces pour l'obtention de la composition chimique globale des émanations volcaniques par l'utilisation de méthodes analytiques largement répendues (chromatographie gaz, HPLC, ICP-MS), et ce en un seul échantillonnage. Ces méthodes sont donc potentiellement porteuses dans des conditions d'observatoires.

- Grâce à son faible encombrement et à sa robustesse, Le VES semble être parfaitement adapté à la surveillance géochimique en continu sur les volcans actifs difficiles d'accès, où seul le panache peut être échantillonné.

-L'ampoule à ammoniac sous vide semble quant à elle être un outil de choix pour l'obtention de la composition chimique complète des gaz volcaniques en un seul échantillonnage.

À l'heure actuelle, cette méthode semble être la plus représentative pour l'étude des concentrations en éléments trace dans les gaz fumeroliens. Cependant, comme nous l'avons vu plus haut, une mauvaise qualité de vide peut engendrer des artefacts d'échantillonnage. Il est donc important de signaler qu'à ce jour, la communauté des volcanologues ne dispose pas de méthode parfaitement fiable pour l'échantillonnage et l'analyse des éléments en trace dans les gaz fumeroliens.

Géochimie des isotopes stables et radiogéniques des éléments trace métalliques dans les gaz volcaniques :

L'objectif principal de cette thèse était de développer la géochimie des isotopes stables et radiogéniques des éléments en trace métalliques dans les gaz volcaniques. Dans ce cadre, les protocoles analytiques MC-ICP-MS, TIMS et ICP-MS qui ont été mis au point, testés et validés dans cette étude, ont permis de réaliser les premières mesures élémentaires et isotopiques du Zn dans les gaz volcaniques, les sublimés et les roches du Mérapi ; ainsi que la première étude isotopique couplée Sr/Pb des gaz fumeroliens et des eaux thermales du Vulcano.

. Isotopes radiogéniques du Sr et du Pb :

L'étude élémentaire et isotopique couplée Sr/Pb effectuée à Vulcano a démontré que les teneurs en Sr/Pb dans les gaz volcaniques et les eaux thermales de l'île résultent de l'interaction des sources naturelles et atmosphérique/anthropique. La majorité des échantillons de gaz indiquent que le Sr résulte du lessivage de la roche ou de contaminations particulaires tandis que le Pb semble issu principalement du dégazage magmatique. Cependant, deux échantillons possédant des signatures Sr/Pb proches des pôles atmosphérique/anthropique indiquent que la variabilité des interactions gaz/eaux météoriques dans un édifice volcanique à perméabilité variable peut modifier temporairement les teneurs et les compositions isotopiques Sr/Pb des gaz fumeroliens. Cette étude suggère aussi que les teneurs en Sr dans les eaux thermales résultent essentiellement du lessivage de la roche par des eaux météoriques infiltrées, sans influence significative de l'eau de mer à l'exception d'un échantillon situé près de la côte. Le Pb semble quant à lui résulter majoritairement des infiltrations d'eau météoriques anthropisées dans les aquifères superficiels de l'île.

. Apports et perspectives de l'étude :

Ce travail démontre l'intérêt de l'utilisation des traceurs radiogéniques pour l'identification des sources des éléments métalliques dans les gaz volcaniques ainsi que pour l'étude des interactions fluides roches dans les systèmes hydro-volcaniques complexes. Cette étude reste cependant très qualitative, principalement en raison de l'absence de données élémentaires et isotopiques sur les eaux météoriques dans la région de Vulcano. L'obtention de ces données permettrait de quantifier précisément les influences des sources volcaniques et atmosphériques/anthropiques sur les teneurs en Sr/Pb dans les gaz volcaniques et les eaux thermales.

Si les variations épisodiques de compositions isotopiques Sr/Pb des gaz fumeroliens sont confirmées, une étude systématique des isotopes Sr/Pb des émanations volcaniques pourrait permettre d'améliorer les calculs des flux de métaux d'origine volcanique à l'atmosphère par correction des phénomènes de recyclage météoriques.

Ce type d'étude peut aussi s'avérer très utile pour tracer l'impact des émissions de métaux d'origine volcaniques à l'atmosphère et quantifier leur influence sur les cycles géochimiques de ces éléments.

. Isotopes stables du Zn :

L'étude élémentaire et isotopique Zn réalisée dans les gaz volcaniques, les sublimés et les roches du volcan Merapi a permis de mettre en évidence d'importantes variations de la compositions isotopiques du Zn entre ces différents échantillons. La composition isotopique des gaz varie de 0,05 à 0,85‰, alors que les échantillons de sublimés présentent les plus hautes valeurs δ^{66}Zn mesurées à ce jour dans les échantillons naturels terrestres (1.48 à 1.68‰). De plus, les compositions isotopiques Zn des gaz et des sublimés semblent clairement dépendantes de la température et suggèrent un processus de fractionnement isotopique à l'équilibre avec condensation préférentielle de l'isotope lourd lors de la réaction : $ZnCl_{2(g)} + H_2S_{(g)} \Leftrightarrow ZnS_{(s)} + 2\ HCl_{(g)}$. Les roches présentant des signatures isotopiques homogènes (valeur moyenne 0.24‰) et inférieures à celles des gaz de haute température, un fractionnement isotopique lors du dégazage magmatique semble probable. Le mécanisme de fractionnement proposé est analogue à ceux déjà observés pour les isotopes légers H, B et C. Il induit un enrichissement de la phase gazeuse en isotope lourd lors du dégazage magmatique en réponse à une diminution de la coordinence du Zn entre le liquide silicaté (coordinence 8 ou 4) et la phase gazeuse (coordinence 2).

. Apports et perspectives de l'étude :

Les données isotopiques présentées dans cette étude sont très prometteuses. Elles suggèrent que les processus de changement de phase en contexte volcanique de haute température induisent des fractionnements isotopiques du Zn significatifs et mesurables.

Dans cette étude, l'influence de la méthodologie d'échantillonnage des gaz volcaniques (condensat acide/ampoule NH_4OH) sur la détermination des compositions isotopiques du Zn a pu être testée sur 3 fumeroles. Même si les variations observées entre les deux modes d'échantillonnage ne modifient pas significativement nos interprétations, il est nécessaire à ce

stade d'entreprendre des systématiques de comparaisons sur un plus grand nombre d'échantillons afin de quantifier précisément cet effet.

La dépendance en température des compositions isotopiques du Zn observée dans les gaz et les sublimés permet d'envisager l'utilisation des isotopes du Zn comme géothermomètres. Ce type d'application pourrait fournir de précieux renseignements sur le comportement des éléments volatils dans les gaz volcaniques mais aussi sur les conditions physico-chimiques de formations des gîtes minéraux.

De même que pour les isotopes du Sr et du Pb, ce type d'étude peut s'avérer utile pour tracer l'impact des émissions de métaux d'origine volcanique à l'atmosphère et leur influence sur les cycles géochimiques de ces éléments.

Ce travail a aussi permis de documenter les bases de données relatives aux variations isotopiques du Zn dans les échantillons naturels en apportant des résultats complémentaires sur les échantillons d'origine volcaniques.

Du fait que le Zn est peu sensible aux changements des conditions d'oxydoréduction, son étude peut aider à la compréhension des processus de fractionnements isotopiques complexes d'éléments possédant plusieurs degrés d'oxydation comme le Se, le Fe ou encore le Cu et ce, dans le cadre d'études isotopiques basées sur des approches multi-élémentaires.

Le développement de ce type d'approches peut aussi fournir un grand nombre de données sur les coefficients de fractionnement isotopiques « naturels » entre phases pour un grand nombre d'éléments métalliques « non traditionnels ». Ces informations peuvent s'avérer fondamentales pour une meilleure compréhension générale des processus de fractionnements isotopiques de ces éléments en contexte naturel. Elles pourraient aussi servir de base de travail pour la validation des modèles théoriques de calculs des coefficients de fractionnements isotopiques de ces nouveaux isotopes stables.

Références bibliographiques citées dans le texte en français

Aiuppa, A., G. Dongarra, G. Capasso, and P. Allard, Trace elements in the thermal groundwaters of Vulcano Island (Sicily), *Journal of Volcanology and Geothermal Research*, *98*, 189-207, 2000.

Albarède, F., The Stable Isotope Geochemistry of Copper and Zinc, *Reviews in Mineralogy & Geochemistry*, *55*, 409-427, 2004.

Anbar, A.D., Iron stable Isotopes: beyond biosignatures, *Earth and Planetary Science Letters*, *217*, 223-236, 2004.

Barbieri, M., and M. Morotti, Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture Volcano, Italy, *Applied Geochemistry*, *18*, 117-125, 2003.

Bernard, A., Les mécanismes de condensation des gaz volcaniques., Ph.D. thesis thesis, University of Brusseles, Belgium, 1985.

Bichler, M., and F. Sortino, Determination and speciation of minor and trace elements in volcanic exhalations by NAA., *J. Radioanal. Nucl. Chem.*, *192*, 183-194, 1995.

Bollhöfer, A., and K.J.R. Rosman, Isotopic source signature for atmospheric lead: The Northern Hemisphere, *Geochimica and Cosmochimica Acta*, *65* (11), 1727-1740, 2001.

Bolognesi, L., Comment on "Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance" by G. Chiodini, R. Cioni, L. Marini, and C. Panichi, *Bulletin of Volcanology*, *58*, 319-320, 1996.

Bolognesi, L., and F. D'Amore, Isotopic variation of the hydrothermal system on Vulcano Island, Italy, *Geochimica and Cosmochimica Acta*, *57*, 2069-2082, 1993.

Capasso, G., R. Favara, S. Francofonte, and S. Inguaggiato, Chemical and isotopic variations in fumarolic discharge and thermal waters at Vulcano Island (Aeolian Islands, Italy) during 1996: evidence of resumed volcanic activity., *Journal of Volcanology and Geothermal Research*, *88*, 167-175, 1999.

Chevrier, R.M., and F. Le Guern, Prélèvement et analyses des condensats de fumerolles sur volcans actifs: Soufrière de la Guadeloupe (1976-1977) et Pouzzoles et Vulcano (Italie) (1978), *Bulletin of Volcanology*, *45*, 173-178, 1982.

Chiodini, G., R. Cioni, and L. Marini, Reactions governing the chemistry of crater fumaroles from Vulcano Island, and implications for volcanic surveillance, *Applied Geochemistry*, *8*, 357-371, 1993.

Chiodini, G., R. Cioni, L. Marini, and C. Panichi, Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance, *Bulletin of Volcanology*, *57*, 99-110, 1995.

Clocchiatti, R., A. Del Moro, A. Gioncada, J.L. Joron, M. Mosbah, L. Pinarelli, and A. Sbrana, Assessment of shallow magmatic system : the 1888-90 eruption, Vulcano Island, Italy, *Bulletin of Volcanology*, *56*, 466-486, 1994.

Cortecci, G., E. Dinelli, L. Bolognesi, T. Boschetti, and G. Ferrara, Chemical and isotopic compositions of water and dissolved sulfate from shallow wells on Vulcano Island, Aeolian Archipelago, Italy, *Geothermics*, *30*, 69-91, 2001.

De Astis, G., L. La Volpe, A. Pecerrillo, and L. Civetta, Volcanological and petrological evolution of Vulcano island (Aeolian Arc, southern Tyrrhenian Sea), *Journal of Geophysical Research*, *102* (B4), 8021-8050, 1997.

De Astis, G., A. Peccerillo, P.D. Kempton, L. La Volpe, and T.W. Wu, Transition from calc-alkaline to potassium-rich magmatism in subduction environments: geochemical and Sr, Nd, Pb isotopic constraints from the island of Vulcano (Aeolian arc), *Contribution to Mineralogy and Petrology*, *139*, 684-703, 2000.

Del Moro, A., A. Gioncada, L. Pinarelli, A. Sbrana, and J.L. Joron, Sr, Nd, and Pb isotope evidence for open system evolution at Vulcano, Aeolian Arc, Italy, *Lithos*, *43*, 81-106, 1998.

Dessert, C., Ph.D. Thesis, Impact du Volcanisme sur le climat et sur les cycles géochimiques globaux, Université Paul Sabatier, Toulouse, France, 2002.

Dongarra, G., and D. Varrica, The presence of heavy metals in air particulate at Vulcano island, *The Science of the Total Environment*, *212*, 1-9, 1998.

Ellam, R.M., C.J. Hawkesworth, M.A. Menzies, and N.W. Rogers, The Volcanism of Southern Italy: Role of Subduction and the Relationship Between Potassic and Sodic Alkaline Magmatism, *Journal of Geophysical Research*, *94* (B4), 4589-4601, 1989.

Esperança, S., G.M. Crisci, R. de Rosa, and R. Mazzuoli, The role of crust in the magmatic evolution of the island of Lipari (Aeolian Islands, Italy), *Contribution to Mineralogy and Petrology* (112), 450-462, 1992.

Faivre-Pierret, R., SO_2, HCl and HF detection and dosing in the volcanic gas phase. In: Tazieff, Sabroux (Eds), in *Forecasting volcanic events*, pp. 399-408, Elsevier, 1983.

Ferrara, G., A. Garavelli, L. Pinarelli, and F. Vurro, Lead isotope composition of the sublimates from the fumaroles of Vulcano (Aeolian Islands, Italy): inferences on the deep fluid circulation, *Bulletin of Volcanology*, *56*, 621-625, 1995.

Finnegan, D.L., J.P. Kotra, D.M. Hermann, and W.H. Zoller, The use of ^{7}LiOH-impregnated filters for the collection of acid gases and analysis by instrumental neutron activation analysis., *Bulletin of Volcanology*, *51*, 83-87, 1989.

Fischer, T.P., G.B. Arehart, N.C. Sturchio, and S.N. Williams, The relationship between fumarole gas composition and eruptive activity at Galeras Volcano, Columbia., *Geology*, *24*, 531-534, 1996.

Fischer, T.P., W.F. Giggenbach, Y. Sano, and S.N. Williams, Fluxes and sources of volatile discharged from Kudryavy, a subduction zone volcano, Kurile Islands, *Earth and Planetary Science Letters*, *160*, 81-96, 1998a.

Fischer, T.P., S. Shuttleworth, and P.A. O'Day, Determination of trace and platinum-group elements in high ionic strength volcanic fluids by sector-field inductively coupled plasma mass spectrometry (ICP-MS), *Journal of Analytical Chemistry*, *362*, 457-464, 1998b.

Freydier, R., and J. Viers, Isotopic study of lead transfer at the interface soil-plants-atmosphere, *Geophysical Reasearch Letters*, *30* (5), 1227, 2003.

Galy, A., N.S. Belshaw, L. Halicz, and R.K. O'Nions, High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry, *International Journal of Mass Spectrometry*, *208*, 89-98, 2001.

Giggenbach, W.F., A simple method for the collection and analysis of volcanic gas samples., *Bulletin of Volcanology*, *39*, 132-145, 1975.

Gioncada, A., R. Mazzuoli, M. Bisson, and M.T. Pareschi, Petrology of volcanic products younger than 42ka on the Lipari-Vulcano complex (Aeolian Island, Italy): an example of volcanism controlled by tectonics, *Journal of Volcanology and Geothermal Research*, *122*, 191-220, 2003.

Goff, F., C.J. Janik, H. Delgado, C. Werner, D. Counce, J.A. Stimac, C. Siebe, S.P. Love, S.N. Williams, T.P. Fischer, and L. Johnson, Geochemical surveillance of magmatic volatiles at Popocatepetl volcano, Mexico., *G.S.A. Bull.*, *110*, 695-710, 1998.

Goff, F., H.A. Wollenberg, D.C. Brookins, and R.W. Kistler, A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California, *Journal of Volcanology and Geothermal Research*, *48*, 265-281, 1991.

Halmer, M.M., H.U. Schmincke, and H.H. Graf, The annual volcanic gas input to the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, *Journal of Volcanology and Geothermal Research*, *115*, 511-528, 2002.

Harris, A.J.L., and A.J.H. Maciejewski, Thermal surveys of the Vulcano Fossa fumarole field 1994-1999: evidence of migration and sealing., *Journal of Volcanology and Geothermal Research*, *102*, 119-147, 2000.

Le Guern, F., and A. Bernard, A new method for sampling and analysing volcanic sublimates - Application to Merapi volcano, Java, *Journal of Volcanology and Geothermal Research*, *12*, 133-146, 1982.

Leeman, W.P., S. Tornarini, M. Penissi, and G. Ferrara, Boron isotopic variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: Implications for evelution of volcanic fluids, *Geochimica and Cosmochimica Acta*, *69* (1), 143-163, 2005.

Marechal, C.N., Géochimie des isotopes du cuivre et du zinc: méthode, variabilité naturelle et application océanographique, Ph.D. thesis, Ecole Normale Supérieure de Lyon et Université Claude Bernard - Lyon I, 1998.

Marechal, C.N., E. Nicolas, C. Douchet, and F. Albarède, Abundance of zinc isotopes as marine biochemical tracer, *Geochemistry Geophysics Geosystems*, *1*, 1999GC000029, 2000.

Marechal, C.N., P. Télouk, and F. Albarède, Precise analysis of copper and zinc isotopic compositons by plasma-source mass spectrometry, *Chemical Geology*, *156*, 251-273, 1999.

Möller, P., P. Dulski, Y. Savascin, and M. Conrad, Rare earth elements, yttrium and Pb isotope ratios in thermal spring and well waters of West Anatolia, Turkey: a hydrochemical study of their origin, *Chemical Geology*, *206*, 97-118, 2004.

Monna, F., A. Aiuppa, D. Varrica, and G. Dongarra, Pb Isotope Composition in Lichens and Aerosols from Eastern Sicily : Insight into the Regional Impact of Volcanoes on the Environment, *Environmental Science and Technology*, *33*, 2517-2523, 1999.

Monna, F., J. Lancelot, I.W. Croudace, A.B. Cundy, and J.T. Lewis, Pb Isotopic Composition of Airborne Particulate Material from France and Southern United Kingdom : Implications for Pb Pollution Sources in Urban Areas, *Environmental Science and Technology*, *31* (8), 2277-2286, 1997.

Pennisi, M., W.P. Leeman, S. Tonarini, A. Penissi, and P. Nabelek, Boron, Sr, O and H isotope geochemistry of grounwaters from Mt. Etna (Sicily) - Hydrologic implications, *Geochimica and Cosmochimica Acta*, *64* (6), 961-974, 2000.

Pichat, S., C. Douchet, and F. Albarède, Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka, *Earth and Planetary Science Letters*, *210*, 167-178, 2003.

Poitrasson, F., A.N. Halliday, C.D. Lee, S. Levasseur, and N. Teutsch, Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms, *Earth and Planetary Science Letters*, *223*, 253-266, 2004.

Quisefit, J.P., J.P. Toutain, G. Bergametti, M. Javoy, B. Cheynet, and A. Person, Evolution versus cooling of gaseous volcanic emmissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations, *Geochimica and Cosmochimica Acta*, *53*, 1989.

Rehkämper, M., M. Frank, J.R. Hein, and A.N. Halliday, Cenozoic marine geochemistry of thallium deduced from isotopic studies of ferromanganese crusts and pelagic sediments, *Earth and Planetary Science Letters*, *219*, 77-91, 2004.

Rehkämper, M., M. Schönbächler, and C.H. Stirling, Multiple Collector ICP-MS: Introduction to Instrumentation, Measurements Techniques and Analytical Capabilities, *Geostandards Newsletter*, *25* (1), 23-40, 2000.

Reviews in Mineralogy, V., Geochemistry of non traditional stable isotopes, in *Reviews in Mineralogy & geochemistry*, edited by C.M. Johnson, B.L. Beard, and F. Albarède, pp. 454, 2004.

Rosman, K.J.R., and P.D.P. Taylor, Isotopic composition of the elements 1997, *Journal of Analytical Atomic Spectrometry*, *13*, 45N-55N, 1998.

Rouxel, O., Y. Fouquet, and J. Ludden, Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: Evidence from sulfur, selenium, and iron isotopes, *Geochimica and Cosmochimica Acta*, *68* (10), 2295-2311, 2004.

Symonds, R.B., Y. Mizutani, and P.H. Briggs, Long term geochemical surveillance of fumaroles at Showa-Shinzan dome, Uzu volcano, Japan, *Journal of Volcanology and Geothermal Research*, *73*, 177-211, 1996.

Symonds, R.B., W.I. Rose, M.H. Reed, F.E. Lichte, and D.L. Finnegan, Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia., *Geochimica and Cosmochimica Acta*, *51*, 2083-2101, 1987.

Taran, Y., A. Bernard, J.C. Gavilanes, E. Lunezheva, A. Cortés, and M.A. Armienta, Chemistry and mineralogy of high temperature gas discharges from Colima volcano,

Mexico. Implications for magmatic gas-atmosphere interaction, *Journal of Volcanology and Geothermal Research*, *108*, 245-264, 2001.

Taran, Y.A., J.W. Hedenquist, M.A. Korzhinsky, S.I. Tkachenko, and K.I. Shmulovich, Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands, *Geochimica and Cosmochimica Acta*, *59* (9), 1749-1761, 1995.

Tedesco, D., Systematic variations in the $^{3}He/^{4}He$ ratio and carbon of fumarolic fluids from active volcanic areas in Italy: Evidence for radiogenic ^{4}He and crustal carbon addition by the subducting African plate?, *Earth and Planetary Science Letters*, *151*, 255-269, 1997.

Tedesco, D., G. Miele, Y. Sano, and J.P. Toutain, Helium isotopic ratio in Vulcano island fumaroles: temporal variations in shallow level mixing and deep magmatic supply, *Journal of Volcanology and Geothermal Research*, 117-128, 1995.

Toutain, J.P., J.P. Quisefit, P. Briole, P. Aloupogiannis, G. Robaye, and P. Blanc, Mineralogy and chemistry of solid aerosols emitted from Mount Etna., *Geochemical Journal*, *29*, 163-173, 1995.

Vallelonga, P., and T.A. Mather, Lead (Pb) fluxes and Pb isotopic compositions from Masaya Volcano, Nicaragua, *Atmospheric Environment*, *37*, 4453-4460, 2003.

Vié le Sage, S., Chemistry of the volcanic aesosols. In Tazieff, Sabroux (Eds.), in *Forecasting Volcanic Events*, pp. 445-474, 1983.

Viers, J., P. Oliva, R. Freydier, and B. Dupre, The use of Zinc isotopes to constrain the biogeochemical cycling of metals in watersheds, Goldschmidt conference, Copenhagen, Denmark, 5-11 June, *Geochimica and Cosmochimica Acta*, *68* (11S), A413, 2004.

Weiss, D.J., T.F.D. Mason, F.J. Zhao, G.J.D. Kirk, B.J. Coles, and M. Horstwood, Isotopic discrimination of zinc in higher plants, *New Phytologist*, *in press*, 2005.

Weyer, S., and J.B. Schwieters, High precision Fe isotope measurements with high mass resolution MC-ICPMS, *International Journal of Mass Spectrometry*, *226*, 355-368, 2003.

Young, E.D., and A. Galy, The Isotope Geochemistry and Cosmochemistry of Magnesium, in *Reviews in Mineralogy and Geochemistry - Geochemistry of non-traditional stable isotopes*, edited by C.M. Johnson, L.B. Brian, and F. Albarède, pp. 197-229, 2004.

Annexe 1 :
Nouveau chapitre de thèse :
Valorisation des compétences

Nouveau chapitre de thèse – Valorisation des compétences

Géochimie élémentaire et isotopique du Zn, du Sr et du Pb des gaz volcaniques.

Méthodologies d'échantillonnage et apports à la compréhension
des interactions fluides/solides.

Anthony NONELL
Allocataire de recherche MENRT (2001 – 2004)

Thèse réalisée
au *Laboratoire des Mécanismes et Transferts en Géologie* (LMTG, Toulouse),
sous la direction de J.P. TOUTAIN et M.MUNOZ

Ecole doctorale « *Sciences de l'Univers, de l'Environnement et de l'Espace* » (SDU2E)

1. PRÉSENTATION RÉSUMÉE DE LA THÈSE

1.1. Titre : Géochimie élémentaire et isotopique du Zn, du Sr et du Pb des gaz volcaniques. Méthodologies d'échantillonnage et apports à la compréhension des interactions fluides roches.

1.2. Domaine scientifique : Géochimie isotopique

1.3. Présentation de la thèse:

Cadre général :

Les volcans sont parfois responsables de catastrophes meurtrières. Par exemple, l'éruption de la Montagne Pelée (Martinique, 1902) fit 28000 morts. Plus récemment, l'éruption du Névado del Ruiz (Colombie, 1985) à fait 25000 morts. De nos jours, des villes entières vivent encore sous la menace d'un volcan. Malgré les progrès réalisés en volcanologie ces dernières années grâce à une approche pluridisciplinaire (géophysique, tectonique, minéralogie, géochimie), l'activité volcanique et son impact sur l'environnement restent encore mal connus. Dans ce cadre, l'étude du comportement des métaux dans les fluides volcaniques peut permettre des avancées significatives dans plusieurs domaines d'intérêts scientifiques et socio-économiques:

- Caractérisation des apports de métaux d'origine volcanique à l'atmosphère.
- Description du rôle des fluides magmatiques dans la formation de minerais.
- Identification de précurseurs d'éruption.
- Compréhension de la dynamique interne des volcans actifs.

Cependant, en raison de difficultés liées à l'échantillonnage et à l'analyse des émanations volcaniques, le comportement des métaux en contexte volcanique reste un domaine peu documenté.

Objectifs de la thèse :

Les objectifs de ce travail de thèse sont multiples:

- Développer de nouveaux protocoles d'analyse et d'échantillonnage permettant l'étude élémentaire et isotopique des métaux traces dans les gaz et minéraux secondaires d'origine volcanique.

- Étudier la distribution élémentaire et isotopique de certains métaux (Sr, Pb, Zn) dans les échantillons précités.
- Utiliser les résultats obtenus pour définir l'origine de ces métaux et décrire leur comportement en contexte volcanique.
- Évaluer l'impact de cette étude sur la compréhension des processus liés à l'activité volcanique.

2. CONTEXTE

2.1. Laboratoire d'acceuil:

Laboratoire des Mécanismes et Transferts en Géologie (LMTG), UMR 5563, 16 Avenue Edouard Belin, 31400, Toulouse, France

2.2. Encadrants:

Directeur de thèse : Jean-Paul Toutain, Physicien-Adjoint, Observatoire Midi-Pyrénées, Laboratoire des Mécanismes et Transferts en Géologie, UMR 5563, 16 Avenue Edouard Belin, 31400, Toulouse, France

Co-directrice de thèse : Marguerite Munoz, CR1 (CNRS), Observatoire Midi-Pyrénées, Laboratoire des Mécanismes et Transferts en Géologie, UMR 5563, 16 Avenue Edouard Belin, 31400, Toulouse, France

2.3. Place de la thèse dans les orientations scientifiques du laboratoire :

Parmi les onze thèmes de recherche du LMTG, ce sujet s'inscrit dans le thème : « Géochimie et minéralogie des processus hydrothermaux et diagénétiques».

2.4. Financement :

Allocation de recherche MENRT (Ministère de l'Education Nationale, de la Recherche et de la Technologie).

2.5. Partenaires académiques :

- Coordination de la recherche Volcanologique, Observatoire de Physique du Globe de Clermont-Ferrand, Université Blaise Pascal & CNRS Campus des Cézeaux, 24, avenue des Landais, 63177 Aubière, France

- École Normale Supérieure de Lyon, Laboratoire des sciences de la Terre, 46 Allée d'Italie, 69364 Lyon cedex 07
- Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, V. Ugo la Malfa,153, 90146 Palermo
- MVO, Merapi Volcano Observatory, Jalan Cendana 15, Yogyakarta, Indonesia

3. COUT DU PROJET

Le coût total de mon projet de thèse a été calculé comme suit:

1) Évaluation des coûts des salaires des personnes impliquées dans le projet en fonction de leur grade, de leur temps de participation et des charges patronales au taux de 45% (Tab.1). Ce calcul a été réalisé à partir des grilles d'indices publiées par le CNRS ou après discussion avec les intéressés.
2) Évaluation des dépenses annexes : missions de terrain, analyses, équipements, frais de formations et de participation aux congrès (Tab.2).

Au total, mon projet de thèse a coûté environ 184000 euros. Les salaires représentant la majorité des sommes engagées (90%).

4. COMPETENCES DÉVELOPPÉES DANS LE CADRE DE LA THÉSE

4.1. Compétences techniques :

4.1.1. Travail sur le terrain :

Une partie de mon travail en tant qu'allocataire de recherche a résidé dans la prospection et l'échantillonnage sur le terrain. Dans ce cadre, j'ai participé à plusieurs missions de prélèvements (préparation de la mission, sélection des sites d'échantillonnage, mesures de paramètres in-situ, conditionnement) sur une grande variété d'échantillons: eaux naturelles, roches, gaz fumeroliens et panaches volcaniques, sublimés volcaniques (minéraux condensés lors du refroidissement des gaz volcaniques).

4.1.2. Géochimie des solides et des solutions naturelles – Géochimie isotopique

Ma thèse m'a permis d'acquérir de solides bases concernant de nombreuses techniques analytiques « classiques » comme le dosage des éléments majeurs par HPLC et AAS, les

techniques d'analyses par colorimétrie et par titration, et le dosage des éléments en trace par ICP-MS (Perkin-Elmer Elan 6000) dans des matrices variées (eaux, roches, condensats de gaz volcaniques, sublimés volcaniques, panaches volcaniques). Dans ce cadre, j'ai été amené à adapter et à développer

1) les protocoles de préparation des échantillons en vue de la détermination des concentrations en éléments majeurs et traces
2) les méthodes de traitement des données brutes ICP-MS (corrections d'interférences pour les matrices chargées).

Je me suis spécialisé dans les techniques d'analyses isotopiques Sr/Pb (utilisation de la spectrométrie de masse à thermo-ionisation, chimie d'élution sur colonne), ainsi que dans les techniques analytiques relatives à la séparation chimique et à l'analyse isotopique des éléments de masses moyennes (Cu, Zn, Fe). Dans ce cadre, j'ai travaillé sur plusieurs MC-ICP-MS, notamment sur Fisons Instruments Plasma 54 (Ecole Normale Supérieure de Lyon), où j'ai effectué mes premières analyses isotopiques Cu/Zn. J'ai ensuite collaboré avec R.Freydier (I.R., CNRS) et J.Viers (M.C., UPS) pour la mise au point des analyses isotopiques Cu/Zn sur Thermo-Finnigan Neptune (Reçu au LMTG en 2003). Durant cette période, j'ai optimisé les paramètres machines, testé les effets de matrices, comparé et sélectionné les méthodes de corrections du fractionnement en masse instrumental et des interférences.

J'ai aussi acquis une bonne expérience en ce qui concerne les calculs et interprétations propres à la géochimie élémentaire et isotopique des eaux naturelles, roches magmatiques, gaz fumeroliens et sublimés volcaniques : approche thermodynamique de la chimie des solutions naturelles et des gaz de haute température, traçage de sources, calculs de mélanges, mise en évidence de processus responsables de fractionnement élémentaires et isotopiques.

4.1.3.Minéralogie

Lors de ma formation universitaire, j'ai étudié l'aspect théorique de l'analyse par diffraction des rayons X, puis j'ai développé une approche plus pratique de cette technique, durant mon contrat en tant qu'allocataire de recherche, en caractérisant les phases minérales contenues dans les sublimés volcaniques.

J'ai aussi suivi une formation théorique et pratique (Institut National des Sciences Appliquées, Toulouse) sur les techniques liées à la microscopie électronique à balayage (MEB) et à transmission (MET).

4.1.4.Modélisation géochimique

Au Laboratoire des Mécanismes de Transferts en Géologie, je me suis sensibilisé à la modélisation de la spéciation des éléments (majeurs et en traces) en phase aqueuse (CHESS, EQ3/6) et gazeuse (Hch, Unitherm) indispensable à toute étude de processus naturels. Cette approche a été abordée, durant mon contrat en tant qu'allocataire de recherche, au travers de la réalisation de modèles conceptuels permettant de décrire les processus de condensation/précipitation de phase minérales à partir de fluides naturels. Par ailleurs, cette description permet de mettre en évidence les processus naturels responsables des fractionnements isotopiques des éléments de masse moyenne lors des processus de changements de phases.

4.2. Compétences personnelles :

4.2.1.Travail en équipe

Pour mener à bien mon travail d'allocataire de recherche, j'ai collaboré avec des personnes aux profils différents : techniciens, ingénieurs, chercheurs, avec qui j'ai régulièrement discuté des stratégies à adopter pour faire aboutir mon projet : acquisition de données, résolution de problèmes analytiques, interprétations des résultats.

4.2.2.Communication scientifique

En plus des articles publiés, soumis ou en cours de rédaction pour des revues scientifiques internationales, j'ai communiqué mes résultats lors de congrès scientifiques nationaux et internationaux sous forme de communications orales (français-anglais) ou sous forme de poster. Ma participation à ces manifestations m'a permis d'établir des contacts avec d'autres laboratoires (ETH Zurich, University of Cambridge, CRPG Nancy, Imperial College London) et de discuter de mon travail avec la communauté scientifique.

J'ai aussi présenté mes résultats lors des « réunions isotopiques » organisées au LMTG et lors d'un séminaire à l'occasion de la venue du Dr. M. Rehkämper (ETH Zurich, Imperial College London), reconnu comme l'un des plus grands spécialistes mondiaux des applications des « nouveaux isotopes stables » à la géochimie et à la cosmochimie.

5. RÉSULTATS ET RETOMBÉES DU PROJET

Du point de vue de la compréhension des processus volcaniques, ce projet a permis de documenter les variabilités élémentaires et isotopiques du Sr, Pb et Zn dans les gaz, panaches, sublimés et roches volcaniques du Merapi(Indonésie) et à Vulcano(Italie). Ceci a permis d'améliorer la compréhension de l'origine (sources) et du comportement de ces ETM dans les sites de volcanisme actif.

Au niveau de l'échantillonnage des gaz et des panaches volcaniques, de nouveaux modes de prélèvement ont été mis au point et validés. Ces nouvelles techniques simplifient grandement la tâche des volcanologues et améliorent la représentativité des prélèvements des émanations volcaniques.

Ce projet a aussi permis de développer de nouveaux protocoles d'analyse des échantillons volcaniques:

1) Amélioration des méthodes d'analyses des concentrations en ETM par ICP-MS (Inductively Coupled Plasma Mass Spectometry).

2) Analyses des compositions isotopiques (strontium et plomb) par TIMS (Thermal Ionisation Mass Spectrometry).

3) Analyses des compositions isotopiques du zinc par MC-ICP-MS (Multiple-Collector Inductively Coupled Plasma Mass Spectometry). Il est important à ce stade de signaler que cet enjeu dépasse de loin le cadre général de ce projet. En effet, depuis son apparition récente (1995), cette technologie novatrice a permis l'exploration du fractionnement en masse des éléments dits « lourds » et commence à trouver des applications de première importance dans des domaines scientifiques autres que la géochimie, comme la médecine (traceurs du métabolisme) ou la cosmochimie (datation des processus de formation du système solaire). Le développement de cette technique est donc de première importance pour pérenniser la reconnaissance analytique internationale du LMTG.

L'aboutissement de ce projet de recherche se traduit par : la rédaction de ma thèse, 2 publications (Journal of Volcanology and Geothermal Reasearch et Geochemistry Geophysics Geosystems), 1 publications soumises (Earth and Planetary Science Letters), 2 publications en préparation, 2 présentations orales et 2 posters dans des conférences

nationales et internationales (Goldschmidt Geochemistry Conference, IAVCEI General assembly, SFIS Réunion jeunes chercheurs, EGS-EGU-EUG Joint Assembly).

J'aspire aujourd'hui à étendre mon expérience analytique sur MC-ICP-MS et à devenir un expert dans ce domaine. Pour atteindre cet objectif, j'ai rédigé, en collaboration avec le Dr. M. Rehkämper (ETH Zurich, Imperial College London) un projet de recherche en vue de l'obtention d'une bourse Marie Curie Intra-European Fellowship. Cette bourse me permettrait d'effectuer un séjour post-doctoral à l'Imperial College de Londres pendant lequel je souhaite développer de nouvelles techniques d'analyses sur MC-ICP-MS et appliquer ces méthodes au contexte cosmochimique. En complément d'une collaboration avec des spécialistes de renommée mondiale dans le domaine de l'analyse par MC-ICP-MS, cette expérience me permettra d'établir un réseau de contacts avec la communauté scientifique européenne, mais aussi de renforcer ma liste de publication en vue d'une candidature future aux concours d'ingénieur de recherche, chargé de recherche ou maître de conférence.

Cette thèse a été une expérience très enrichissante sur le plan personnel. Les compétences acquises dans le cadre de ce travail sur le plan du savoir faire méthodologique, sur la gestion globale d'un projet scientifique ou encore sur les méthodes de communication scientifiques, se montreront utiles quelles que soient mes expériences professionnelles futures. C'est donc sans aucune hésitation que je réitèrerais cette expérience, si elle était à renouveler.

Tableau 1 : *Evaluation des coûts des salaires des principaux acteurs de la thèse en fonction de leur participation au projet.*

(a) Personnels internes au LMTG :

	nombre de personnes	temps passé estimé (%, jours)	coût estimé (euros)
Allocatiare	1	100%	65082
Encadrants			
Physicien adjoint	1	25%	40600
Chargée de recherche	1	25%	40600
Personnels techniques			
Techniciens	3	80j	4480
Assistants ingénieurs	3	50j	3950
Ingénieurs d'étude	1	30j	3780
Ingénieurs de recherche	2	30j	4560
total			**163052**

(b) Personnels extérieurs au LMTG :

	nombre de personnes	temps passé estimé (%, jours)	coût estimé (euros)
Ingénieur de recherche ENS Lyon	1	10j	1520
Assistants ingénieurs	1	10j	790
total			**2310**
Coût total des salaires			**165362**

Tableau 2 : *Evaluation des dépenses nécessaires à la réalisation du projet (hors salaires).*

types de dépenses	coût estimé (euros)
missions de terrain	4750
Analyses	
analyses LMTG	4500
services communs	750
prestations extérieures	0
Equipement	
informatique	500
Prélèvement et conditionnement des échantillons	5000
formations	0
congrès	3000
total	**18500**

Annexe 2 :
Measurements of Zn isotopic composition in a soil-plant system of a tropical watershed: a new tool to constrain the biogeochemical cycles of metals?

Measurements of Zn isotopic composition in a soil-plant system of a tropical watershed: a new tool to constrain the biogeochemical cycles of metals?

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Abstract

The objective of the present study was to determine for the first time the natural variation in zinc (Zn) isotopic compositions of different soil horizons, parent rocks (silicate), litters, and plants from the same watershed (Nsimi, south Cameroon, Africa). The $\delta^{66}Zn$ ($\delta^{66}Zn = [(^{66}Zn/^{64}Zn)_{sample}/(^{66}Zn/^{64}Zn)_{JMC\ 3\text{-}0749L}) -1] *10^3$) measured in the soils, litters and rocks range from -0.22 to 0.65‰.

From the bottom (i.e., saprolite/granite weathering front) to the top soil profile (loose clayey horizon), the soils exhibit increasing degrees of weathering and alteration into a mature soil profile and a preferential enrichment in the light isotopes. The organs (i.e., root, shoot, leave) of six plants were analyzed for their Zn isotopic compositions. $\delta^{66}Zn$ varied from -0.91‰ to 0.75‰. Plants roots and shoots are generally enriched in heavy Zn ($\delta^{66}Zn$ of +0.32 to +0.86‰) relative to the litter layer while tree leaves have more negative values, suggesting that both root uptake and internal Zn transport cause isotopic fractionation. Contrary to the significantly lower $\delta^{66}Zn$ values of shoots, relative to roots, observed by Weiss et al. [9], we find no significant difference among shoots and roots. Similar to their study we find the most negative $\delta^{66}Zn$ values in the leaves.

The results obtained were discussed in order to interpret the isotopic composition of the weathered soil profile; one hypothesis considers fractionation during adsorption process of Zn onto mineral surfaces while another one implies the role of plants when they incorporate elements from the soils. At present time, it is difficult to use Zn isotopes to reach a better understanding of metals cycling. However, this paper represents a starting point to evaluate the potential use of these isotopes and should help the community to plan further investigations.

Keywords: Zinc isotopes, soil, vegetation, weathering, cycle

1. Introduction

The understanding of the elements (major and trace) cycling within a watershed or at the Earth Surface scale requires to consider both biotic and abiotic processes that control minerals chemical weathering rates and elements fluxes between the different reservoirs [1, 2]. Among the various elements, Zinc (Zn) cycling is particularly investigated. Indeed, Zn is a trace element found in all soils, plants, and animals and it is one of the eight trace elements (with boron, chlorine, copper, iron, manganese, molybdenum and nickel) essential for the normal healthy growth of plants, animals, and humans [3]. For instance, Zn is a regulatory cofactor of a large number of enzymes that play a key role in several processes such as carbohydrate and protein metabolism, or biochemical reactions maintaining membrane integrity [4]. Due to the complexity of natural systems, it is difficult to constrain the role of the different processes involved in the metal cycling. Among these processes, the role of plants and plant-induced biological activity is crucial but still misunderstood [2].

The recent development of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) enable us to measure with significant precision mass-dependent isotope variations occuring in natural environments (see references in [5]). Recently, Cloquet [6] has compiled most of the Zn isotopic composition data available in the literature for bio-geological samples. The δ^{66}Zn (relative to JMC 3-0749L) of all these samples ranges from -0.5‰ (incinerator ash, [6]) to 1.34‰ (deep-sea carbonate, [7]). Direct evidence for biological fractionation was shown by Zhu et al. [8] who reported a fractionation of 1.1‰ (relative to Zn nutrient solution) for Zn proteins synthesized by yeast. In controlled plant growth studies, Weiss et al. [9] observed heavy Zn isotopes enrichment in roots (0.04-0.09‰ per atomic mass unit), and a depletion (up to -0.26‰ per atomic mass unit) from roots to shoots in rice, lettuce and tomato. It was suggested that these fractionations result from surface adsorption, solution speciation and membrane-transport controlled uptake.

If Zn isotopes are fractionated during incorporation by plants relative to the soil/rock system, then the isotopic signatures of the different reservoirs can be used as a new tracer to understand metals cycling within a watershed. The objective of the present study is to determine the natural variation in Zn isotopic compositions of different soil horizons (including litters), parent rocks (silicates), and plants from the small tropical watershed Nsimi-Zoétélé (Cameroon, Africa) [10]. The obtained data will then be used as a starting point to evaluate the potential use of Zn isotopes to constrain transfer of metals between plants and soils and during pedogenetic processes.

2. Description of the study area

2.1. General characteristics

Rocks, soils, and plants samples were collected at the Nsimi-Zoetele site in the Mengong watershed (Fig. 1). This watershed is located ~120 km to the southeast of the city of Yaoundé, southern Cameroon (3°10'N-11°51'E), 200 km East of the Atlantic coast, and is covered by a tropical rainforest. The geomorphology is characterized by 700m high convex rounded hills surrounding a flat swamp zone, the latter representing about 20% of the whole basin area (0.6 km^2). Such a geomorphology is characteristic of the erosion surface of the "South Cameroon Plateau" [11]. The Mengong watershed belongs to the Nyong basin, a larger basin that has a drainage area of 27,800 km^2, located between the latitudes 2°48'N and 4°32'N and the longitudes 9°54'E and 13°30'E. The climate is of equatorial type and marked by four different seasons, including two three-month wet seasons (from September to November and from April to June), a four-month dry season (from December to March) and a short dry season from July to August. The mean annual rainfall is 1751 ± 143 mm and the mean annual air temperature is 24°C ± 1 [12].

2.2. Soils and bedrock descriptions

The soil cover in the Nsimi watershed consists mainly of thick lateritic formations which can reach 40m depth at hill tops**.** This lateritic cover started to develop during the Miocene (6-20 Ma) [11]. The parent rock is a mixture of two granitoid rocks originating from late Archean crustal evolution of the Congo Craton (calco-alkaline differentiation) [13]. These rocks are a gray blue-colored granodiorite, that is fine to medium grained, and a leucocratic monzogranite, that is medium to coarse grained. A description of the mineralogy of these two rocks are given in Viers and Wasserburg [14]. These authors reported a Nd model age of 2.81 Ga for these two rocks. For the present study, the granodiorite was sampled in the hill zone (close to the pit 1L6, Fig. 1) while the monzogranite was sampled in the swamp zone (close to the SZ pit, Fig. 1). The lateritic soil cover can be divided into four main horizons from the bottom to the surface: a saprolite zone, a mottled clay horizon, a nodular ferruginous horizon, and a soft clayey horizon that supports the litter layer [10, 14, 15]. The main minerals in these soils are 1) primary resistant minerals (i.e., quartz, and to a lesser extent K-feldspar in the saprolite zone), and 2) iron- and aluminum-rich weathering products (i.e., kaolinite, goethite, and hematite) [10, 14, 15]. Less abundant minerals are mainly Ti-oxides and zircon. In the swamp zone organic rich sandy soils have evolved. These are partly affected by colluviation and show hydromophic features that are typical of tropical swamp zones (tropical podzols) [16].

3. Sample Collection, Treatment and Analytical Techniques

3.1. Sample collection

The soils, rocks, and plants samples are listed in Tables 1 and 2 together with their sampling location in the watershed (Fig. 1). In the text, soil samples are indicated by the pit name followed by the sampling depth in cm (e.g., 5L6-675).

3.1.1. The soil and rock samples

Samples of parent rocks (1 to 4 kg) were collected from drill cores (i.e., 1L6) located in the hill zone (granodiorite) and from outcrops located in the bed brook (monzogranite). Bulk soil samples of about 2 kg were collected from drill cores or pedological pits. These samples were collected in soft plastic boxes to preserve the soil structure. The porosity of the soil, close to 0.50 in all the soil horizons, has been calculated using the bulk density (obtained by the paraffin method) and the grain density (obtained by the air picnometer method) [10].

3.1.2. The plant samples

More than twenty different plant species were collected of which six were chosen for Zn isotopic measurements. The sampling locations and the species classification is given in Table 2. After collection, plant materials (i.e., roots, shoots, leaves) were first carefully cleaned on the site with ultrapure water to remove particles from the surface, and stored in clean plastic bags. Back to the laboratory, samples were again washed and dried at 80°C in an oven during 24 hours and then finely ground. All these procedures (cleaning, drying, and homogenization) have been carefully reviewed by Markert [17]. To avoid compositional variability in trea leaves [18, 19], a mix of old and young leaves from several trees were collected and considered as representative samples.

3.2. Sample treatment and analytical techniques

Each powdered sample (between 100 and 200 mg of plant, soil, rock) was submitted (in clean room) to hydrogen peroxide (H_2O_2) digestion during 24 hours at ambient temperature and acid digestion on a hot plate : HNO_3 + HF, during 36 hours, at 80°C, then HCl, during 36 hours, at 80°C and finally HCl-HNO_3, during 36 hours, at 80°C. Blank tests were performed to estimate the level of contamination induced by the acid digestion and were found to be less than 0.2% of the less concentrated sample. Soils and rocks were also analyzed after an alkaline fusion. Zn concentrations obtained by the two methods are in good agreement suggesting complete dissolution of Zn during the acid digestion.

Zn concentrations were measured using a quadrupole ICP-MS (Elan 6000, Perkin Elmer SCIEX). The international geostandards GA (granite, from CRPG, France) for the rocks and soils, and SRM 1515 (Apple Leaves, from NIST, USA) for plants were used to check the validity and the reproducibility of both the acid digestion and ICP-MS analyses. The relative difference between our Zn concentrations values and the certified data (given for the international standards) is close to 5%.

Zn has five stable isotopes of mass 64, 66, 67, 68 and 70 whose average abundances are 48.63%, 27.90%, 4.10%, 18.75% and 0.62%, respectively. Zn isotopes have been measured at Lyon (Ecole Normale Supérieure) on the P54 MC-ICP-MS (VG Elemental) and at Toulouse (LMTG) on the Neptune MC-ICP-MS (ThermoFinnigan). Firstly, Zn was isolated from the bulk sample using the purification procedure of Maréchal et al. [20] on the AG-MP-1 (100-200 mesh, chloride form) anion exchange resin (Bio-Rad laboratories, CA, USA). The same procedure was used for the different kinds of samples (soils, rocks, plants). An aliquot containing about 300 ng of Zn was loaded on the column (polyethylene column, Bio-Rad laboratories, CA, USA). Because isotopic fractionation may occur during the elemental separation on the ion-exchange resin [21], we analyzed only the samples for which the separation procedure gave a yield of 100% taking into account the analytical uncertainties. The ^{62}Ni signal was simultaneously measured to evaluate the isobaric interference of ^{64}Ni on the ^{64}Zn signal; no significant interference was found. For a Zn and Cu concentration of about 300 µg/L, and 100 µL/min sample uptake, we obtained intensities of ~8.6 V and 5 V for the ^{65}Cu and ^{66}Zn isotopes, respectively. Instrumental mass fractionation was corrected following the method described by Maréchal et al. [20] and by Mason et al. [22, 23]. A Cu standard (NIST 976) was added to the purified Zn fractions and a Cu (NIST 976) + Zn (JMC 3-0749L) standard mixture was run as a bracketing standard**.** The ratio of Cu and Zn fractionation factors (i.e., f_{Cu}/f_{Zn}) was found to be constant over a single analytical session (i.e., one day measurement) for both P54 and Neptune instruments. As already observed by Maréchal et al. [20] and Pichat et al. [7] this f_{Cu}/f_{Zn} ratio does not remain constant from one day to another. The slope of the fractionation line derived from the standard mixture raw data in a Log (^{66}Zn/^{64}Zn) *versus* Log (^{65}Cu/^{63}Cu) plot was used to correct the data on the Zn sample + Cu standard mixtures. The Zn isotopic results in this study are given in the recommended delta notation for the ^{66}Zn/^{64}Zn ratio [5] :

$$\delta^{66}Zn = [(({}^{66}Zn/{}^{64}Zn)_s/({}^{66}Zn/{}^{64}Zn)_{JMC}) -1] *1000 \quad (\text{in } ‰) \qquad (2)$$

where s stands for sample and JMC represents the Zn isotopic standard solution. Note that the JMC 3-0749L solution is not a referenced material but an elemental standard solution used by

several laboratories. The $\delta^{67}Zn$ and $\delta^{68}Zn$ were also considered to check the validity of the measurements and to insure that the different Zn isotopes fit on a theoretical mass-dependent fractionation line.

The external reproducibility for $\delta^{66}Zn$ is 0.1‰ (2σ). This value is an upper limit based on 5 samples that have been submitted twice to the whole procedure (acid attack, separation) and analyzed at Lyon and Toulouse. In the following, we will consider 0.1‰ to be the individual sample uncertainty even if for most samples, the uncertainty may be lower. The basalt BCR-1 (from USGS, USA) and lichen BCR-CRM 482 (from BCR, Belgium) standards have been analyzed for Zn isotopes on the Neptune (LMTG, Toulouse) using the chemical and analytical protocol described in this paper. The three isotopes plot obtained for our BCR-1 and BCR CRM 482 data are reported in figure 2. The $\delta^{66}Zn$ is 0.26 ± 0.05‰ (n=8, 95% confidence level) and 0.14 ± 0.03‰ (n=8, 95% confidence level) for BCR-1 and BCR-CRM 482, respectively. Our data agree with recent measurements of the BCR-1 standard by Archer and Vance [24] ($\delta^{66}Zn$ is 0.20 ± 0.09‰) and by Clocquet [6] ($\delta^{66}Zn$ is 0.32 ± 0.13‰), and of the BCR CRM 482 standard ($\delta^{66}Zn$ of 0.07 ± 0.1‰ [6]).

4. Results

4.1. Zn Concentrations in rocks, soils, and plants

Zn concentrations measured in the different rocks and soils samples are given in Table 1. In the 5L6 hill zone soil profile, Zn concentrations range 85 µg/g in the parent rock (granodiorite) to (40 ± 5) µg/g in the upper soils and the litter. The 5L6-400 soil sample corresponds to the ferruginous horizon (see Table 1). This sample was separated into two fractions, the first one constituted by the iron hydroxide nodules (5-400 hy) and the second one constituted by the clay matrix (5-400 cl). These two fractions exhibit similar Zn concentrations. In the swamp zone soil profile (SZ-soil profile, Table 1), the Zn concentration in the monzogranite parent rock and the different soil horizons are lower than those of the granodiorite (14-31 µg/g). Zn concentrations are similar in the parent rock and the saprolite horizon, lower in the sandy horizon and enriched in the litter, relatively to the monzogranite.

The behavior of Zn in the overlying soil profiles can be evaluated through comparison with refractory elements such as Zr, Ti or Sc [25]. Zirconium (Zr) concentrations in the rocks and soils samples are also reported in the Table 1. We calculated Zn depletion factors relative to Zr in the soil profiles, DF_{Zn}, as follows:

$$DF_{Zn} = \frac{([Zn]/[Zr])_{sample}}{([Zn]/[Zr])_{parent-rock}}$$

DF_{Zn} values for both soil profiles are shown in Figure 3A and 3B, respectively for the hill zone and swamp zone soil profiles. Both soils evidence a 70-85 % depletion of Zn during weathering while the litter layers show an apparently lower depletion of Zn.

Table 2 reports the average concentrations of Zn in the different parts of different plant species. Zn concentrations vary as a function of the plant species and for a given species as a function of the organ as illustrated by a range from 264 to 2600 µg/g in the different organs of *Lasimorpha senegalensis* (herbaceous species), while *Raphia vinifera* (palm tree) has all values lower than 48 µg/g. With the exception of the *Lasimorpha senegalensis* species, Zn concentrations range from 19 µg/g to 116 µg/g in the different organs of the different species. All plant species have higher Zn concentrations in the roots than in the shoots or the leaves. The efficiency of plant washing and rinsing was evaluated from Zr concentrations (Table 2). Zr concentrations measured in the plant samples are low (0.01-1.7 µg/g) suggesting that the washing procedure was efficient and that the Zn concentrations measured in the plant samples are not affected by soil or atmospheric particles.

Except for *Lasimorpha senegalensis*, the range of Zn concentration measured in all plants is in good agreement with published data for non contaminated tropical and temperate environments [26, 27].

4.2. Zn isotopic composition in rocks, soils, plants

The Zn isotopic composition ($\delta^{66}Zn$) of selected plants, soils, and rocks of the Nsimi-Zoetele watershed are reported in Tables 1 and 2 and Figures 3A, 3B and 4. Note that the range of variation (-0.91 to 0.75‰) is 15 times larger than the overall analytical uncertainty. These results extend the range of observed depleted Zn isotopic compositions in plant samples from –0.61‰ [9] (original values recalculated for 2 amu mass difference, and relative to JMC 3-0749L) to –0.91‰.

4.2.1. Zn isotopic composition in soils and rocks

In the 5L6 profile the parent rock (granodiorite) has a $\delta^{66}Zn$ of 0.41‰. The $\delta^{66}Zn$ of the 5L6-soil profile ranges from 0.64 ‰ (5L6-675 sample, saprolite horizon) to -0.05 ‰ for the ferruginous soil horizon (Figure 3A). Note that when progressing from the bottom (parent rock and saprolite) to the top of the profile (ferruginous and clay horizons), the $\delta^{66}Zn$ decreases,

indicating that the soils become enriched in the lighter isotopes. In the swamp zone profile (SZ, Figure 3B), the parent rock (monzogranite) has a δ^{66}Zn value of 0.47‰ that is not significantly different from the granodiorite. The two soil samples of SZ also have similar δ^{66}Zn values, 0.55 and 0.42 for the SZ-425 and SZ-125, respectively. The litter layer has a significantly lower value of +0.25 ‰ compared to the soil and parent rock.

4.2.2. Zn isotopic composition in the plants

In the plants δ^{66}Zn fluctuates from -0.91‰ to 0.75‰ (a 1.7 ‰ range) (see Table 2 and Figure 4), which encompasses the variation observed for the soils and rocks (from 0.64‰ to -0.05‰). The roots of the different species have a δ^{66}Zn between 0.51 and 0.75‰. Values obtained for the shoots range from 0.09 to 0.76‰ and those for the leaves from 0.63 to -0.91‰. If we consider the different organs of a single plant, there is a difference in isotopic composition between the roots and the shoots and the leaves for some species (*Musanga cecropioides, Raphia vinifera, Renealmia cincinnata*). For these species, the leaves are generally enriched in the light isotopes (more negative δ^{66}Zn) compared with the roots and the shoots. For example, the roots of the *Raphia vinifera* species exhibit a value of 0.51‰. The δ^{66}Zn is significantly different in the other organs of the plant, with a value of 0.76‰ in the shoots and -0.91‰ in the leaves. Taking account the analytical uncertainties, there is no difference in the isotopic composition of the different organs of the *Lasimorpha senegalensis* and *Megaphrynium macrostachyum* species.

5. Discussion

5.1. Zn in plants.

It has been shown that zinc concentration in plants varies as a function of species and plant organ (i.e., root, shoot, leave). Zn concentrations are similar for all the analysed trees while herbaceous species shown large variations, with values diminishing from roots to leaves. As concerns Zn isotopic composition, several important observations were made: *1)* The inter-compartment variation in δ^{66}Zn is largest for leaves (1.54‰), then shoots (0.67‰), and finally roots (0.24‰); *2)* Out of 4 root-shoot pairs, only one pair has significantly different root δ^{66}Zn from shoot δ^{66}Zn (*Megaphrynium macrostachyum*); *3)* Herb species leaves do not have significantly different δ^{66}Zn from their roots or shoots. By contrast, leaves of tree species display strongly negative δ^{66}Zn values that are different from their shoots. Additional observations can be made by comparing the plant compartments to the soils. Poszwa et al. [28] and others have shown, based on Ca, Sr and ^{87}Sr/^{86}Sr tracers, that deep roots do not play an important role in

nutrient uptake by tropical rainforest species. This was shown for old and nutrient-depleted soils. Adhering to this general view that nutrient cycling occurs mainly in the upper soil layer, we will compare δ^{66}Zn values of plants with δ^{66}Zn values of the litter layer (+0.12 to +0.25‰): *4)* Considering the roots, all plants are significantly enriched in heavy Zn relative to the litter ; considering the shoots and the roots, four out of five plants species are significantly enriched in heavy Zn (+0.42 to +0.76‰). A comparison of Zn isotopic fractionation in our study on natural tropical plants with controlled growth experiments of rice (*Oryza sativa*), lettuce (*Lactuca sativa*), and tomato (*Lycopersicon esculentum*) by Weiss et al. [9] reveals both similarities and differences. In both studies, the incorporation of Zn by roots seems to induce a fractionation of Zn isotopes with a preferential incorporation of the heavier isotopes (compared with the litter or the most surficial soils in this study, or compared with nutrient solutions in Weiss et al ' study). Also, similarly to their study we find the most negative δ^{66}Zn values in the leaves. Additionally it appears that there is a correlation between plant biomass (trees>herbs and tomato>lettuce>rice) and Zn fractionation intensity in leaves. Although we do not wish to speculate on the exact mechanisms, such as covalency of Zn complexes, responsible for isotopic fractionation of Zn during uptake and transport in plants, it appears that diffusion controlled transport is compatible with the observations. However, contrary to the significantly lower δ^{66}Zn values of shoots, relative to roots, observed by Weiss et al., we find no significant difference among shoots and roots.

A discussion of the negative δ^{66}Zn values of tree leaves needs to address the potential contribution of the atmospheric dust because plants, and particularly trees, may incorporate elements directly from the barks or the leaves [29]. The significant contribution of atmospherically derived components to the budget of elements in soils has been already reported for old hawaiin soils and unpolluted temperate forests [30, 31]. Unfortunately, the only data available is a value of 0.17‰ for Saharian particles [32]. This value does not necessarily reflect the atmospheric deposits on this watershed and thereby eliminate a possible source effect. Also the explanation of the negative values will require to consider a potential fractionation during the translocation of Zn inside the plants or during the incorporation of Zn at the leaf surface. Finally, mechanisms involved during the transport of Zn and its accumulation (chemical forms) should be investigated in order to understand and be able to use these signatures as a tracer.

5.2. Zn in soils and litters

The results plotted in Fig 3A and 3B show that the two weathering profiles display similarities as well as differences. The saprolite horizons of the two soil profiles displays insignificantly fractionated δ^{66}Zn values, although a tendency towards heavier δ^{66}Zn values is present (compared to the parent rock). Overall, the swamp zone soil profile (i.e., SZ-soil profile) shows δ^{66}Zn similar values (+0.42 to +0.55‰ range) throughout the soil profile. In contrast, the hill slope soil profile (i.e., 5L6-soil profile) reveals a significant depletion in heavy Zn isotopes in the shallower ferruginous horizon (-0.22 to +0.06‰) compared to the parent rock. The δ^{66}Zn values in the litter layer of both soils (+0.12 to +0.25‰) are depleted in heavy Zn isotopes relative to the parent rocks. The SZ-soil profile has been suspected by previous studies [10, 15] to be a mix between allochtonous and autochtonous materials while the 5L6-soil profile is considered to be an "*in situ*" profile, derived from the local parent rock. Considering the weathered 5L6-soil profile, we observe two important trends : *i)* a weathering regime at depth that involves strong Zn depletion (DF_{Zn} of 0.3), yet negligible Zn isotopic fraction, and ii) a shallower weathering regime that causes significant depletion in heavy Zn isotopes for the fully developed lateritic hill slope soil. Note that these surficials soils developed from the saprolite horizon [10] and exhibit again a Zn depletion with DF_{Zn} of 0.15. These are the first observations on Zn isotopic fractionation during soil formation.

From the bottom (overlying granodiorite) to the top of the profile, the soils exhibit increasing degrees of weathering and alteration into a mature soil profile (loose clayey horizon). Globally, it signifies that the most weathered soil horizons exhibit a preferential enrichment in the light isotopes. The main question is to understand what processes induce or have induced this isotopic composition shift between the saprolite and the most superficial and weathered soil horizons. At present time, it is difficult to answer to these questions, because of the lack of data in the literature about the mechanisms that control Zn isotope fractionation [5]. In the case of Fe several experimental works have shown that Fe isotopes can be fractionated during mineral weathering. Brantley et al. [33] showed that Fe released during the dissolution of hornblende (i.e., silicate mineral) in the presence of organic acids was lighter than the substrate. Another experiment by Beard et al. [34] showed an enrichment in the substrat of the light isotopes during Fe hydroxide dissolution mediated by Fe reducing bacteria. Even if some data are lacking concerning the mechanisms that control Zn fractionation, some hypotheses should be primarily investigated.

5.2.1 A source effect?

The Zn content in the granodiorite constituting the geological substratum is controlled by ZnS minerals (P. Oliva, pers. comm.). It is therefore likely that the isotopic composition of the bulk rock is the isotopic composition of ZnS minerals. The isotopic composition of the soil derived from this granodioritic rock will depend on the evolution of the ZnS mineral during chemical weathering and on the behavior of Zn after being released from the dissolution of primary minerals. We don't know the distribution of Zn in the soils between the different reservoirs (i.e., crystal lattice of secondary minerals, adsorbed onto mineral surfaces) and the percentage that is exchangeable. An extensive review by Alloway [3] on Zn behavior in different soils, classifies old ferralitic soils developed from granitic rocks, such as in the Nsimi-Zoétélé wateshed, as Zn deficient. It is likely that Zn is mainly adsorbed onto the mineral (i.e., clays, oxyhydroxides) and humics surfaces of the soils. Based on the Zn depletion (i.e., DF_{Zn}) and the isotopic composition of the surficial soil horizons (see Table 1), we can estimate the isotopic composition of the Zn component that has been removed during the saprolite – ferruginous horizon transition, by using a simple mass balance calculation. This mobilized Zn component is calculated to have a δ^{66}Zn value of +1.39‰. Considering the isotopic composition of the bulk rock (δ^{66}Zn of +0.41‰), it seems unlikely to explain the isotopic composition of the soils by removing ZnS minerals during rock weathering and soil formation.

5.2.1 Fractionation processes?

The isotopic composition may result from fractionation process; the normal procedure is to check if the data follow a distillation curve of Rayleigh. Unfortunately, there is no literature reference that can give us experimental fractionation factors (α) to correctly model the data. Something more complicate than a Rayleigh distillation should occur because the isotopic composition of the whole soil profile does not go in the same way considering the saprolite horizon (heavier than the parent rock) and the surficial horizons (lighter than the parent rock). Recently, Pokrovsky et al. [35] performed some experiments on Zn adsorption onto different solid phases (e.g., goethite, gibbsite) and evidenced that these adsorption processes only induce light isotopic fractionation. Zinc stable isotopic fractionation induced by adsorption on most mineral surfaces does not exceed 0.2‰ (negative or positive according to mineral type) that is the order of magnitude we obtained between the rock and the soil constituting the laterite cover of the Nsimi-Zoétélé site. Based on these previous results, adsorption process may explain the isotopic composition of these soils. In the SZ-soil profile, the sandy horizon (see Figure 3B) does not exhibit isotopic fractionation compared with the parent rock. The much lower proportion of

clays in this horizon (see [14]) seems to suggest that adsorption process onto clays surface may induce fractionation and explain the diffence of isotopic composition encountered in the Nsimi-Zoétélé soil system. In the 5L6-soil profile, the clay and hydroxyde fractions of the 5L6-400 sample (see Table 1) exhibit isotopic composition significantly different to that of the parent rock.

We observed that globally the plants are enriched in heavy isotopes compared to the most superficial soil horizons (see Figure 4). It is true that we have seen that tree leaves exhibit depletion in light isotopes, but they account for less than 20% of the total biomass of the forest ([36]). During the first stage of chemical weathering, plants may have preferentially incorporated heavy isotopes leaving in the residual weathered products a Zn component enriched in light isotopes. We have seen that the Zn that have been removed should have had a isotopic composition of 1.39‰. If we consider the progressive formation of soil through time (i.e., progressive thickening) and the progressive uptake of elements by the changing vegetation, we don't need to have a such high value (i.e., δ^{66}Zn of 1.39‰) for the vegetation to explain the actual Zn heavy isotopes depletion. Indeed, small and continuous fractionation through time could involve the depletion encountered today. However, a last point should be questionned. Indeed, if nowadays Zn cycling is mainly controlled by a transfer between the litter and the plants, the isotopic composition of the litter should be more negative because leaves of trees account for the major proportion of litter biomass [36]. Indeed, we have seen that tree leaves can reach -0.91 ‰ value for δ^{66}Zn. The values we found for the litter (0.12-0.25‰) suggest that the processes involved (e.g., litter decay, atmospheric dust contibution) are more complicated and should be investigated in the future.

6. Summary

In this study, we reported a number of new and important observations such as: *1)* the difference of isotopic composition between the fresh parent rock and the very mature tropical soils (i.e., both ferruginous horizon and loose clayey horizon) and *2)* the difference in the isotopic composition of plant species and between the different organs of a single species.

As concerns the soil/rock system, there is a need to acquire more data from other lateritic soil profiles presenting similar organisation and to see if our results are a general rule for such systems. If this is the case, then Zn isotopes will be considered as serious tracers of laterite formation. However, two hypotheses were proposed to explain the Zn isotopic composition of the weathrerd soil profile. The first one considers that isotopes fractionation occurs during the adsorption onto minerals (e.g., clays) surface. The second one deals with a fractionation that

occurs during the incorporation of Zn by roots in the soil system. This last hypothesis is based on the assumption that the plant biomass is globally enriched in heavier isotopes.

Discussing the actual cycling of Zn particularly within the influence of the vegetation based on Zn isotopes is at present time too much speculative. Indeed, there is a crucial need to improve our understanding of factors controlling the incorporation of the elements by plants and the mobility within the plants.

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References

[1] J. Drever, D.W. Clow, Weathering rates in catchments, in: A.F. White, S.L. Brantley (Eds.), Chemical weathering rates of silicate minerals, Min. Soc. of America 31, 1995, pp. 463-481.
[2] Y. Lucas, The role of plants in controlling rates and products of weathering: importance of biological pumping, Annu. Rev. Earth Planet. Sci. 29 (2001) 135-163.
[3] B.J. Alloway, Zinc in soils and crop nutrition, online book, www.zinc-crops-org, 127 pp.
[4] P.H. Brown, I. Cakmak, G. Zhang, Form and function of zinc in plants, in: A.D. Robson (Ed.), Zn in soils and plants, Kluwer Academic Publishers, 1993, pp. 93-106.
[5] C.M. Johnson, B.L. Beard, F. Albarède (Editors), Geochemistry of non-traditional stable isotopes, Reviews in Mineralogy and Geochemistry. Mineralogical Society of America 55 (2004) Washington.
[6] C. Cloquet, Géochimie élémentaire et isotopique des métaux lourds. Applications environnementales en tissus urbains et industriels. PhD, Institut National Polytechnique de Lorraine, 2005, Nancy, France.
[7] S. Pichat, C. Doucet, F. Albarède, Zinc isotope variations in deep sea carbonates from the eastern equatorial Pacific over the last 175 ka, Earth and Planetary Science Letters 210 (2003) 167-178.
[8] X.K. Zhu, Y. Guo, R.J.P. Williams, R.K. O'Nions, A. Matthews, N.S. Belshaw, G.W. Canters, E.C. de Waal, U. Weser, B.K. Burgess, B. Salvato, Mass fractionation processes of transition metal isotopes, Earth and Planetary Science Letters 200 (2002) 47-62.
[9] D.J. Weiss, T.F.D. Mason, F.J. Zhao, G.J.D. Kirk, B.J. Coles, M.S.A. Horstwood, Isotopic discrimination of zinc in higher plants, New Phytologist 165 (2005) 703-710.
[10] J-J. Braun, J-R. Ndam Ngoupayou, J. Viers, B. Dupré, J-P. Bedimo Bedimo, J-L. Boeglin, H. Robain, B. Nyeck, R. Freydier, L. Sigha Nkamdjou, J. Rouiller, J-P. Muller, Present weathering rates in a humid tropical watershed: Nsimi, South Cameroon, Geochim. Cosmochim. Acta 69 (2005) 357-387.
[11] Y. Tardy, C. Roquin, Dérive des continents, Paléoclimats et altérations tropicales, BRGM Ed, 1998, 473 pp.
[12] J.C. Olivry, Fleuves et rivières du Cameroun, *Monographies Hydrologiques*, ORSTOM, Paris, 9, 1986, 733pp.
[13] R. Tchameni, Géochimie et géochronologie des formations de l'Archéen et du Paléoprotérozoique du sud Cameroun (Groupe du Ntem, Craton du Congo), Thèse de Doctorat, Université d'Orléans I, France, 1997, 395 pp.
[14] J. Viers, G.J. Wasserburg, Behavior of Sm and Nd in a lateritic soil profile, Geochim. Cosmochim. Acta 68 (2004) 2043-2054.
[15] P. Oliva, J. Viers, B. Dupré, J.P. Fortuné, F. Martin, J.J. Braun, D. Nahon, H. Robain, The effect of organic matter on chemical weathering: Study of a small tropical watershed: Nsimi-Zoétélé site, Cameroon, Geochim. Cosmochim. Acta 63 (1999) 4013-4035.
[16] Y. Tardy, Pétrologie des latérites et des sols tropicaux, Masson, Paris, 459p.
[17] B. Markert, Sample preparation (cleaning, drying, homogenization) for trace element analysis in plant matrices, The Science of the Total Environment 176 (1995) 45-61.
[18] R.M. Palma, R.L. Defrieri, M.F. Tortarolo, J. Prause, J.F. Gallardo, Seasonal changes of bioelements in the litter and their potential return to green leaves in four species of the Argentine subtropical forest, Annals of Botany 85 (2000) 181-186.
[19] N.E. Longnecker, A. Robson, Distribution and transport of zinc in plants, *In* Zn in soils and plants, Edited by A.D. Robson, Kluwer Academic Publishers, 55, 1993.
[20] C.N. Maréchal, P. Télouk, F. Albarède, Precise analysis of copper and zinc isotopic compositions by plasma source mass spectrometry, Geochim. et Cosmochim. Acta 156 (1999) 251-273.

[21] C.N. Maréchal, F. Albarède, Ion exchange fractionation of copper and zinc isotopes, Geochim. et Cosmochim. Acta, 66 (2002) 1499-1509.
[22] T.F.D. Mason, D.J. Weiss, M. Horstwood, R.R. Parrish, S.S. Russel, E. Mullane, B.J. Coles, High-precision Cu and Zn isotope analysis by plasma source mass spectrometry, Part 1: Spectral interferences and their correction, J. Anal. At. Spectrom., 19 (2004) 209-217.
[23] T.F.D. Mason, D.J. Weiss, M. Horstwood, R.R. Parrish, S.S. Russel, E. Mullane, B.J. Coles, High-precision Cu and Zn isotope analysis by plasma source mass spectrometry, Part 2: Correcting for mass discrimination effects, J. Anal. At. Spectrom., 19 (2004) 218-226.
[24] C. Archer, D. Vance, Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes, J. Anal. At. Spectrom., 19 (2004) 656-665.
[25] G.H. Brimhall, C.J. Lewis, C. Ford, J. Bratt, G. Taylor, O. Warin, Quantitative geochemical approach to pedogenesis: Importance of parent material reduction, volumetric expansion, and eolian influx in lateritization, Geoderma 51 (1991) 51-91.
[26] J. Chiarenzelli, L. Aspler, C. Dunn, B. Coussens, D. Ozarko, K. Powis, Multi element and rare earth element composition of lichens, mosses and vascular plants from the Central Barrenlands, Nunavut, Canada, Applied Geochemistry 2001 (16) 245-270.
[27] J. Vanderlei Martins, P. Artaxo, E.S.B. Ferraz, M.H. Tabacniks, Chronological studies of tree-rings from the Amazon basin using thick target PIXE and porton backscaterring analysis, Nuclear Instruments and Methods in Physic Research 150 (1999) 240-270.
[28] A. Poszwa, E. Dambrine, B. Ferry, B. Pollier, M. Loubet, Do deep tree roots provide nutrients to the tropical rainforest? Biogeochemistry 60 (2002) 97-118.
[29] R. Freydier, J. Viers, Isotopic study of lead transfer at the interface soil-plants-atmosphere, Geophysical Research Letters, 30(5) (2003) N°1227.
[30] O.A. Chadwick, L.A. Derry, P.M. Vitousek, B.J. Huebert, L.O. Hedin, Changing sources of nutrients during four million years of ecosystem development, Nature 397 (1999) 491-497.
[31] M.J. Kennedy, L.O. Hedin, L.A. Derry, Decoupling of unpolluted temperate forests from rock nutrient sources revealed by natural 87Sr/86Sr tracer addition, PNAS 15(99) (2002) 9639-9644.
[32] C. Maréchal, Géochimie des isotopes du cuivre et du zinc: méthode, variabilité naturelle et application océanographique, PhD Université Joseph Fourier, Grenoble, France, 1998, 261 pp.
[33] S.L. Brantley, L. Liearmann L., T.D. Bullen, Fractionation of Fe isotopes by soil microbes and organic acids, Geology 29 (2001) 535-538.
[34] B.L. Beard, C.M. Johnson, J.L. Skulan, K.H. Nealson, L. Cox, H. Sun, Application of Fe isotopes to tracing the geochemical and biological cycling of Fe, Chem. Geol. 195 (2003) 87-117.
[35] O. Pokrovsky, J. Viers, R. Freydier, Zn stable isotope fractionation during its adsorption on oxides and hydroxides, Journal of Colloïd and Interface Science (2005) (in press)
[36] W.H. Schlesinger, Biogeochemistry: an analysis of global change, Second Edition, Academic Press, 1997, 588 pp.

Figure captions

Figure 1: A) Location of the Nsimi-Zoétélé watershed, B) A three-dimensional representation of the watershed (0.6 km^2) with the localities of the soil/rock sampling points. Filled circles are for pits. Sampling sites are 5L6 pit (hill zone soil profile), and SZ pit (swamp zone soil profile).

Figure 2: Three isotopes plot obtained for the measurements of the BCR-1 and BCR CRM 482 standards with $\delta^{6X}Zn = [((^{6X}Zn/^{64}Zn)_s/(^{6X}Zn/^{64}Zn)_{JMC}) -1] *1000$ (in ‰).

Figure 3: A) 5L6-soil profile ; Evolution of DF_{Zn} (see Table 1 for definition) and $\delta^{66}Zn$ (‰) as a function of depth. B) same data for the SZ-soil profile.

Figure 4: Zn isotopic composition of the herbaceous and tree species. The isotopic composition of the litters in the same location than plants has been reported for comparison.

Table 1: Zn, and Zr concentrations and Zn isotopic composition ($\delta^{66}Zn$) for the soils and rocks samples.

Sample name	Sample type	Location	Zn content	Zr content	DF_{Zn}[1]	$\delta^{66}Zn$ (‰)[2]
			µg/g	µg/g		
5L6-soil profile						
Granodiorite	parental rock	Hill zone	85	120	1	0.41[4]
5L6-675	soil (saprolite horizon)	Hill zone	37	182	0.29	0.64
5L6-400 cl	soil (ferruginous horizon)	Hill zone	38	303	0.18	-0.22
5L6-400 hy	soil (ferruginous horizon)	Hill zone	41	443	0.13	0.06
5L6-400[3]	soil (ferruginous horizon)	Hill zone	40	390	0.14	-0.05
5L6-150	soil (loose clayey horizon)	Hill zone	45	443	0.14	-0.03
LHZ1	litter	Hill zone	38	120	0.45	0.12
SZ-soil profile						
Monzogranite	parental rock	Swamp zone	23	70	1	0.47
SZ-425	soil (saprolite horizon)	Swamp zone	26	256	0.31	0.55[4]
SZ-125	soil (sandy horizon)	Swamp zone	14	183	0.23	0.42[4]
LSZ1	litter	Swamp zone	31	94	0.98	0.25

[1] DF_{Zn} represents the Zn/Zr concentration ratio in the sample divided by the same ratio in the parent rock
[2] $\delta^{66}Zn$ is the conventional delta notation for the $^{66}Zn/^{64}Zn$ ratio ($\delta^{66}Zn = [(({}^{66}Zn/{}^{64}Zn)_S/({}^{66}Zn/{}^{64}Zn)_{JMC}) -1] *1000$ with s the sample and JMC the Zn standard solution).
[3] total 5L6-400 sample values calculated using the respective percentage of the clay matrix and iron nodules fractions
[4] sample used to test the external reproducibility of the general method (see chapter 3, paragraph 3.2).

Table 2 : Zn, and Zr concentrations and Zn isotopic composition ($\delta^{66}Zn$) for the plant samples.

Classification (order / family / species)	Sample type	Plant organ	Location	Zr content	Zn content	$\delta^{66}Zn$ (‰)
				µg/g	µg/g	
Zingiberales / Marantaceae / *Megaphrynium macrostachyum*	Herbaceous species	root	Hill zone	1.7	32	0.75[1]
		shoot	Hill zone	0.34	27	0.42[1]
		leaves	Hill zone	0.05	19	0.52[1]
Urticales / Moraceae / *Milicia excelsa*	Tree	leaves	Hill zone	0.35	21	-0.03
Urticales / Cecropiaceae / *Musanga cecropioides*	Tree	shoot	Hill zone	0.01	25	0.09
		leaves	Hill zone	0.15	30	-0.27
Arales / Araceae / *Lasimorpha senegalensis*	Herbaceous species	root	Swamp zone	1.30	2583	0.57
		shoot	Swamp zone	0.13	264	0.69
		leaves	Swamp zone	0.04	492	0.63
Arecales / Arecaceae / *Raphia vinifera*	Palm Tree	root	Swamp zone	0.17	48	0.51
		shoot	Swamp zone	0.08	22	0.76
		leaves	Swamp zone	0.16	20	-0.91
Zingiberales / Zingiberaceae / *Renealmia cincinnata*	Herbaceous species	root	Swamp zone	1.04	116	0.57
		shoot	Swamp zone	0.02	62	0.61
		leaves	Swamp zone	0.07	26	0.26

[4] sample used to test the external reproducibility of the general method (see chapter 3, paragraph 3.2).

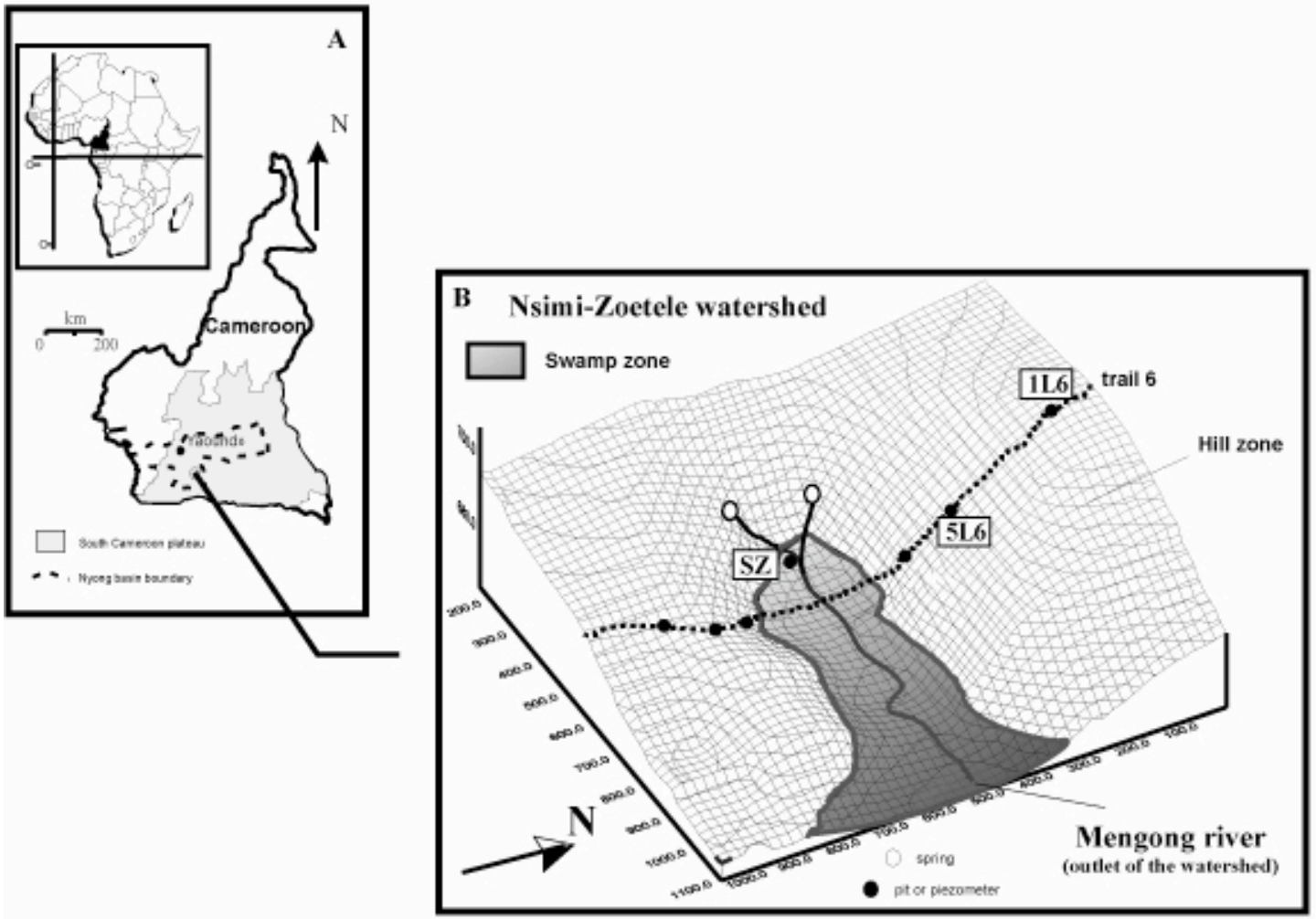

Figure 1 (Viers et al., 2005)

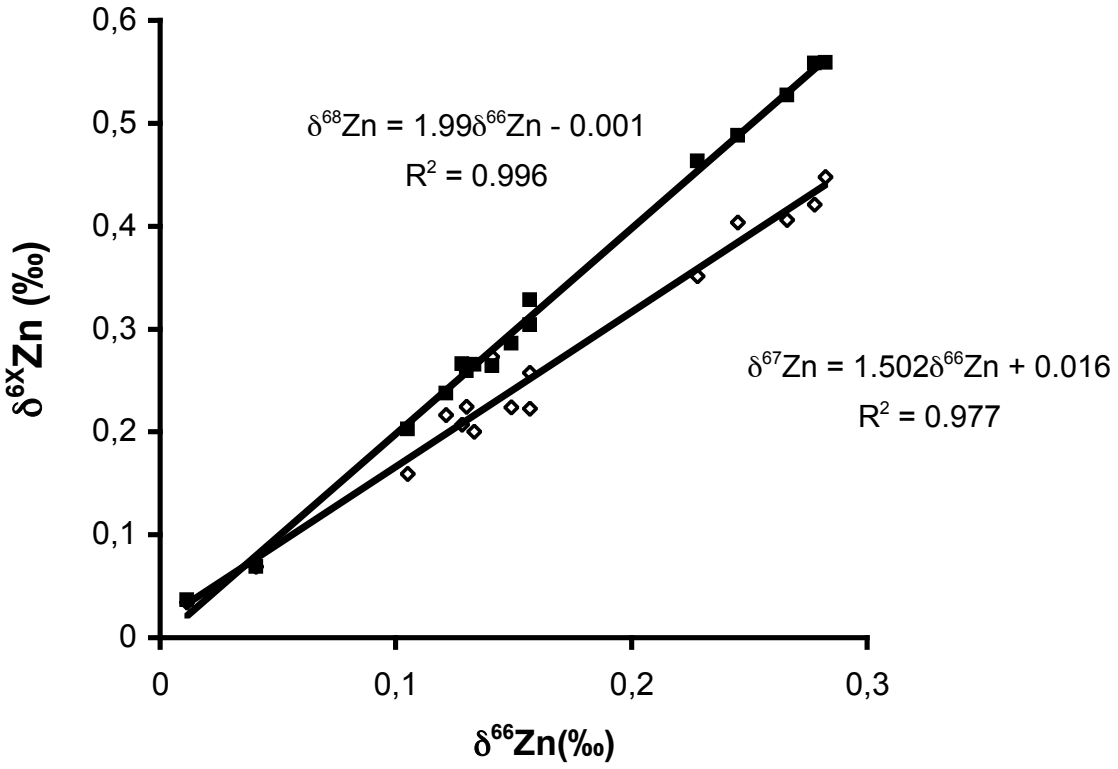

Fig 2.

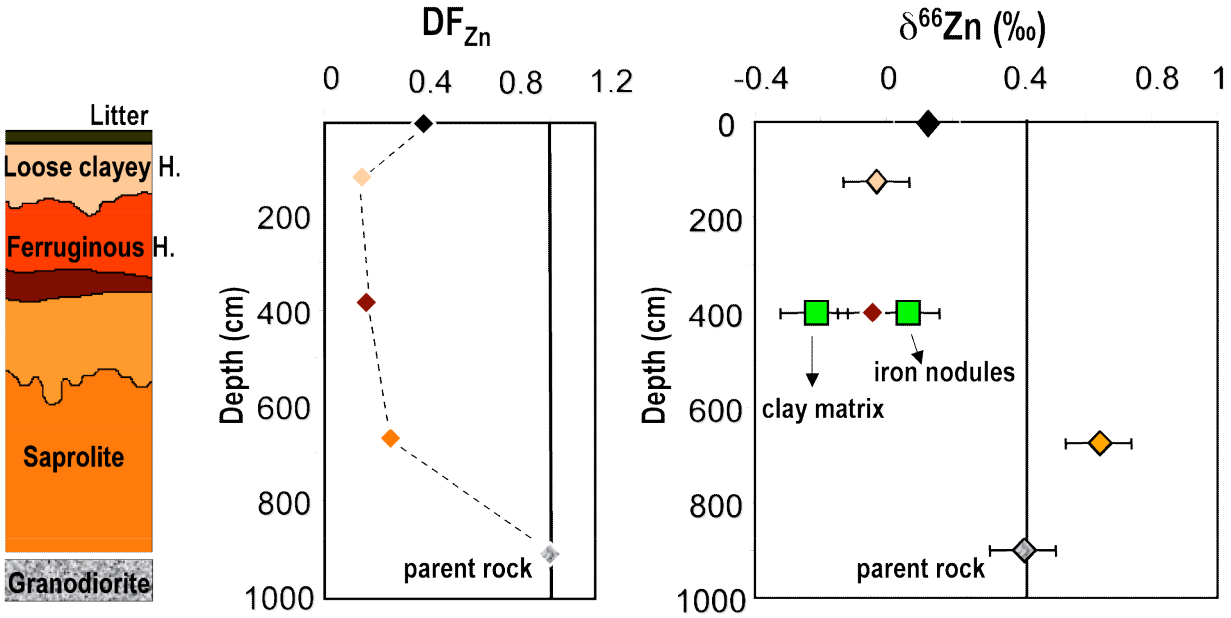

Figure 3A (Viers et al., 2005)

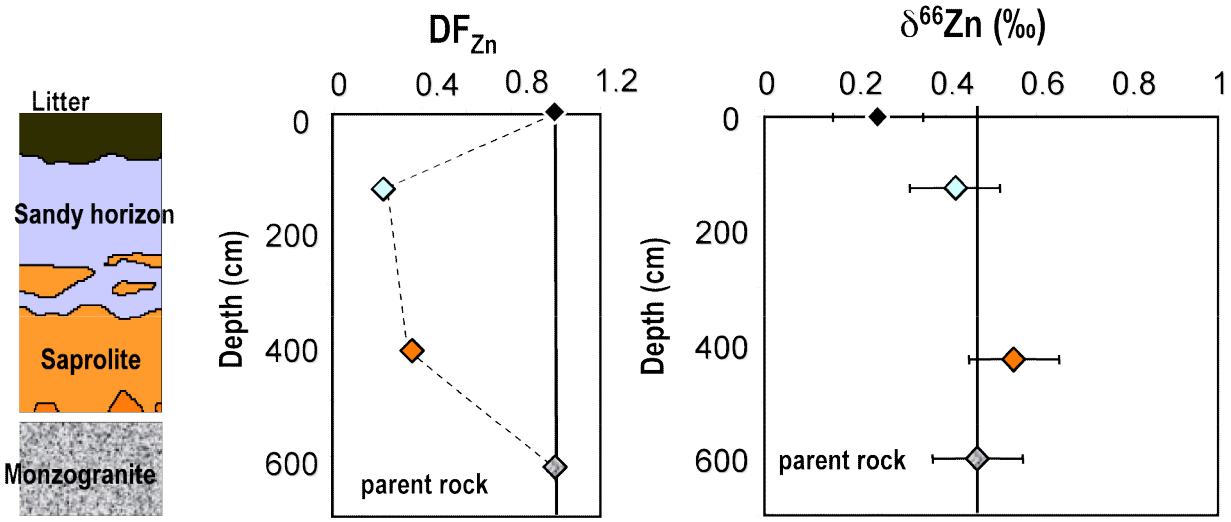

Figure 3B (Viers et al., 2005)

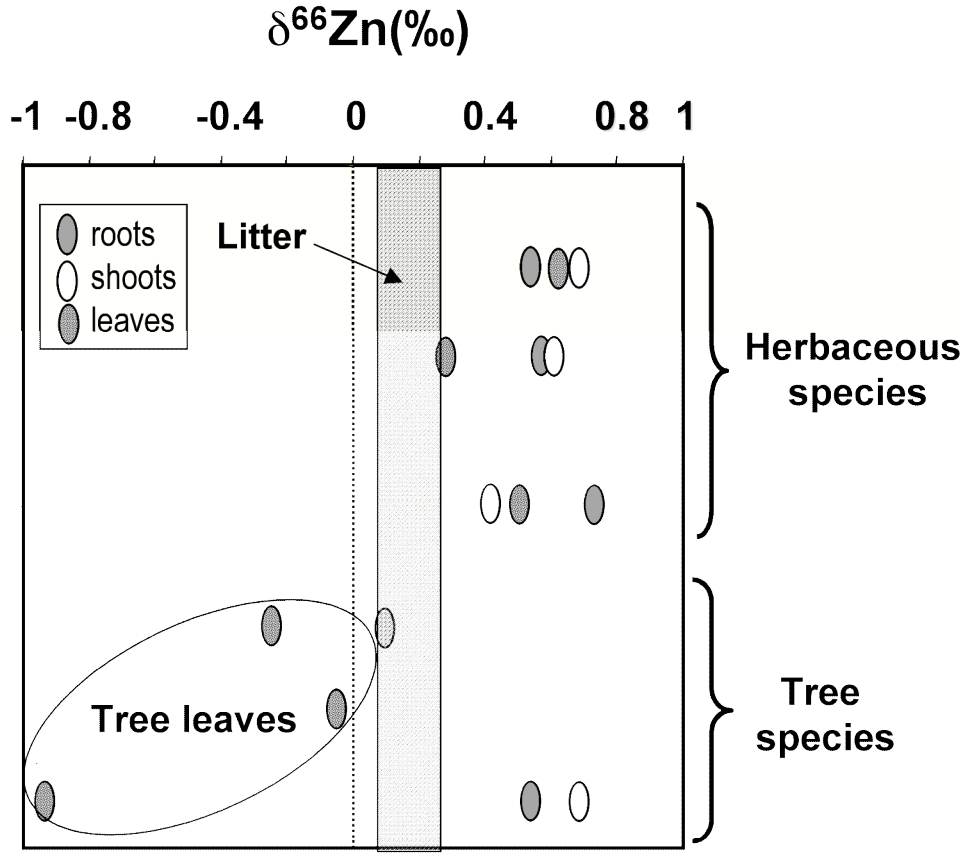

Figure 4 (Viers et al., 2005)

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TITRE : Géochimie élémentaire et isotopique du Zn, du Sr et du Pb dans les gaz volcaniques. Méthodologies d'échantillonnage et apports à la compréhension des interactions fluides/solides.

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RESUME

Ce manuscrit présente les premiers résultats d'études élémentaires et isotopiques du Zn, du Sr et du Pb, réalisées dans les principaux types d'échantillons liés aux gaz volcaniques (gaz, sublimés, eaux thermales, roches), ainsi que deux nouvelles méthodologies d'échantillonnage des émanations volcaniques. Les variations isotopiques du Zn observées au Merapi suggèrent que les processus de changement de phase (fluides/solides) provoquent des fractionnements isotopiques significatifs des éléments trace métalliques en contexte volcanique. L'étude couplée Sr/Pb réalisée à Vulcano indique que les compositions en éléments trace métalliques des fumerolles et des eaux thermales sont influencées par les sources naturelles et anthropiques. Ce travail a aussi permis la mise au point de nouvelles méthodologies d'échantillonnage et d'analyse des gaz et des panaches volcaniques, permettant d'accéder à la composition chimique complète de ces manifestations gazeuses de manière simple et efficace.

Mots-clés : gaz volcaniques, panaches volcaniques, isotopes stables, isotopes radiogéniques, Zn, Sr, Pb, fractionnements isotopiques, sources, MC-ICP-MS, TIMS, ICP-MS.

ABSTRACT

This manuscript presents the first results concerning the study of Zn, Sr, and Pb elementary and isotopic variations in samples linked to volcanic exhalations (gas, sublimates, thermal waters, rocks), together with two new volcanic gas and plumes sampling methodologies. Zn isotopic variations observed at Merapi suggests that phase changing processes (fluid/solid) might generate significant isotopic fractionation of metallic trace elements in a volcanic context. The coupled Sr/Pb isotopic study performed at Vulcano shows that both natural and anthropogenic sources might influence the trace metal compositions of fumaroles and thermal waters. This work also describes new methods for sampling and analyzing volcanic gases and plumes, allowing a complete characterization of these volcanic exhalations with simple and efficient methods.

Keywords: volcanic gas, volcanic plumes, stable isotopes, radiogenic isotopes, Zn, Sr, Pb, isotopic fractionation, end-members, MC-ICP-MS, TIMS, ICP-MS.

DISCIPLINE: Géochimie isotopique

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