# PRODUCTION D'H<sub>2</sub> IN-SITU

Résumé de l'article de Marcaillou et al. (2011) publié dans le journal Earth and Planetary Science Letters

En contexte de dorsale lente, l'altération hydrothermale des péridotites produit de grandes quantités d'hydrogène. Cette production est associée à l'oxydation du  $Fe^{2+}$ , initialement présent dans les minéraux du produit de départ, en  $Fe^{3+}$  incorporé dans des phases secondaires (Moody, 1976 ; Frost, 1985 ; Janecky et Seyfried, 1986). En particulier, l'expérience menée par Seyfried et al. (2007) a montré que le  $Fe^{3+}$  n'est pas uniquement incorporé dans la magnétite, mais qu'il intègre également la structure de la serpentine. Cependant, ces auteurs n'ont pas pu quantifier les teneurs respectives en magnétite et serpentine dans leur échantillon expérimental sous forme de poudre. Aussi, les rôles respectifs joués par ces deux minéraux restent mal compris. De plus, Seyfried et al. (2007) n'ont caractérisé que les produits solides récupérés en fin d'expérience. Par conséquent, ni l'évolution de l'assemblage minéralogique, ni la répartition du  $Fe^{3+}$  au cours du processus de serpentinisation, ne sont connues. Enfin, aucune étude expérimentale n'a été réalisée dans le but de comparer la production d'hydrogène et l'état d'oxydation du fer moyenné dans un échantillon serpentinisé. Il n'est donc pas possible de savoir si l'hydrogène résulte de l'oxydation du seul élément fer, ou si le changement de degré d'oxydation d'autres éléments (Cr, Ni, Al) entre en jeu dans cette production.

Afin de contraindre le rôle des différentes espèces minérales dans la production d'hydrogène au cours du temps, il faut donc effectuer une altération expérimentale dans laquelle les phases minérales et l'état d'oxydation du fer seront précisément quantifiés sur des échantillons présentant divers degrés d'altération. L'état général d'oxydation du fer mesuré sur les produits d'altération devra être rigoureusement comparé aux concentrations d'hydrogène mesurées.

Pour cela, nous avons conduit une expérience basée sur l'altération d'une lherzolite finement broyée (1 µm) dans de l'eau à 300°C/300 bar, de 0 à 70 jours. A la fin de chaque série d'expérience, l'hydrogène gaz a été mesuré à l'aide d'un chromatographe en phase gazeuse. Les produits d'altération ont été récupérés, rebroyés, puis préparés sous forme de pastille (voir Figure 25) pour être analysés par DRX, spectrométrie Raman, et spectroscopie d'absorption des rayons X au seuil K du fer. En parallèle, les solutions aqueuses ont été analysées par ICP-AES. Une méthode originale, spécialement adapté à ce système chimique et basée sur la spectroscopie d'absorption X, a été développée dans le but de caractériser et quantifier les teneurs en fer et phases minérales présentent au sein d'un échantillon sous forme de poudre. Ainsi, nous avons déterminé, au cours de l'altération hydrothermale, l'évolution des concentrations minéralogiques de l'olivine, du pyroxène, et de la magnétite, ainsi que la teneur en fer de la serpentine.



Figure 25 : Pastilles (4mm de diamètre) des différents produits d'altération en fonction du temps d'expérience (en jour).

Après 70 jours d'altération, l'olivine et le pyroxène ont été remplacés par un assemblage composé de serpentine et magnétite, indiquant que le processus de serpentinisation a été mené à son terme. Le rapport  $Fe^{3+}/Fe_{total}$  apparait comme linéairement dépendant de la production d'hydrogène et évolue de 0, en début, à 0,66 en fin d'expérience. Les résultats soulignent également les fortes variations dans les concentrations de  $Fe^{3+}$  incorporé dans la serpentine, qui vont de 0 à 100%, dont 12% sont intégrés dans les tétraèdres. Finalement, le processus de production d'hydrogène a été séparé en trois étapes principales : (1) un premier stade durant lequel la production d'H<sub>2</sub> atteint un maximum à 18 jours et est contrôlée par la cristallisation de magnétite, (2) un stade intermédiaire durant lequel la serpentine incorpore du  $Fe^{3+}$  et joue donc un rôle majeur (jusqu'à 50%) dans la formation d'hydrogène, en enfin (3) un stade finale pendant lequel la quantité de magnétite augmente à nouveau fortement, allant de ~2% à ~5% de l'assemblage minéralogique final. Le dernier stade d'altération est également souligné par une faible augmentation du rapport  $Fe^{3+}/Fe_{total}$  en accord avec une diminution de la production d'hydrogène. On en conclu que les concentrations en fer ferrique mesurées dans les roches ultrabasiques peuvent constituer un excellent marqueur pour estimer les réserves énergétiques d'un site hydrothermal donné.

# Mineralogical evidence for $H_2$ degassing during serpentinization at $300^{\circ}C/300$ bar

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#### Abstract

Hydrogen is produced in large amounts during hydrothermal alteration of peridotite in lowspreading-rate mid-ocean ridges. This production is directly linked to reducing conditions in hydrothermal fluids induced by the oxidation of  $Fe^{2+}$  in primary minerals (olivine and pyroxene) to Fe3+ in secondary minerals (magnetite and serpentine). A better knowledge of iron speciation in serpentine is therefore crucial to the quantification of hydrogen production during the serpentinization process. For the first time, we have determined the amount of ferric iron in altered peridotite as a function of alteration time. We investigated experimentally the alteration of powdered lherzolite in pure water at 300 °C/300 bar. For each experimental run (0, 7, 18, 34 and 70 days), H2 degassing was measured using in-situ gas chromatography and the experimental products were analyzed using XRD, Raman and X-ray absorption spectroscopy at the iron K-edge. In parallel, aqueous solutions were analyzed by ICP-AES. Our results show quasi-complete serpentinization at 70 days with replacement of primary olivine and pyroxene by secondary lizardite and magnetite. TheFe3+/Fetotal ratio is linearly dependent on the hydrogen production and ranges from 0 to 0.66 at the end of the experiment. Our results reveal strong variations in Fe<sup>3+</sup> in serpentine for different alteration times, from 0 to 100% of ferric iron, including up to 12% of tetrahedral iron. Hydrogen was produced in three main stages: (1) a first stage during which the H2 production rate reaches a maximum at 18 days and is controlled by the crystallization of magnetite, (2) an intermediate stage during which serpentine incorporates ferric iron and thus plays a major role (up to 50%) in the hydrogen formation, and (3) a final stage during which magnetite amount increases from  $\sim 2$  to  $\sim 5\%$ of the mineral assemblage. The last alteration stage is accompanied by a slight increase of the Fe3+/Fetotal ratio, while the rate of hydrogen production decreases at the end of the experiment. Consequently, variations of the ferric iron contents in natural oceanic peridotites may constitute a good indicator of the "hydrogen-potential" of various ultramafic hydrothermal fields.

# 1. Introduction

At slow spreading mid-ocean ridges, interaction between mantle (i.e., ultramafic) rocks and seawater produces large volumes of serpentinized peridotite (Cannat, 1993; Cannat et al., 1992; Mével, 2003). The hydrothermal alteration of ferro-magnesian minerals like olivine and pyroxene produces iron oxides, magnesium hydroxide and hydrated phases belonging to the serpentine group. Serpentinization is accompanied by the release of hydrogen, which has been measured in high concentration in the fluids expelled in two well-studied hydrothermal fields: Lost City (Foustoukos et al., 2008; Früh-Green et al., 2003; Fu et al., 2007; Kelley et al., 2001; Kelley et al., 2005) and Rainbow (Allen and Seyfried, 2003; Bach et al., 2006; Charlou et al., 2002; Charlou et al., 2010; Douville et al., 2002; Sleep et al., 2004). It is commonly assumed that the H2 production results from the reduction of H2O, which accompanying the oxidation of ferrous iron in primary minerals (e.g., olivine and pyroxene) into ferric iron in secondary minerals, as in the following reactions:

Olivine serpentine magnetite hydrogen  
2 
$$\mathbf{Fe_{0.5} Mg_{1.5}SiO_4 + 7/3 H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + 1/3 Fe_3O_4 + 1/6 H_2}$$
 (Eq. A1)  
opx serpentine magnetite hydrogen  
2  $\mathbf{Fe_{0.5} Mg_{1.5}Si_2O_6 + 7/3 H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + 1/3 Fe_3O_4 + 1/6 H_2 + 2 SiO_2(aq)}$  (Eq. A2)

The nature and the amount of reaction products depend on the water/rock (w/r) ratio, the proportion of olivine and pyroxene in the starting peridotite, and the P-T conditions. Although the concentration of magnetite has been accurately related to the degree of alteration in natural peridotites using magnetic susceptibility measurements (Oufi et al., 2002; Toft et al., 1990), the evolution of the Fe3+ content during serpentinization has never been constrained. Indeed, several studies based on Mössbauer spectrometry have demonstrated that trivalent iron can also be incorporated in natural serpentine (Blaauwet al., 1979; Fuchs et al., 1998; Gonzalez-Mancera et al., 2003; Klein et al., 2009). In addition, Seyfried et al. (2007) showed that Fe<sup>3+</sup> is also incorporated in serpentine formed during the experimental alteration of lherzolite at 200 °C/ 500 bar. The lack of magnetite in the experimental products suggests that the production of H<sub>2</sub> was permitted by the formation of Fe<sup>3+</sup>-bearing chrysotile, which casts some doubt on the validity of the reactions described in Eqs. (1) and (2). The thermodynamic modeling of Klein et al. (2009) and McCollom and Bach (2009) suggests that other reactions might be responsible for the production of H<sub>2</sub>. These authors showed that both the partitioning and the oxidation state of iron are sensitive to temperature and w/r ratio while the formation of magnetite depends on the availability of an external source of silica. However, the thermodynamic simulations were performed at equilibrium

conditions and the influence of kinetics was neglected. Moreover, the thermodynamic calculations did not consider the possible incorporation and evolution of the  $Fe^{3+}$  concentration in serpentine during the serpentinization process. The present study was aimed at quantifying the evolution with time of the oxidation state of iron and the production of hydrogen associated with the serpentinization of peridotite. For this purpose, we performed several experiments at 300 °C/300 bar and of various durations. The H2 produced during reaction was measured by gas chromatography, and the mineral products were characterized using different spectroscopic tools, including XANES (X-ray Absorption Near Edge Structure) spectroscopy at the iron K-edge to quantify their  $Fe^{3+}$  contents.

#### 2. Experiments and analyses

#### 2.1. Synthesis procedure

The high concentration of Ca measured in fluid vent at the Rainbow hydrothermal field (66 mM) is consistent with the alteration of a lherzolite-type peridotite (Charlou et al., 2002). For that reason, this experimental study was conducted using a non-altered spinel-lherzolite composition as starting material. The peridotite was sampled at Borée (Massif Central, France), where it occurs as xenoliths in a basaltic flow. This granular peridotite, the so-called G-type peridotite, was investigated in several previous studies (e.g., Leggo and Hutchison, 1968; Mercier and Nicolas, 1975; Xu et al., 1998) and is composed of about 65 vol% olivine, 30 vol% pyroxene and 5 vol% spinel. The mineral phases were individually analyzed by XRF spectroscopy. The inferred compositions are in agreement with the data published by Xu et al. (1998). The bulk analysis of the peridotite was performed by ICP-AES. The chemical analyses of the bulk and the individual minerals are both referenced in Supplementary Table.

Peridotite fragments were ground in agate mortars to fine particles (~1  $\mu$ m in size). The experiments were run in a 0.25 L hastelloy PARR autoclave with a w/r of 3/2, i.e. 180 mL distilled water and 120 g of peridotite. The experimental pressure and temperature conditions were defined according to the thermodynamic simulations of Klein et al. (2009) and McCollom and Bach (2009), which predict the most efficient production of hydrogen at 30 MPa and around 300 °C. The setting pressure was regulated at the beginning of the run and after each gas sampling during the run by pumping neutral gas (Argon) into the autoclave, and it was measured with a pressure gauge. The temperature was measured by two thermocouples located at the top and 4 cm above the bottom of the autoclave. The operating temperature was controlled by the thermocouple to  $\pm 1$  °C. The cumulative uncertainties on temperature and pressure are about 3 °C and 5 bar, respectively. Four experimental runs, of 7, 18, 34 and 70 days duration were performed. At the end of each run, the sample was quenching from 300 °C to 30 °C in 10 min with a flow of compressed air.

#### 2.2. Fluid sampling and analysis

2.2.1. Gas chromatography : Gas phases were sampled in-situ using a regulator system coupled with a 5 cm 141 3 hastelloy tube. The hastelloy tube was first quenched in a 15 °C water for 3 min before the gas was injected in the chromatograph (Varian) at 3 bar. Then, the composition was measured over 10 min using two thermal conductivity detectors (TCD). The absolute uncertainty of these detectors for the measurement of  $H_2$  gas concentration is about 1.25%. For each run, four

analyses were performed to check reproducibility. The "Galaxie Chromatograph" software provides peak processing and gas fraction calculations.

2.2.2. ICP-AES : The liquid phases were diluted in 2% HNO3 and then analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) at the Laboratoire de Géodynamique des Chaînes Alpines (LGCA; Grenoble; France). Results are listed in Table A1.

Time (day)	0	7	18	34	70
Mg (mol/L)	0	1.32e-3	6.58e-4	4.12e-5	4.02e-5
Si (mol/L)	0	3.56e-5	2.62e-4	7.12e-5	1.75e-4
Ca (mol/L)	0	3.25e-4	2.5e-4	1.68e-4	2.33e-4
Fe (mol/L)	0	< DL	< DL	< DL	< DL
pН	ND	5.1	5.2	5.5	5.8
$\log a(Mg^{2+})$	-	-2.88	-3.18	-4.38	-4.38
log a(SiO <sub>2</sub> )	-	-4.45	-3.58	-4.14	-3.76
$\log a(Mg^{2+}/H^+)$	-	7.32	7.22	6.61	7.21

Table A1: Evolution of the fluid composition during the serpentinization process (< DL = concentrations below the detection limit; ND = No Data.)

# 2.3. Mineralogical characterization

The solid phases recovered after the experiments were dehydrated at 50 °C for 3 h. They were ground in an agate mortar to obtain micrometric grain size and compressed to 4 mm diameter pellets for mineralogical characterization. Each pellet was then characterized by X-ray diffraction (XRD), Raman and Fe K-edge XANES spectroscopy.

2.3.1. X-ray diffraction : XRD analyses have been performed with a Siemens D501 diffractometer at the LGCA. A large X-ray beam was emitted by a cobalt source with a 40 kV accelerating voltage and a 37.5 mA current.

2.3.2. Raman spectroscopy : Raman measurements were performed with an InVia Renishaw Raman spectrometer using a green laser light at 514 cm<sup>-1</sup> with a beam size of 20  $\mu$ m on the sample in Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI; Grenoble; France). The spectra were recorded between 3600 and 3750 cm<sup>-1</sup>; area that corresponds to the structural OH group vibrations. At minimum, 3 acquisitions per sample were done at

different locations in order to check reproducibility and sample homogeneity. The spectra were then averaged to obtain better statistics.

2.3.3. X-ray absorption spectroscopy : XANES spectra were collected at the Swiss Light Source (SLS), on the "super bending magnet" (i.e., 2.9 T) beamline, SuperXAS. The storage ring operating conditions were 2.4 GeV electron energy and 400 mA electron current in the "Top-up" injection mode. A Si(111) double monochromator was used to provide a flux on the sample of  $10^{12}$  ph/s, with a beam-size of  $100\times100 \,\mu$ m and an energy resolution of 1.4 eV at the Fe K-edge (i.e., 7712 eV). Energy calibration of the monochromator was based on the acquisition of XANES spectra in the transmission mode for an iron metallic foil. The incident beam intensity was measured using a "low-noise" ion chamber filled with He-gas. XANES spectra were collected at the Fe K-edge, between 7100 and 7230 eV, in the fluorescence mode using a "Ketek" silicon-drift detector positioned at 90° to the incident beam. For each XANES spectra, three measurements were made in the step-by-step mode with appropriate energy step and dwell times for the different regions of the spectra: 0.3 eV and 4 s for the pre-peak region; 0.5 eV and 3 s for thewhite line region; 2 eV and 2 s for the rest of the spectra. Data normalization (i.e., edge-jump and slope correction) was performed using the appropriate function of the XasMap program (Muñoz et al., 2006; Muñoz et al., 2008).

# 3. Results

#### 3.1. Fluid composition

Between 0 and 7 days, the fluid composition is characterized by the strong increase of the Mg and Ca concentrations, from 0 to  $1.32.10^{-3}$  and  $3.25.10^{-4}$  mol.L<sup>-1</sup>, respectively. Then the concentrations of these two elements decrease to reach, respectively,  $4.12.10^{-5}$  and  $1.68.10^{-4}$  mol L<sup>-1</sup> after 34 days, and are then stabilized until 70 days. The concentrations obtained for Si are in the same order of magnitude compared to those of Ca. However, the maximum Si content is observed at 18 days ( $2.62 \ 10^{-4} \ mol \ L^{-1}$ ) whereas it is located at 7 days for Ca. Note that the Fe concentrations were not measured since they remain below the detection limit.

#### 3.2. Mineralogical evolution

*3.2.1. X-ray diffraction :* The diffraction patterns for each altered sample are shown in Fig. A1. The mineral assemblage in the starting sample (i.e., 0 days) comprises forsterite, enstatite and clinopyroxene (diopside). After 7 days of hydrothermal alteration, the intensities of the diffraction peaks for these three minerals decrease significantly, suggesting degradation of the crystal structure. No other mineral species is observed at this stage. From then on, the diffractions peaks for the three departure minerals decrease progressively until 70 days, while the peaks for lizardite appear at 18 days and increase until the end of the experiment. Even after 70 days of exposure time, residual forsterite is still observed in the mineral assemblage, but the diffraction pattern is largely dominated by lizardite. As previously observed by Seyfried et al. (2007), magnetite seems to crystallize only in the latest stages of alteration since the related diffraction peaks only appear in the 70 days diffraction pattern. However, even small amounts of magnetite could potentially drive to the release of significant amounts of di-hydrogen, and detection limits using such "traditional" laboratory XRD apparatus (in contrast with X-ray synchrotron sources for instance) may not allow the detection of magnetite in the early serpentinization stages.



Figure A1: XRD patterns of serpentinized lherzolite for different alteration time. The 70 days spectrum is plotted with a larger vertical scale at the top of figure.

*3.2.2.* Raman spectroscopy : Raman spectroscopy analyses were carried out in order to determine the amount of structural water (i.e., hydroxyl groups) in the different mineralogical assemblages. This technique has already been used to quantify the water concentration for different types of minerals by calibrating the area of the Raman bands (Muñoz, 2003; Thomas, 2000). In our case, since lizardite, a mineral containing 13 wt.% water (Mellini, 1982), is the only hydrated mineral, this method can be used to determine the amount of lizardite in the alteration products. In order to derive the amount of lizardite in the different samples from the area of the OH bands, a calibration curve has first to be established. Thus, we prepared different mechanical mixtures between peridotite and natural "pure" serpentine in ratios ranging from 0 to 100 wt.%.



Figure A2: (a) Raman spectra corresponding to the structural OH bands. Mechanical mixtures are represented by dotted lines. Bold black lines correspond to the altered samples after 0, 7, 18, 34, 70 days of serpentinization. (b) Model presenting percentage of serpentine as a function of OH peak area. White diamonds correspond to the mechanical mixtures and full black circles correspond to the experimental samples.

The spectra obtained from the standard mixtures and samples are given in Fig. A2a. A graph of the "serpentine percentage vs. peak areas" is shown in Fig. A2b. The calibration curve, plotted as a dotted line, follows a two-degree polynomial function. The results indicate 7, 43, 77 and 88 wt.% of lizardite for assemblages that correspond to 7, 18, 34 and 70 days of alteration, respectively. At 70 days, serpentine represents about 90 wt.% of the sample, indicating a quasi-complete serpentinization of the starting peridotite, in good agreementwith the XRD data. These data are presented in the Fig. A7a, and will be discussed further in this article.

#### 3.2.3. X-ray absorption spectroscopy

3.2.3.1. Qualitative description. Fig. A3a shows the normalized XANES spectra collected at the Fe K-edge for the different mineralogical assemblages. The four standard spectra used for the linear combination fits are also presented in the lower part of the figure. Feature A, which corresponds to pre-edge region, will be discussed later in the paper. The white line for the standards as well as for the "mixed" spectra is in the form of a doublet, identified as features B and C. Feature B is higher than C for the olivine and pyroxene spectra, while feature C is more intense for the magnetite and serpentine spectra. The series of "mixed" spectra shows a progressive evolution for these features as a function of time. At 0 days, B is slightly higher than C, in agreement with a mix between the olivine and pyroxene spectra. Then, with increasing experiment duration, the intensity of B decreases while that of C increases. At 70 days, the C is higher than B, in good agreement with

significant contributions of the magnetite and serpentine spectral signatures. Feature D is well identified for all standard spectra except for the one of magnetite, which is subdued and difficult to identify. When compared to the "mixed" spectra, we observe that this feature is relatively well identified at the first stages of alteration and become increasingly subdued and indistinct with the experiment duration, suggesting a significant contribution of the magnetite spectrum at 70 days. Similarly, the feature E shifts towards high energies with increasing experiment duration, in agreement with the shift observed in other spectra; between olivine and pyroxene on one hand, and magnetite and serpentine on the other.



Figure A3: (a) Normalized Fe K-edge XANES spectra of standard minerals and mineralogical assemblages for the different experimental runs. Solid lines represent the experimental data and open circles represent their respective fits using linear combination with four standards (olivine, magnetite pyroxene, and serpentine). Standard deviation (b) calculated for the set of spectra is displayed as a function of energy. The optimized range for linear combination fits is located between 7120 and 7162 eV.

3.2.3.2. Specific quantitative methodology. The interpretation of the XANES spectra is based on linear combinations using the appropriate standard components. Since each mineral species identified by XRD (i.e., olivine, pyroxene, lizardite and magnetite) includes some iron in its structure, the XANES measurements of our powdered samples produce weighted averages, in

variable proportions, of the spectral signatures of these minerals. This analytical approach, which involves Fe K-edge XANES spectra measured for mixtures of iron-rich minerals, was recently used to determine the amounts of different minerals or the distribution of iron between coexisting minerals (see previous studies of Andrault et al., 2010; Muñoz et al., 2008). The general equation used to resolve such data can be written as:

$$X_{mixture} = \sum_{n} X_{n} \cdot C_{n}^{Fe} \cdot x_{n}$$
(Eq. A3)

in which X is a XANES spectrum either for the *mixture* or each mineral species *n* (i.e., the spectra of the standards);  $c^{Fe}$  and x are, respectively, the iron molar concentration and the molar fraction of the mineral n. In our specific case, the minerals involved are olivine (Ol), pyroxene (Px), lizardite (Lz) and magnetite (Mgt). Ol and Px constitute the starting materials of the alteration experiments. Therefore, their iron concentrations are known and only their respective molar fractions decrease during the alteration process. Note that, as shown by the XRD data, two types of pyroxenes are present in the initial peridotite: enstatite and diopside. However, because their spectral signatures (i.e., XANES at the Fe K-edge) are similar (see for example the spectrum of diopside in Wilke et al., 2001) and the amount of diopside is much lower than enstatite, we made the assumption that only one spectrum is required to efficiently fit our data. The spectrum used is the weighted average of the two spectra, relative to their respective abundance in the rock. Magnetite an alteration product with a constant iron content and its molar fraction can be easily determined from Equation A3. In lizardite, main alteration mineral in our experiments, both the iron concentration and the molar fraction can vary. Therefore, the Lz concentrations obtained by Raman spectroscopy (described in the previous section) will be introduced as molar fractions in the calculation process. The resulting values obtained from the least square minimization (i.e., XANES "mixture" vs. XANES "standards") correspond, for each mineral, to the product  $c^{Fe}$ .x. The parameters required for the linear combination calculations therfore are the molar fractions, x, of Ol, Px and Mgt, and the iron concentration,  $c^{Fe}$ , of lizardite. In order to determine the optimized energy range for the linear combinations, we calculated the standard deviation of the complete set of data following the method of Muñoz et al. (2008). The result is shown in Figure A3b. The pre-edge region is a priori not directly correlated to the XANES shape so that we did not take it into account for the calculations. The standard deviation curve shows that variability is less than 25 % above 7162 eV, so that we define an optimum energy range for the calculations between 7120 and 7162 eV. The models obtained from the linear combinations are displayed as grey-circle curves in Figure A3a.

In order to determine the error bars due to the normalization of the XANES spectra, the fit quality was tested by random variations of both height and slope of the spectra, based on a Monte-Carlo algorithm. The maximum height and slope variations applied in this algorithm are  $\pm$  3 % and  $\pm$  0.3 keV<sup>-1</sup>, respectively. For each experimental run (7, 18, 34, and 70 days), 50,000 iterations were calculated for each spectrum, including the "mixture" and the standard spectra. Fig. A4a shows effect of both parameters - height (grey dotted lines) and slope (black dotted lines) - using the 7-day spectrum as a reference. For better understanding, black solid lines represent the extreme shapes authorized for the spectra after 20,000 iterations. Note that extreme shapes are really distorted and would be not usually considered as correctly normalized spectra. As an example, Fig. A4b shows the binomial distribution of the magnetite content for the 18-day run. Results obtained for the phase concentrations, together with associated error bars, are shown in Fig. A7a. Note that the errors bars never exceed more than 7 mol%, even for the minerals containing low concentrations of iron (i.e., olivine and pyroxene). In the 70 days experiment, the concentration of the residual forsterite observed in XRD spectra (Fig. A1) matcheswith the inferred error bars. On the other hand, the error bars are smaller than symbol size in the case of magnetite since this mineral contains high concentration of iron (Fe<sub>3</sub>O<sub>4</sub>). The determination of magnetite concentrations are thus extremely well constrained.



Figure A4: (a) Random sampling of 50000 XANES spectra using a measured XANES spectrum as a reference (here 7 days spectrum). (b) Number of iterations plotted as a function of magnetite percentage in order to estimate the error bar on magnetite amount at 18 days.

3.2.3.3. Quantitative results. Fig. A7a shows the mineral evolutions as a function of alteration time. The serpentinization reaction begins slowly in the early alteration stages, reaches amaximum after around 15 days, and then decelerates progressively to reach a quasi-plateau with a slightly

positive slope from about 40 days. According to the Raman results, after 70 days of alteration, the amount of serpentine in the mineralogical assemblage is 52 mol%. In parallel, the amount of olivine decreases relatively symmetrically compared to that of serpentine, from 71 mol% at the beginning, to  $\sim 0$  mol% after only 34 days of alteration. In contrast, the amount of pyroxene decreases quasilinearly from 29 mol% in the starting material to 0 mol% after 70 days. Finally, this diagram reveals that the crystallization of magnetite starts in the very early stage of serpentinization, to reach around 5 mol% at the end of the experiment. Despite its low concentration in the final product, magnetite produces a strong signal in the XANES "mixture" spectra. Therefore, XANES spectroscopy offers a much better detection limit for magnetite compared to our XRD measurements, which only reveal the presence of magnetite at the latest alteration stage. Finally, based on the linear combinations, the concentration of iron in serpentine could be calculated using Eq. (A3). The values are listed in Table A2 and will be used to constrain the iron speciation in the serpentine.

#### 3.3. Iron speciation in serpentine

Pre-peaks of the K-edge XANES spectra of transition metals are particularly sensitive to the oxidation state of the cation probed as well as the geometry (degree of symmetry) of its crystallographic site; the latter being generally correlated to the coordination number (e.g., Farges et al., 2001a,b; Wilke et al., 2001). Serpentine is a phyllosilicate with a "T-O" sheet structure, i.e., tetrahedral (coordination IV) and octahedral (coordination VI), so that the geometry effects on prepeaks can be directly related to coordination numbers. The pre-peaks were fitted according to the method of Wilke et al. (2001) that involves four pseudo-voigt functions (i.e., Gaussian and Lorentzian components). The full-width half-maximum was fixed at 1.5 eV and the Gaussian-Lorentzian ratio was fixed at 1. A fifth function was used to fit the baseline between 7109 and 7117 eV. The area and centroid values obtained for the pre-edge features were calibrated using the following model phases: diopside for <sup>[VI]</sup>Fe<sup>2+</sup>, staurolite for <sup>[IV]</sup>Fe<sup>2+</sup>, and radite for <sup>[VI]</sup>Fe<sup>3+</sup> and sanidine for <sup>[IV]</sup>Fe<sup>3+</sup>. The calibration curve used to derive the oxidation state of iron from the centroid position will be explained later. The baseline-corrected pre-peaks are shown in Fig. A5 for the spectra collected at 0, 7, 18, 34 and 70 days. The figure shows the experimental data as circles, the fitted pre-peaks as solid lines and for each spectrum, the four individual peaks used to fit the data (dotted lines). Additionally, two vertical dotted lines indicate the energies of the pre-peak centroids that correspond to 100% of Fe<sup>2+</sup> in the sample(left line) and 100% of Fe<sup>3+</sup> (right line). These values were determined from the analysis of the pre-edges of our model compounds.



Figure A5: Normalized Fe-K pre-edge spectra of the experimental powders. Pre-edge fits are represented as open black circles. The two vertical dotted lines indicate the energy positions of the pre-edge centroids, both for ferrous and ferric iron.

Fig. A6 clearly shows that the main components of the pre-peaks are located around the  $Fe^{2+}$  position at 0 days, and they shift progressively towards higher energies, i.e., toward the Fe<sup>3+</sup> position, as the duration of the experiment increases. This observation indicates an increasing  $Fe^{3+}/Fe_{total}$  in the assemblage. In addition, there is a slight increase in the peak area from 0 to 70 days. These observations most likely suggest that the

oxidation state of iron increases with the alteration of the sample, and that part of it undergoes a transition towards lower coordination number. The results obtained for the centroid energies and the integrated areas are plotted in Fig. A6a. The template defined by the four grey circles is based on our model compounds as defined in the preliminary work of Wilke et al. (2001). The starting material is located close to the <sup>[VII]</sup>Fe(II) end-member, in agreement with the speciation of iron in olivines and pyroxenes. The integrated areas increase with time with a distinct change in slope at 34 days. Wilke et al. (2001) show a quasi-linear relationship between the integrated pre-edge area and the coordination number of iron. We infer that the amount of tetrahedral iron increased from 0% at the beginning of the experiment to about 25% of total iron after 70 days of alteration. The two distinct regimes observed most likely correspond to a change in the crystallization process.

In order to quantify these variations in terms of oxidation state of iron, we calculated a calibration curve using model compounds (i.e., iron "end-members" with different oxidation states and coordination numbers). Curves 1 and 3 in Figure A6b show the evolution from a starting product with <sup>[VI]</sup>Fe<sup>2+</sup> towards two final products, <sup>[VI]</sup>Fe<sup>3+</sup> and <sup>[IV]</sup>Fe<sup>3+</sup> (from Wilke et al., 2001). The curvature radius of the two curves is inversely proportional to the amount of tetrahedral iron in the final product. In our system, iron is essentially included in magnetite with 2/3 <sup>[VI]</sup>Fe<sup>3+</sup> and 1/3 <sup>[IV]</sup>Fe<sup>3+</sup>. The calibration model used to quantify the Fe<sup>3+</sup>/Fe<sub>total</sub> ratio in our samples is thus defined by 2/3 of the curve 1 and 1/3 of the curve 3.



Figure A6: (a) Diagram indicating the area and centroid-energy of pre-edges for the 0, 7, 18, 34 and 70 days samples (black full circles). Larger gray circles correspond to end-members of four pure phases incorporating iron with different oxidation states and coordination numbers (olivine  ${}^{[VI]}Fe^{2+}$ , staurolite  ${}^{[IV]}Fe^{2+}$ , andradite  ${}^{[VI]}Fe^{3+}$ , sanidine  ${}^{[IV]}Fe^{3+}$ ). (b) Evolution of ferric iron content as a function of pre-edge centroid energy. The quantification curves change as a function of the amount of tetrahedral iron in the oxidized end-member (top right). Curve 1 corresponds to the evolution between  ${}^{[VI]}Fe^{2+}$  and  ${}^{[VI]}Fe^{3+}$  end-members, while curve 3 corresponds to the evolution between  ${}^{[VI]}Fe^{2+}$  and  ${}^{[IV]}Fe^{3+}$  end-members.

The result is curve 2 in Figure A6b. Each centroid energy value is then reported on this calibration curve, and the values obtained for the  $Fe^{3+}/Fe_{total}$  ratio are 2, 23, 47, 66 % ± 2% for 7, 18, 34 and 70 days, respectively. The  $Fe^{3+}/Fe_{total}$  (or  $Fe^{3+}$  number; i.e.,  $\#Fe^{3+}$ ) ratios obtained can be expressed in the following way:

$$Fe_{total}^{3+} = \left(C^{Fe} . x.\# Fe^{3+}\right)_{mgt} + \left(C^{Fe} . x.\# Fe^{3+}\right)_{serp}$$
(Eq. A4)

in which  $e^{Fe}$  is the iron concentration and x the molar fraction for the different phases. Since  $e^{Fe}$  and  $\#Fe^{3+}$  for magnetite are fixed and equal to 3/7 and 2/3, respectively, x values are known for both minerals, and, because  $e^{Fe}$  has been previously calculated for serpentine (Fig. A7b), it is possible to calculate the  $\#Fe^{3+}$  for the serpentine phase. Moreover, using the same logic, it is possible to calculate the amount of tetrahedral iron in the serpentine with the following equation:

<sup>[IV]</sup> Fe<sub>serp</sub> = 
$$\frac{{}^{[IV]} Fe - ({}^{[IV]} Fe_{mgt} . C_{mgt}^{Fe} . x_{mgt})}{C_{serp}^{Fe} . x_{serp}}$$
 (Eq. A5)

The results obtained from the Eq. A5 and A6 are reported in Figures A7c and A7d. For a better understanding, we distinguished three stages of serpentinization – "early", "intermediate" and

"final" – that correspond to the periods 0-18, 18-34 and 34-70 days. Figure A7c shows that  $\#Fe^{3+}$  in serpentine remains close to 0 in the early stage, then increases strongly to 35% in the intermediate and to 66% at the end final stage. Figure A7c shows that the tetrahedral component of  $Fe^{3+}$  in serpentine is negligible until 34 days and then slightly increases in the final stage to reach about 15% at the end of the experiment. This speciation information means that the Si<sup>4+</sup>–Fe<sup>3+</sup> substitution in the tetrahedral sites of the serpentine is significant, in agreement with previous qualitative investigations of natural samples (O'Hanley and Dyar, 1993; Gonzalez-Mancera et al., 2003; Andréani et al., 2008; Klein et al., 2009).

Figure A7d displays the evolution of the total amount of trivalent iron in either magnetite or serpentine. In the early stage of alteration, the increase of Fe<sup>3+</sup> results essentially from the crystallization of magnetite, while serpentine incorporates only ferrous iron. This trend is completely inverted in the intermediate stage, when the serpentine massively incorporates ferric iron in its structure as magnetite crystallization declines. At 34 days, the contribution of serpentine and magnetite in the Fe<sup>3+</sup> storage is similar since they both contain about ~ 1/3 of total ferric iron. Beyond 34 days of alteration, Fe<sup>3+</sup> is preferentially incorporated into magnetite, to reach a balance at the end of the experiment when 3/4 of ferric iron is incorporated in magnetite and 1/4 in serpentine.



Figure A7: (a) Evolution of the amount of mineral phases during serpentinization. (b) Calculated #Fe in serpentine throughout the alteration. (c)  $Fe^{3+}/\Sigma Fe$  calculated for serpentine (bold line) as a function of alteration time. Octabedral and tetrahedral components are displayed in dotted lines.  $Fe^{3+}/\Sigma Fe$  in magnetite is constant and equal to 2/3. (d) Evolution of  $Fe^{3+}/\Sigma Fe$  for the experimental powders (bold line). The magnetite and serpentine components are presented as solid line and dotted line, respectively.

# 4. Discussion

As abundantly documented in the literature, and in agreement with our experiments, serpentinization is accompanied by the oxidation of iron and the reduction of water into molecular hydrogen. The process was modeled thermodynamically using the Arxim software (http://www.emse.fr/~moutte/thermodyn/programs/index.html), already used in previous studies (e.g., Garcia et al., 2010; Kowalewski et al., 2008), which allows one to calculate the evolution of the mineral assemblage and the composition of fluid during serpentinization. The modeling was carried out using the thermodynamic data of Helgeson et al. (1978) and the kinetic data of Panadri and Kharaka (2004), with a water-rock ratio of 3/2 and a  $10^{-6}$  m grain size for all solids. Calculations of the evolution of mineral proportions, displayed in Supplementary Figure, are in excellent agreement with the proportions deduced fromspectroscopicmeasurements (see Fig. A7a). The Arxim software was also used to calculate the pH values of the aqueous solutions at the pressure-temperature conditions of the experiments and the measured concentrations of Mg, Si and Ca reported in Table A2, as well as the activities of dissolved species. The evolution of calculated and measured fluid compositions are shown in a  $\log(aMg^{2+}/(H^{+})^{2})$  vs.  $\log(aSiO_{2})$  diagram (Supplementary Figure). The calculated evolution of the solution is shown colored as a function of time. Both the experimental and calculated values of  $aMg^{2+}/aH^+$  and  $aSiO_2$  are located close to the serpentine-solution limit during the entire serpentinization process. These results indicate that serpentine is the only silicate that buffers the composition of the aqueous solution throughout the experiment. Considering the data from the experimental and thermodynamic calculations, the serpentinization process can be divided into three main stages.

#### 4.1. Early serpentinization (between 0 and 18 days)

According to the liquid composition and the relative amounts of minerals given in the Table A2, the serpentinization reaction between 0 and 18 days can be written as:

olivine enstatite 
$$cpx$$
  
1.18  $Mg_{1.7}Fe_{0.3}SiO_4 + 0.4101 Mg_{1.7}Fe_{0.3}Si_2O_6 + 0.00157 CaMg_{0.8}Fe_{0.2}Si_2O_6 + 2.056 H_2O + 0.0022 H^+$   
 $\rightarrow$   
 $Mg_{2.7}Fe_{0.3}Si_2O_5(OH)_4 + 0.059 Fe_3O_4 + 0.00094 Mg^{2+} + 0.00016 Ca^{2+} + 0.0002 SiO_2(aq) + 0.057 H_2$   
serpentine magnetite (Eq. A6)

The concentration of iron in serpentine was fixed in agreement with XANES results. Diffraction patterns reveal that serpentine crystallizes as the lizardite polymorph.

Although chrysotile and lizardite are both stable at the P-T conditions of our experiments, lizardite is generally the first polymorph to form while chrysotile is frequently considered as a secondary phase in natural rocks (O'Hanley and Offer, 1992; Normand et al., 2002). Moreover, at slow-spreading mid-ocean ridges, lizardite is the main product of olivine and pyroxene hydration (Caruso and Chernosky, 1979; Wicks and Plant, 1979).

Time (day)	0	7	18	34	70
X <sub>mgt</sub> (mol%)	0.061	0.07	0.98	2.16	4.56
$X_{ol} \pmod{\%}$	76.05	69.87	39.46	0.0000	0.0000
$X_{px} \left( mol\% \right)$	23.89	25.95	24.94	17.94	0.00
X <sub>serp</sub> (mol%)	0.00	4.03	34.61	79.68	89.49
[Fe] <sub>mgt</sub> (mol%)	0.428	0.428	0.428	0.428	0.428
[Fe] <sub>ol</sub> (mol%)	0.0285	0.0285	0.0285	0.0285	0.0285
[Fe] <sub>px</sub> (mol%)	0.02	0.02	0.02	0.02	0.02
[Fe] <sub>serp</sub> (mol%)	No serp.	0.00242	0.00749	0.00822	0.00280
$(Fe3+/\Sigma Fe)_{bulk}$	0.01	0.02	0.23	0.48	0.66
$(Fe3+/\Sigma Fe)_{mgt}$	0.66	0.66	0.66	0.66	0.66
$(Fe3+/\Sigma Fe)_{serp}$	No serp.	0.00	0.00	0.23	0.67
$(Fe(IV)/\Sigma Fe)_{bulk}$	0.00	0.00	0.05	0.08	0.31
$(Fe(IV)/\sum Fe)_{mgt}$	0.33	0.33	0.33	0.33	0.33
$(Fe(IV)/\sum Fe)_{serp}$	No serp.	0.00	0.00	0.00	0.12
H2-experiment (mol)	0.0000	0.0004	0.0019	0.0071	0.0138
H2-theory (mol)	0.0000	ND	0.0063	0.0115	0.0131

Table A2: Evolution of the parameters shown in Fig. A7 and A8, as a function of the alteration time (see text for further information).

During this step, the production of hydrogen indicates that oxidation of ferrous iron begins during the very first days of the experiment. At the end of this early stage, the integrated amount of hydrogen reaches 1.5 mmol, produced by the oxidation of 23 % of the total iron. The concentration of Fe<sup>3+</sup> in serpentine remains close to zero, which indicates that the early production of H<sub>2</sub> is exclusively associated with the crystallization of magnetite. As it was the case in the experiments conducted by Seyfried et al. (2007), magnetite was not detected by XRD. However, the presence of magnetite in the run products of the short-duration experiments is confirmed by the XANES measurements. In the same time, the release of Mg<sup>2+</sup> and SiO<sub>2</sub> into the fluid phase is consistent with

the dissolution of pyroxene and olivine. The reaction also consumes protons, which is consistent with the observed slight increase of pH. The evolution of clinopyroxene and enstatite was defined separately in the calculations. The thermodynamic calculations predict that enstatite is entirely dissolved before 30 days, while the amount of clinopyroxene remains unchanged. According to these results, the dissolution of pyroxene before 18 days mainly corresponds to the breakdown of enstatite, although the slight increase of calcium concentration in the aqueous phase suggests at least a minor dissolution of clinopyroxene (see Eq. A6).

#### 4.2. Intermediate serpentinization stage (between 18 and 34 days)

As the concentration of calcium in the liquid phases does not significantly evolve during this step, clinopyroxene does not appear in the corresponding reaction (Eq. A7). This result is supported by thermodynamical modeling (see Cpx curve in Supplementary Figure). Therefore, the decrease of the pyroxene amount (Fig. A7a) must be assigned entirely to the breakdown of orthopyroxene. The mass of serpentine increases from 43 to 77 wt%, together with the complete dissolution of olivine. In parallel, the production of hydrogen, which is associated with the incorporation of Fe<sup>3+</sup> in serpentine, increases, Our data show that  $\#Fe^{3+}$  in serpentine increases from 0 to 0.37 between 18 and 34 days, (Fig. A7c). These are averaged values that integrate the previously crystallized serpentine, so that the serpentine formed at 24 days has most likely a  $\#Fe^{3+} > 0.37$ . The best reaction accounting for the 18- to 34-day experimental results is obtained with a  $\#Fe^{3+}$  of 0.5. As is the case for  $\#Fe^{3+}$ , this value is not an integrated value from 0 and 34 days, and is thus different from those calculated by XANES (Table A3). Based on the measured proportions of mineral phases between 18 and 34 days (Table A3), the following reaction is inferred:

Olivine enstatite 1.184  $Mg_{1.7}Fe_{0.3}SiO_4 + 0.408 Mg_{1.7}Fe_{0.3}Si_2O_6 + 2.0624 H_2O + 0.0002 SiO_2(aq) + 0.00088 Mg^{2+}$   $\rightarrow$   $Mg_{2.707}Fe^{2+}_{0.120}Fe^{3+}_{0.120}Si_2O_5(OH)_4 + 0.0018 H^+ + 0.0779 Fe_3O_4 + 0.0624 H_2$ serpentine magnetite (Eq. A7)

Note that the charge balance due to the incorporation of ferric iron into serpentine requires vacancies in the octahedral sheet. Consequently, the number of cations in the octahedral sheet of serpentine is slightly less than 3 in Equation A7. In contrast to the early stage of serpentinization, magnetite does not crystallize in large amounts, while the serpentine phase contributes up to 50 % of the total hydrogen production at the end of the intermediate stage (Fig. A7d).

#### 4.3. Final serpentinization stage (between 34 and 70 days)

After 70 days of alteration, the integrated hydrogen production reaches 14 mmol. During this stage, the crystallization of serpentine is exclusively due to the dissolution of pyroxene. Considering the mineral amount and the fluid composition after 70 days of serpentinization process, the best stoichiometry matches the dissolution of up to 50% of any remaining clinopyroxene. However, the concentration of calcium in the solid fraction (3 wt%) is identical in the initial peridotite and in the most altered sample. This result suggests the crystallization of a very small amount of calcic phyllosilicate like that okenite that is sometimes observed in this kind of environment (Spiridonov et al., 2009). This calcic phase is probably free of iron, which explains why it was not detected by the XANES measurements. Moreover, the chemical balance (Eq. A8) requires a concentration of only 2.7 mol% of this hypothetical mineral, which is clearly below the detection limit of our XRD measurements. In order to reach the amount of magnetite observed in our experiments, and considering the observed decrease of #Fe<sup>3+</sup> in the newly-formed serpentine, the previously-formed serpentine (0-18 days) must be considered the reactive species, and the following reaction is inferred :

enstatite
 cpx
 Fe-rich serpentine

 
$$0.154 Mg_{1.7}Fe_{0.3}Si_2O_6 + 0.154 CaMg_{0.8}Fe_{0.2}Si_2O_6 + 0.926 Mg_{2.7}Fe^{2+}_{0.122}Fe^{3+}_{0.122}Si_2O_5(OH)_4 + 0.67 H_2O$$
 $\rightarrow$ 
 $Mg_{2.9}Fe^{3+}_{0.07}Si_2O_5(OH)_4 + 0.0744 Fe_3O_4 + 0.159 SiO_2(aq) + 0.0514 Ca_3Si_6O_{15}(H_2O)_6 + 0.058 H_2$ 
 Mg-rich serpentine

 magnetite
 calcic silicate

 (Eq. A8)
 (Eq. A8)

The optimized serpentine composition is reached for a  $\#Fe^{3+}$  of 1. This is in agreement with the results presented in Figure A7c, which shows a significant increase of tetrahedral iron in serpentine at the end of the experiment. This process is likely driven by the saturation of ferric iron in the octahedral sheet of the serpentine. In the mineral assemblage recovered after 70 days of alteration, up to ~ 27 % of total Fe<sup>3+</sup> is in the tetrahedral position. This result is consistent with the highest concentration of tetrahedral iron measured by Klein et al. (2009) on natural mesh rims (25-27 %). Other studies performed on natural rocks have revealed the presence of trivalent iron in the tetrahedral sheets of serpentine (Whittaker and Wicks, 1970; Blaauw et al., 1979; Rozenson et al., 1979; Gonzalez-Mancera et al., 2003; Andréani et al., 2008). However, our results provide for the first time details about the incorporation of Fe<sup>3+</sup> in serpentine as a function of the degree of alteration of the rock.



Figure A8: (a) Hydrogen production as a function of the alteration degree. Black squares correspond to the experimental hydrogen ( $H_2(gas) + H_2(aq)$ ). White diamonds correspond to the hydrogen calculated by chemical balancing (see Eq. A6, A7 and A8; fit is displayed as solid line). The maximum of the hydrogen production is highlighted, at 18 days, by the derivative of the fit (dotted line). (b) Correlation diagram between Fe<sup>3+</sup> and H<sub>2</sub> amounts (in mol). Hydrogen amounts obtained from chemical balancing show a linear coorelation (solid line), while experimental hydrogen presents deficits at 34 and 70 days (see explanations in text).

To further illustrate the relation between the oxidation of iron and the production of hydrogen, Figure A8b shows the total amount of Fe<sup>3+</sup> in the recovered mineralogical assemblages as a function of the amount of hydrogen produced. The experimental data (black squares) are compared to an "ideal" model of hydrogen formation (dotted line) in which two moles of produced Fe<sup>3+</sup> correspond to one mole of H<sub>2</sub>. The ideal model corresponds to the hydrogen concentrations obtained from the chemical balance of equations A6, A7 and A8 (data in Table A3), which are shown by the white diamonds in the same diagram. Figure A8b shows that the measured concentrations of hydrogen overlap the ideal model at 7 and 70 days. In contrast, a significant deviation is observed at 18 and 34 days, where the measured H<sub>2</sub> content is lower than expected. This deviation is due to a leak of hydrogen or to a diffusion process in the walls of the autoclave

(Kishimoto et al., 1984; Kishimoto et al., 1985). The absence of pressure drop during the experiments is attributed to the low weight of hydrogen and the very low concentrations of hydrogen produced in the Ar gas injected at 300 bar.

The quantities of  $H_2$  obtained from the chemical balance based on the mineralogical characterization are reported in Figure A8a (white diamonds). These data can be correctly fitted using an arctangent function (solid line), and the derivative of the fit curve is shown as a dotted line. The derivative curve clearly highlights a maximum (inflection point of the arctangent) that corresponds to the maximum production rate of hydrogen, which in our experiment, was observed after about 17 days of alteration, at the end of the "early" alteration stage. When considering the full-width at half-maximum of the peak, the  $H_2$  production appears efficient from the day 10 to the day 25, i.e., from the middle of the "early" stage to the middle of the "intermediate" stage.

# 5. Conclusions

Our study emphasizes the role of magnetite in the early stage of hydrogen production and serpentinization. The incorporation of ferric iron into serpentine contributes up to 30 % of the total hydrogen production, while the other 70 % is associated with the crystallization of magnetite. The experimental data are in fair agreement with the results of thermodynamic-kinetic calculations. Both magnetite and serpentine contain ferric iron and are thus major actors of the production of H<sub>2</sub> during serpentinization in natural environments. The balancing of chemical reactions based on the mineral characterization confirms that the production of hydrogen is linearly correlated to the amount of ferric iron. Direct measurements by gas chromatography underestimate the amount of produced hydrogen and lead to erroneous estimates of the optimum gas production as a function of the degree of serpentinisation. In contrast, our results demonstrate that an accurate mineralogical characterization allows the ex-situ quantification of the H<sub>2</sub> degassing for a given volume of altered rock. Since the experimental procedure presented in this study aims at characterizing the whole rock mineralogy, and since no mineral selection is needed, this method can potentially be easily transposed to natural rocks in order to evaluate the "hydrogen-potential" of different hydrothermal sites. Obviously, the experiment presented in this study, conducted at 300°C/300 bar, is not representative of all types of hydrothermal systems which display strong variations in terms of temperature and fluid chemistry. To further our understanding of natural ultramafic hydrothermal systems, new experimental studies will be conducted, involving, among others, 1) various pressure and temperature conditions and w/r ratios, 2) comparisons between the alteration of powders and the alteration of centrimetric rock fragments.

Supplementary materials related to this article can be found on the two next pages.



Supplementary Figure: (a) Concentrations of dissolved species in aqueous fluid coexisting with altered peridotite for different alteration time. (b) Thermodynamic modeling of the evolution of mineral phases as a function of time. (c) Activity diagram in the MgO-SiO<sub>2</sub>-H<sup>+</sup>-H<sub>2</sub>O system showing the evolution of the fluid composition during the serpentinization process. Colored circles correspond to fluid compositions extracted by thermodynamic modeling.

Element				
(mass fraction)	Olivine	Opx	Срх	Bulk
CaO	0.0066	0.0269	0.1817	0.0203
$Al_2O_3$	0.0135	0.0355	0.0362	0.0218
MgO	0.4731	0.3388	0.1896	0.4242
FeO	0.0843	0.0788	0.0668	0.0832
$SiO_2$	0.4128	0.5113	0.5235	0.4449
Total	0.9903	0.9914	0.9978	0.9944

Supplementary Table: Composition, in mass fraction, of the lherzolite minerals, determined by ICP-AES.

Cette expérience montre donc que la production d'hydrogène est directement corrélée à la quantité de fer oxydé et qu'aucun autre élément ne semble entrer en ligne de compte. En fonction du degré d'altération, nous montrons que le Fe<sup>3+</sup> incorpore soit la magnétite, soit la serpentine. Nous concluons que l'incorporation du Fe3+ dans la magnétite participe majoritairement à cette cette production en début et fin du processus de serpentinisation alors que la serpentine semble jouer un rôle plus important dans les stades intermédiaires d'altération.