SERPENTINISATION D'UNE PÉRIDOTITE SOUS FORME DE FRAGMENTS

Jusqu'à présent, les processus d'altération ont été contraints sur des roches finement broyées dans le but de maximiser les surfaces de réactions, et ainsi d'accélérer la vitesse de serpentinisation. Évidemment, les roches de la croûte océanique ne se présentent pas sous forme de poudre et les processus physico-chimiques mesurés sur nos échantillons expérimentaux, notamment la cinétique réactionnelle et les vitesses de percolation des fluides, doivent nécessairement être réévalués pour s'appliquer aux conditions naturelles. Si de nombreuses études ont permis de caractériser les serpentinites océaniques (Aumento et Loubat, 1971 ; Wicks et Whittaker, 1977 ; Prichard, 1979 ; Dilek et al., 1997 ; Stamoudi, 2002 ; Andréani et al., 2007, 2008), aucune étude expérimentale n'a pour l'instant déterminé à la fois 1) la cinétique de cristallisation sur une roche non broyée, 2) le mode de cristallisation de la serpentine lors des premiers stades d'altération, et 3) l'évolution spatiale de la spéciation du fer dans les veines nouvellement formées. Pour cela, nous avons expérimentalement altéré des fragments centimétriques et cubiques de lherzolite dans un autoclave à gros volume. Ces cubes ont été récupérés après différents temps d'altération : de 15 à 84 jours. L'étude de ces fragments altérés fait l'objet de deux parties, dont la première est présentée sous la forme d'un article.

4.1) **Estimation de la taille d'un réseau hydrothermal à partir de la cinétique de réaction**

Résumé étendu de l'article 3 en préparation (à soumettre dans Contribution to Mineralogy and Petrology) :
La première partie constitue une étude cinétique de la serpentinisation dans une roche non broyée. Les cubes expérimentaux présentent des bordures altérées et de couleur brune, alors que leurs cœurs sont constitués de péridotite saine, de couleur verte.

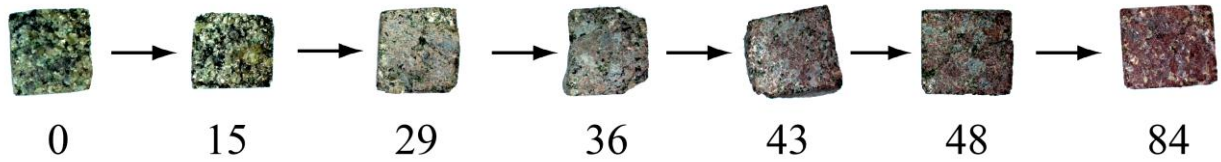


Figure 45 : Évolution de l'état de surface des fragments en fonction du nombre de jours d'altération.

Malgré un important changement de couleur (Figure 45), la zone altérée n'est que partiellement serpentinisée. Celle-ci est en réalité constituée d'un réseau plus ou moins développé de veines de serpentine localisées aux joints de grains, entre les olivines et les pyroxènes, observable sur une coupe médiane de chaque cube. Ainsi, deux paramètres ont été précisément mesurés sur chaque échantillon.

1. Le premier correspond à la largeur de la zone partiellement serpentinisée, qui est mesurée depuis les bords du fragment. Calculé sur chaque échantillon, ce paramètre nous donne la vitesse d'avancée du front de serpentinisation dans une roche naturelle. La vitesse calculée dans cette expérience est de 3,8 cm.an^{-1} (longueur « a » dans la figure 46).

2. Le second paramètre est le pourcentage de la surface serpentinisée dans la zone partiellement altérée. Cette surface est calculée dans une zone bien définie, entre le bord de l'échantillon et la limite du front d'altération (rectangle gris sur Figure 46). Pour réaliser ce calcul, nous avons défini la surface couverte par les veines. Pour cela, les images acquises en microscopie sur des lames minces ont été digitalisées, puis numériquement traitées pour définir le pourcentage de surface correspondant à de la serpentine nouvellement formée. Par extrapolation tridimensionnel (le long d'un plan de faille par exemple), cette surface peut être traduite en volume serpentinisé pour chaque échantillon. Nous obtenons ainsi l'évolution du degré d'altération au cours du temps. Il résulte que le volume serpentinisé augmente de 33 wt% par an sur une épaisseur de 3,8 cm.

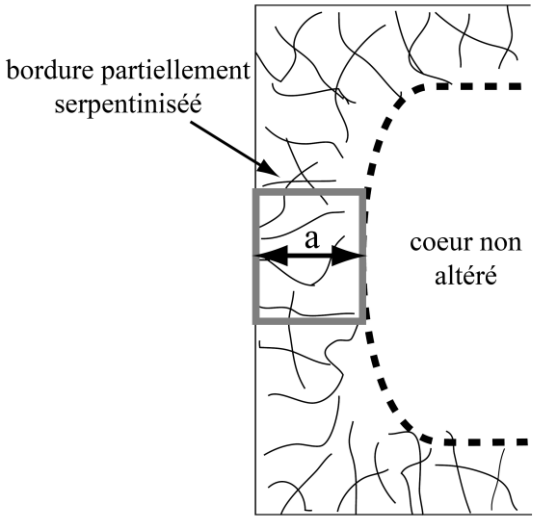


Figure 46 : Schéma simplifié représentant l'altération observée dans les échantillons. Le premier paramètre « profondeur d'altération » est indiqué par la lettre « a ». Le paramètre « surface serpentinisée » est calculé dans le rectangle gris.

À l'aide de ces deux paramètres expérimentaux, nous avons construit deux modèles numériques qui permettent de contraindre, au premier ordre, les processus de croissance d'un système hydrothermal : soit par densification du réseau au cours du temps (Fig. 47), soit par extension du réseau avec une égale densité de fracture.

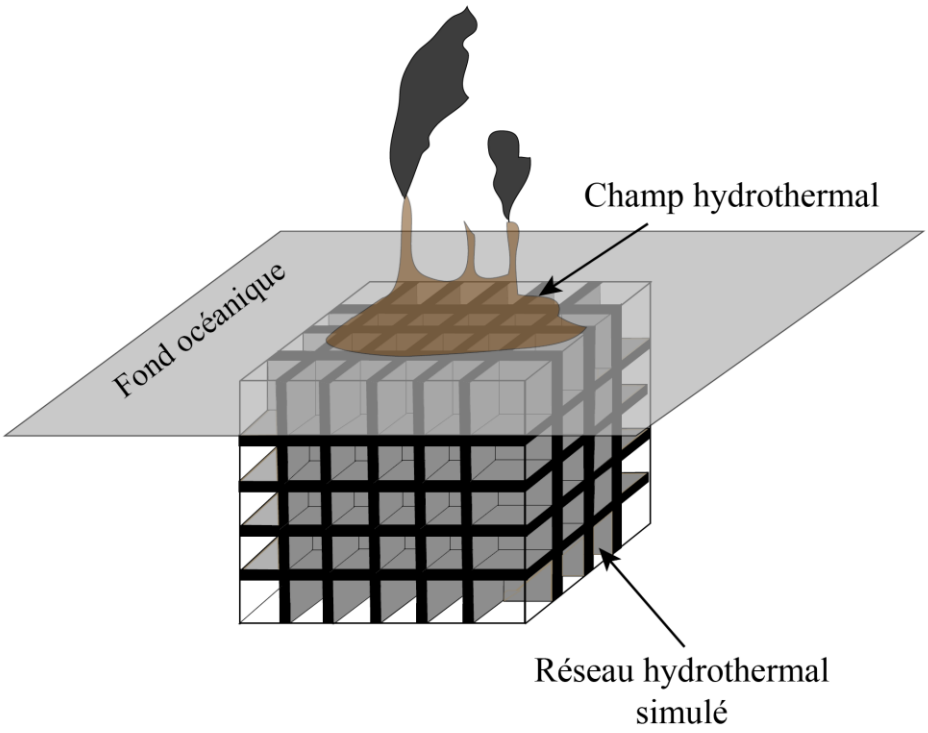


Figure 47 : Représentation schématique du réseau hydrothermal simulé dans cette étude.

En intégrant les deux paramètres définis plus hauts dans le premier modèle, il est possible de calculer un volume serpentinisé en fonction 1) du temps et 2) de la maille utilisée. Le modèle permet alors de définir, en fonction du temps, l'évolution la densité de fracturation (ou la taille de maille) dans un cube de péridotite de volume fixe. Les volumes serpentinisés au cours du temps sur Rainbow ont été comparés à ce modèle. Ces derniers ont été estimés en couplant les données de notre première expérience avec les flux d'hydrogène mesurés sur Rainbow (Charlou et al., 2002). Il en résulte que la maille calculée est trop importante (80 m) par rapport à celles que l'on devrait attendre pour assurer la pérennité de la circulation hydrothermale (1-10m, Lister, 1980).

À l'aide de nos paramètres cinétiques, nous avons donc calculé le nombre de m^3 de roches partiellement altérés qui sont nécessaires à la production d'hydrogène mesurée, à chaque instant *t*, sur les fumeurs. En considérant à la fois les contraintes de températures vis-à-vis de la cinétique de serpentinisation, mais aussi le gradient thermique estimé dans le contexte de dorsale lente,

nous avons estimé que le réseau hydrothermal se situait autour de 2 km de profondeur et avait une épaisseur moyenne de 1 km. Nous avons donc considéré que le réseau hydrothermal s'étendait au cours du temps en prenant la forme d'un cylindre haut de 1 km. Après 10 000ans de fonctionnement, le réseau hydrothermal du site Rainbow représente ainsi un cylindre de 2 km de diamètre très essentiellement composé de péridotite entièrement altérée. La partie partiellement altérée contribuant à la production d'hydrogène constitue une fine enveloppe cylindrique de moins d'un mètre d'épaisseur. On en conclu que la production d'hydrogène sur ce site devrait être effective à une distance minimale de 1 km par rapport au champ de fumeurs.

Experimental alteration of centimetric fragments of peridotite at 300°C/300 bar

Marcaillou C.[a], Vidal O.[a], Muñoz M.[a], Parra T.[b], Guillot S.[a]

[a]LGCA-OSUG, UMR 5025, Université Joseph Fourier, Grenoble, France.

[b]Geology-Geochemistry-Geophysics Division, IFP, BP311, 92506 Rueil-Malmaison, France.

Corresponding author:

E-mail address: marcaillou.clement@gmail.com

Present address: Laboratoire de Géodynamique des Chaînes Alpines, Maison des geosciences, boite poste 53, 38041 Grenoble Cedex 9.

Phone number: +33 (0)4 76 51 40 60

Fax number: +33 (0)4 76 51 40 58

Abstract

The size of the ultramafic hydrothermal fields at mid oceanic ridges remains mainly unknown because drilling and seismic data are sparse, and because the rate of serpentinization in natural settings is poorly constrained. The rate of serpentinization of compacted peridotite fragments was constrained in high volume autoclaves, for time duration ranging from 1 to 84 days, at 300°C, 300 bar. The degree and rate of serpentinization were constrained by a numerical treatment based on the acquisition of microscopic images on thin sections. The serpentinization front progressed from the rim to the center of the fragments at a rate of 4 cm.year^{-1} , and the amount of serpentine increased by 33 vol% per year into this front. These two fundamental parameters were then incorporated in a 3D-kinetic model to estimate the volume of the hydrothermal network.

Since the serpentinization process mostly occur in the 200°C-range of temperature (200-400°C), we assume that hydrothermal network has a cylindrical shape with a maximal height of 1100 m according to the thermal gradient inferred in such context (175°C.km^{-1}). In the case of Rainbow, the actual hydrothermal network represents a cylinder having a diameter close to 2 km. In parallel, the volume of rock in which serpentinization permanently occurs to ensure the constant production of hydrogen only constitutes a small part of this hydrothermal network at the present time, and can be represented as a thin sheath (< 1 m) surrounded a large inactive core of serpentinite. We conclude that the production of hydrocarbons nowadays happens at 1 km (at less) from the active vent field.

1. Introduction

Deep lithospheric ultramafic rocks along low-spread mid-oceanic ridges are exposed to aqueous alteration at 200-400°C, which leads to the crystallization of magnesium-rich serpentine and iron oxides (Wicks and Whittaker, 1977; Bach et al., 2006, Paulick et al., 2006; Marques et al., 2006, Andreani et al., 2007, 2008 ; Epp & Suyenaga, 1978 ; O'Hanley and Wicks, 1995 ; Früh-Green et al., 1996 ; Agrinier and Cannat, 1997 ; Mével, 2003). Serpentinization induces a strong modification of the rheology and magnetization (e.g., Escartın et al., 1997, Oufi et al., 2002), petrophysic (e.g., Christensen, 1972; Carlson and Miller, 1997; Miller and Christensen, 1997) and chemical (e.g., Janecky and Seyfried, 1986) properties of the oceanic lithosphere. The process of serpentinization at low-spread mid oceanic is also a source of hydrogen and hydrocarbon-rich fluids that are used by primitive microbial activity at hydrothermal vents (Janecky and Seyfried, 1986; Charlou et al., 1998; Holm and Charlou, 2001; Kelley et al., 2001), and which are central to a hypothesis positing that life emerged at an alkaline hydrothermal vent (Früh-Green et al., 2004; Konn et al., 2006; Martin and Russel, 2007; Russel et al., 2010, Lang et al., 2010). During serpentinization, hydrogen is generated by the reduction of water into molecular hydrogen that accompanied the oxidation of Fe^{2+} contained in primary olivines into Fe^{3+} incorporated mainly into secondary magnetite (Moody, 1976a ; Moody, 1976b ; Frost, 1985; Janecky and Seyfried, 1986, Bach et al., 2006) and to some extend into serpentine (Seyfried et al., 2007, Marcaillou et al. (submitted)).

Numerous experimental simulations of serpentinization have been conducted over the last two decades (Seyfried and Dibble, 1980 ; Berndt et al., 1996 ; Wetzel and Shock, 2000 ; Allen and Seyfried, 2003 ; Seyfried et al., 2007), which all show that olivine breakdown and serpentine growth is a very fast process. The experimental results of Marcaillou et al. (2011 and submitted) showed that 80 vol% of a natural lherzolite is serpentinized after ~150 days between 250 and 350°C, 30 bars, and a water-to-rock ratio equal to 1. These results are consistent with the kinetic laws available in the literature (Martin and Fyfe, 1970 ; Rudge et al., 2010 ; Marcaillou et al., 2011). However, the above-mentioned experimental studies were conducted with extremely thin powdered natural rocks with a high reactive surface, which greatly enhances the rate of alteration. The rate of serpentinization of compact natural rocks can be very different. The paucity of seismic data and drilling on Rainbow limits our ability to precisely estimate the volumes of serpentinized rock formed per time unit at the crustal scale (Canales et al., 2004 ; Blackman et al., 2009 ; Collins et al., 2009). Extensive serpentinization (<50%) detected by seismic velocity profile occurs where an open system of hydrothermal circulation operates, but the early 5 to 30% serpentinization between the seismic Moho and about 4 km that occurs in the absence of hydrothermal circulation is not detectable. This

early serpentinization is believed to be a fast process (<2000 years, Andreani et al., 2007), but the lack of reliable experimental data on rock fragments hampers any reliable estimates of its rate and the volumes of serpentine generated with time remains unknown. Not only the kinetics but also the physico-chemical processes involved in the serpentinization of natural ultramafic rocks is different from that observed during the experimental alteration of powdered peridotite. It follows that the modalities of serpentinization and the evolution of the mineral composition (in particular the iron concentration and speciation) as a function of time remains poorly constrained.

In order to improve our knowledge of the serpentinization process under more realistic conditions than those corresponding to the experimental studies using powdered peridotite, we have conducted an experimental alteration on centimetric rock fragments at 300°C, 300 bar, from 1 to 84 days. The first goal of this study was to quantify the progress of serpentinization through a compacted peridotite. The alteration width was measured for each alteration time, from the edges to the core of the fragments. The experimental results were used to perform a diffusion-like model with the aim to constrain at a first order the size and the 3D-geometry of the hydrothermal network in natural context.

2. Experimental method

Experimental – Following Marcaillou et al. (2011 and submitted), the experiments were conducted with a fresh spinel-lherzolite sampled from xenoliths at Borée (Massif Central, France), which has been studied in details by Leggo and Hutchison (1968), Mercier and Nicolas, (1975) and Xu et al. (1998). It is composed of 65 vol% olivine, 30 vol% pyroxene and 5 vol% of spinel.

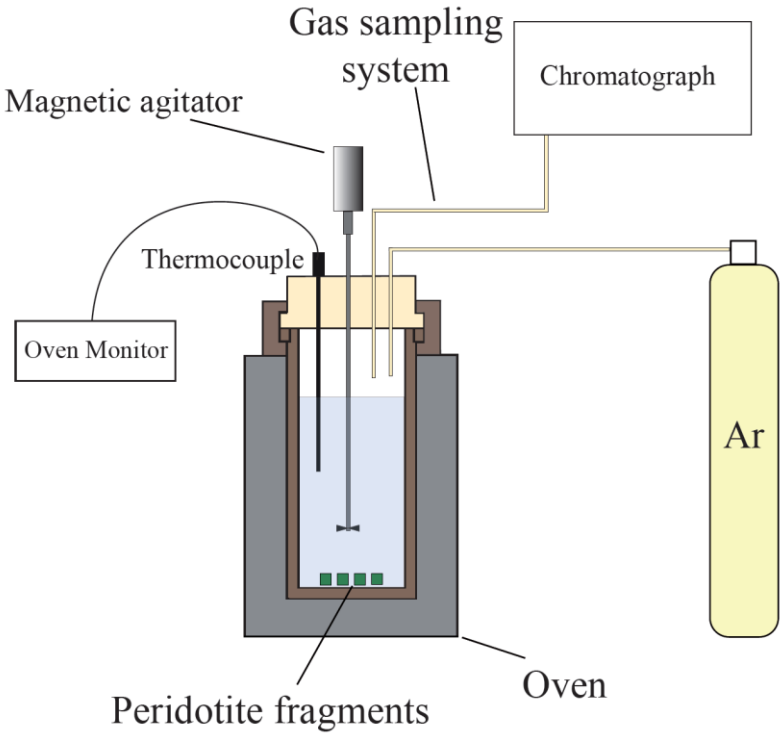


Figure C1: Diagram representing the high volume autoclave used in this study.

The experiments were conducted with 15*15*15 mm rock cubes cut in the freshest part of the rock. Six experiments were realized at 300°C and 300 bar for different time durations with two rock fragments placed in a 0.25 L hastelloy PARR autoclave with 200 mL distilled water (Fig. C1). The setting pressure, measured with a pressure gauge, was adjusted at the beginning of the experiment by pumping neutral gas (Argon) into the autoclave. The temperature was measured with two thermocouples located at the top and at 4 cm above the bottom of the autoclave. The setting temperature of liquid was controlled to $\pm$ 1°C by a thermocouple located 4 cm above the bottom of the autoclave. The cumulative uncertainties on pressure and temperature are ~5 °C and ~15 bar, respectively. In order to quantify the rate of serpentinization, six runs were made for 15, 29, 36, 43, 48 and 84 days. At the end of the experiment, the autoclave was cooled at ambient temperature in

half an hour, the rock fragment were collected and dried in a sterilizer at 50°C for two hours, and impregnated with epoxy. The fragments were then cut in two pieces and 80 μm-thin sections were prepared.

3. Experimental Results

Optical miscroscopy - The colour of the sample surfaces evolves from the greenish fresh peridotite for the short time experiments to red-brownish after 84 days of alteration (Fig. C2).

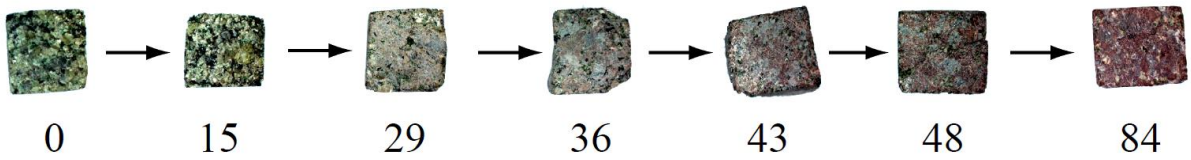


Figure C2: Picture displaying the evolution of the surface colour as a function of the alteration degree, from fresh peridotite (left) to the most altered sample (right). The duration of the experiment is indicated in days below each fragment.

Similar variations of colour were observed from the core (green) to rim (brown) of the fragment after 84 days (Fig. C3a). Thin veins of serpentine were observed to develop at the grain boundaries (Fig. C3b) of all fragments for run durations longer than 15 days. These veins have an isotropic aspect with homogeneous brown colour in natural light and black colour in cross-polarized light, and they contain aggregates of black oxides grains (Fig. C3b) at their walls. These features are similar to those of the early V1 veins defined by Andreani et al. (2007) in natural rocks. The veins do not exceed 80 μm in thickness and they are often empty in their centre. In that case, the serpentine may present undulated/folded structures, which possibly results from the shearing of olivine grains during serpentine growth (Fig. C4).

The intergranular network of serpentine veins with a brownish color compared to the fresh olivine and pyroxens was contoured from digitalized optical micrograph of the thin sections prepared from the rock fragments of the > 36 days experiments (Fig. C3c). For the shorter time duration experiments, the low degree of serpentinization does not allow one to quantify the network with enough precision. Four depths of penetration of the serpentine veins were then measured from each border toward the center of the rock cubes (see black arrows on Fig. C3d: x1, x2, x3, and x4) and an average "alteration width" was estimated.

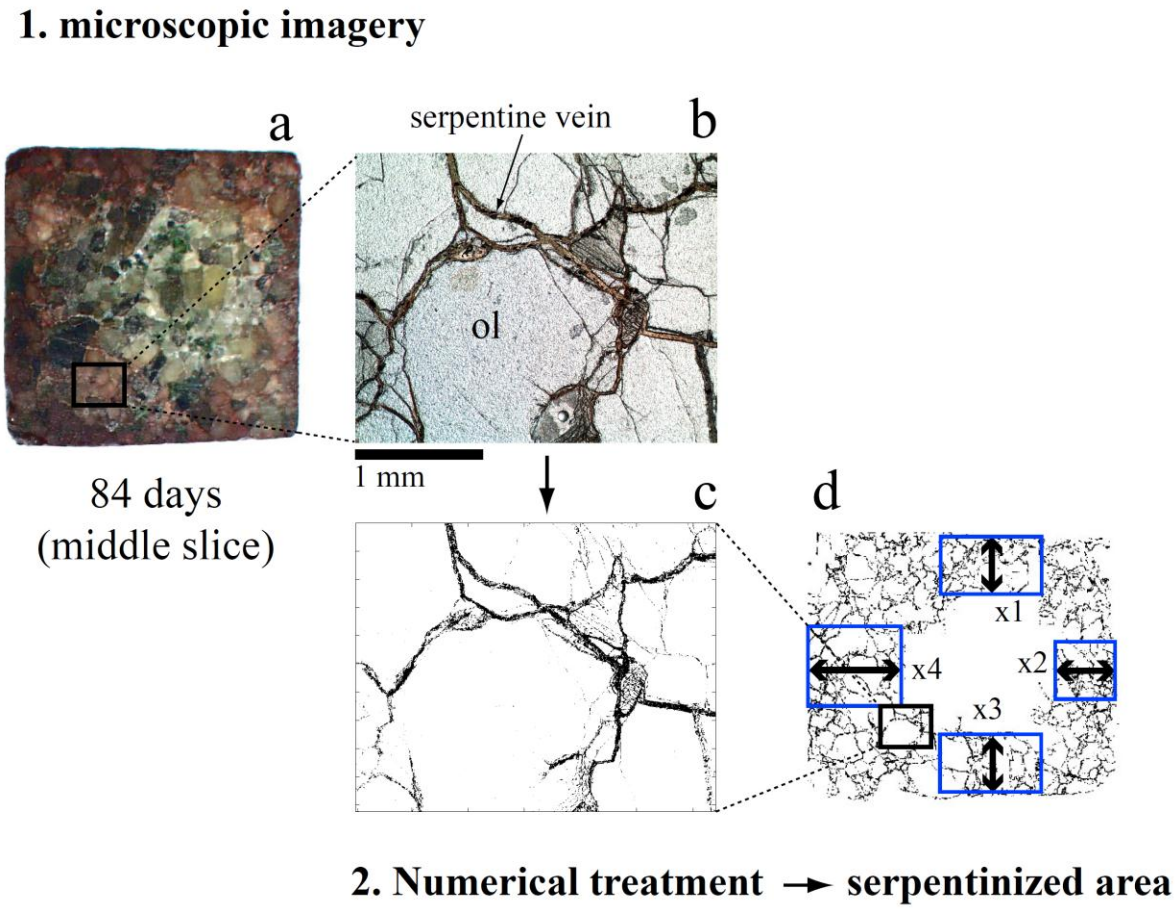
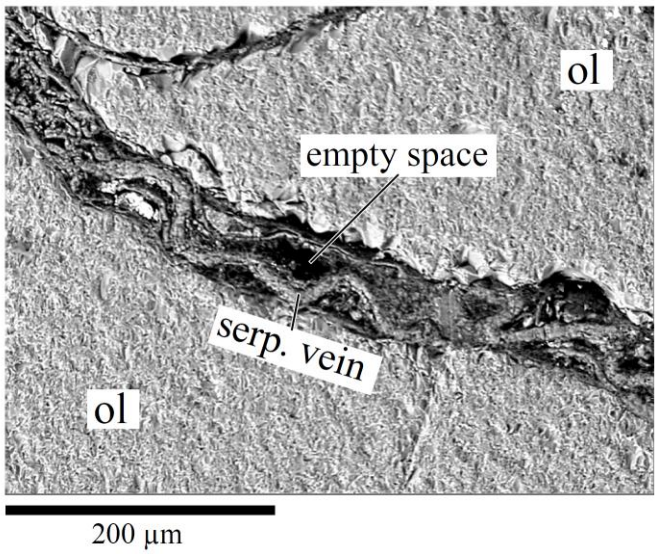


Figure C3: (a) Section of the sample altered during 84 days. Borders appear as brown in agreement with the crystallization of serpentine. (b) Microscope image obtained in LPnA on the altered part of the sample, displaying the serpentine network at grain joints. (c) Numerical treatment permitting to extract the pixel corresponding to serpentine. (d) Measured of the front progress (x1, x2, x3, and x4) and the area serpentinized (blue boxes) for the altered sample.



The serpentinized area comprised between the outer rim of the fragments and the inner position of the veining front was determined in four areas located at the edges of the fragments (see blue rectangles on Fig. C3d).

Figure C4: A folded vein of serpentine stucked between two olivine grains, seen in back scattering electron microscopy.

The abundance of serpentine from the rim to the centre of the fragments was estimated from the number of serpentine pixels in the rectangle AB shown in Fig. C5a.

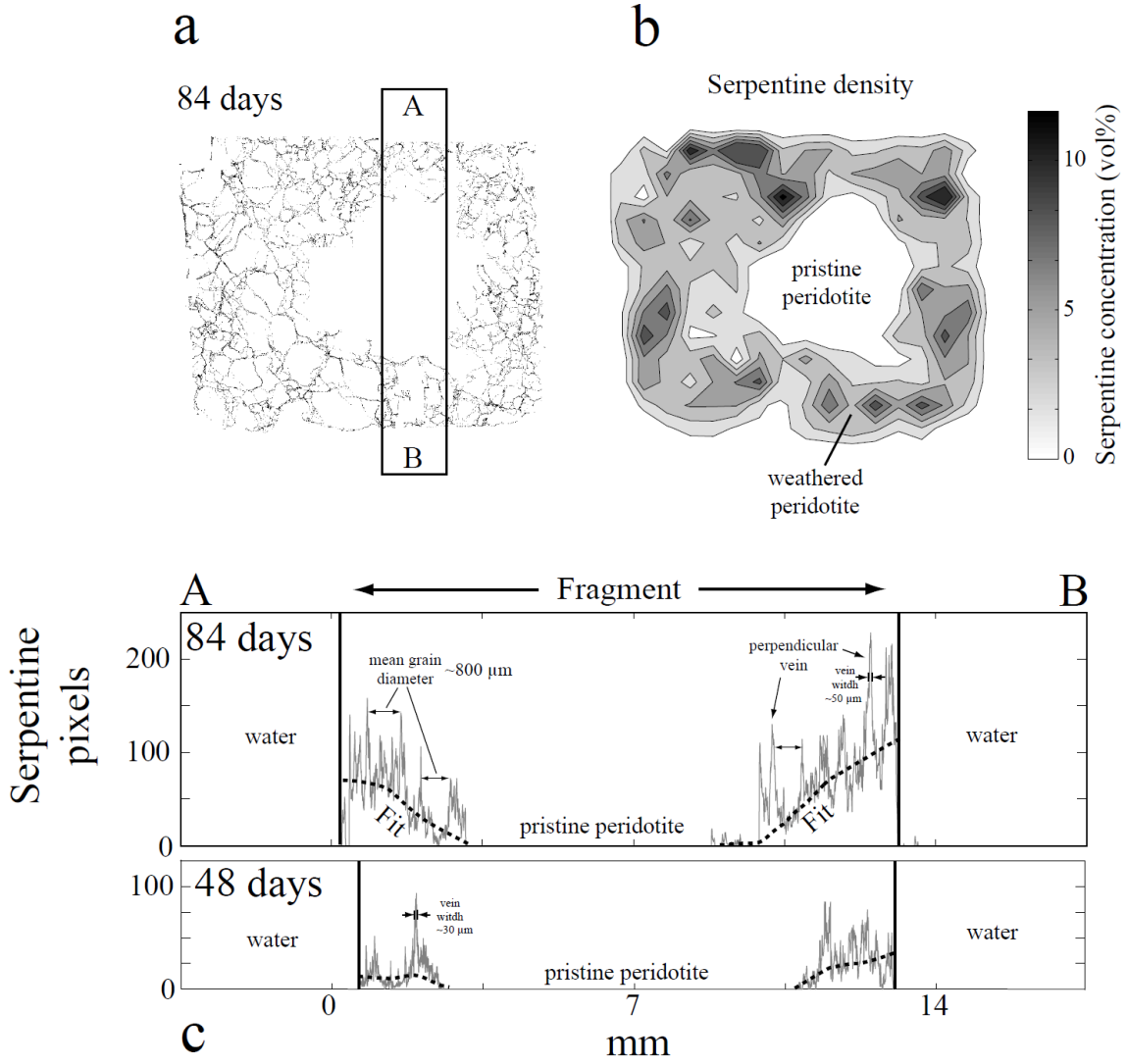


Figure C5: (a) Serpentinized network in the most altered sample. AB corresponds to the profile displayed below (c). (b) Serpentine density map showing permitting to identify the vein distribution. (c) Profiles, in number of pixel, obtained on the 84 and 48 days samples. The dotted line represents a 50% weigthed fit.

The percentage of serpentine was numerically calculated and represents the ratio between the number of pixels corresponding to serpentine and the full number of pixel in the rectangle. Results are shown for the 48 and 84 days experiments in Fig. C5c. The sharp peaks correspond to the veins at the grain boundaries oriented perpendicularly to the profile, which have an average width of about 50 µm. The distance between the main peaks corresponds to the diameter of the initial olivine and pyroxene (~800µm). This distance does not seem to change significantly along the profile, which indicates the lack of grain fracturing and the restriction of serpentine veins at the grain boundaries. To better visualise the evolution of the serpentine amount, the concentration profiles were fitted by

weighted functions (bold dotted curves). The fits indicate a main concentration trend which globally decreases toward the unaltered core, in agreement with the numerical simulations performed by Rudge et al. (2010). Both the serpentine concentration and width of the alteration front increase from the 48 to 84 days. As the density of the vein network does not increase as a function of time (no fracturing), the increase of the serpentine amount is balanced by the widening of the veins (from ~30 μm at 48 days to ~50 μm at 84 days).

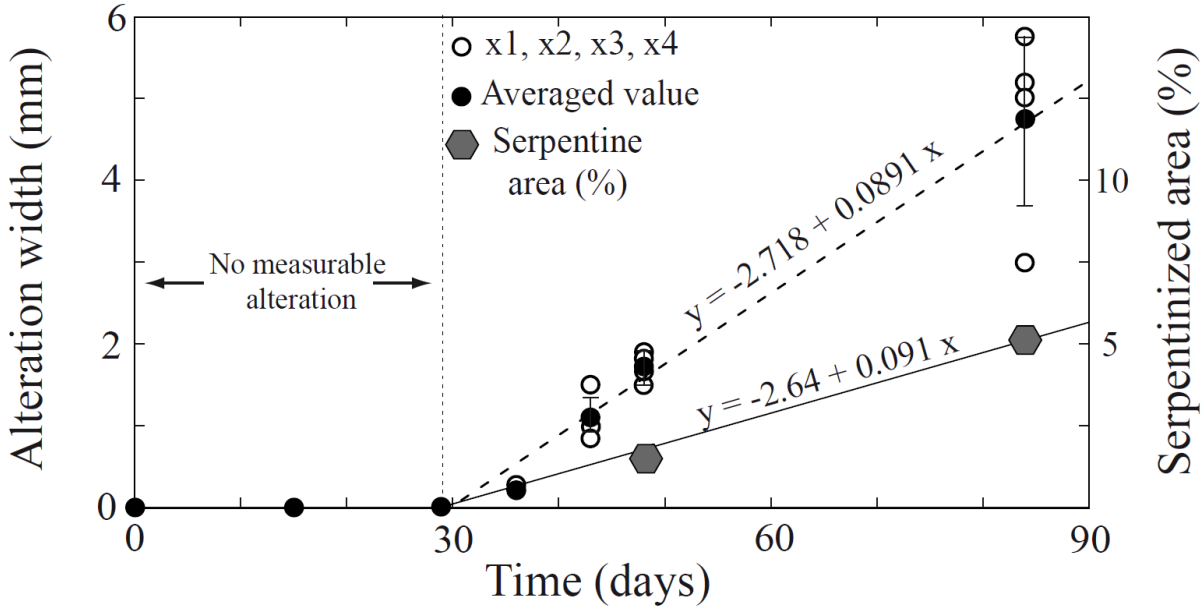


Figure C6: Diagram displaying the front width (full and empty circles) and the serpentine area (gray diamonds) calculated in blue boxes, as a function of the alteration time.

After a first period (0-30 days) during which the veins do not penetrate into the compacted rock, the width of the alteration front (aw) increased linearly as a function of time (black full circles in Fig. C6) and reaches almost 6mm-depth after 84 days:

$$aw(t) = -2.718 + 0.0891 \cdot t \quad (R^2 = 0.9938) \qquad \text{(Eq. C1)}$$

where t is the run time duration in day. This relation predicts that the vein propagation in peridotite at 300°C and 300 bars is about 3.8 cm.year^{-1}. The serpentinized area in the boxes displayed in Fig. C3d also increased linearly with time, and reached 5.036 ± 0.5 % for the 84 days sample:

$$sa(t) = -2.78 + 0.0926 \times t \quad (R^2 = 0.997) \qquad \text{(Eq. C2)}$$

The relation (2) predicts that after 100 days, 6.5% of the rock surface is occupied by serpentine. Considering that the water/rock interface is a fault plan, the relative volume of serpentine in the altered edge of the rock fragment equals the relative surface measured in 2D (see sketch in Fig. C7).

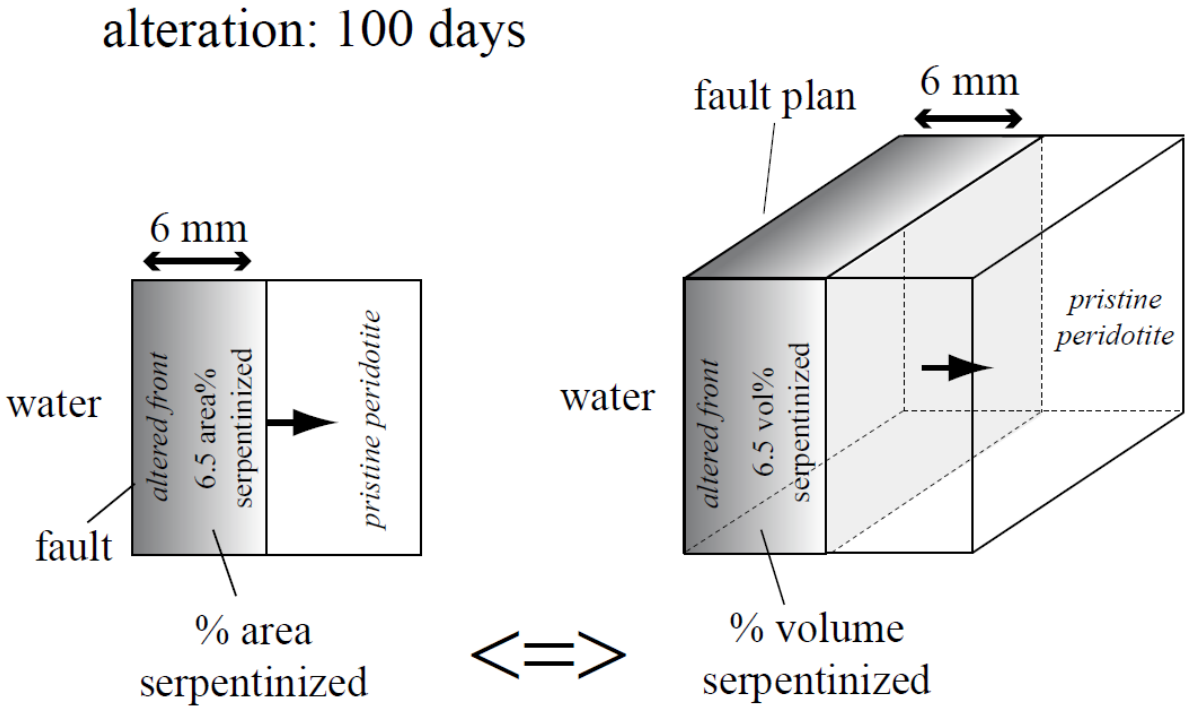


Figure C7: Sketch representing the serpentinized front in a 2D plan and 3D block diagram. The percentage of serpentinized volume is equal to the percentage of serpentinized area.

The molar volume of serpentine (five anhydrous oxygen basis) and olivine (four oxygen basis) are 44 and 53 $cm^3.mol^{-1}$, respectively. Assuming that the fresh sample was made of 100% olivine, the amount of serpentine after 100 days predicted by (2) is limited to about 5 mol%. After 100 days experiments at the same P-T conditions but using a 1 µm grain size powder of lherzolite, Marcaillou et al. (2011) showed that more than 60 mol% of the initial olivine was replaced by serpentine. The same extend of reaction is predicted by the kinetic law of Rudge et al. (2010) for a water/rock ratio, temperature conditions and a grain size similar to those of Marcaillou et al. (2011, and submitted) experiments. The amount of serpentine calculated with the kinetic law of Rudge et al. (2010) for the average 800 µm grain size used in the present experiments is lower (1.8 mol%) than the value determined experimentally (5 mol%). The amount of serpentine calculated as a function of time with the size-dependant kinetic model of Rudge et al. (2010) is compared to that obtained with Eq. 2 in Fig. C8 (see appendix B).

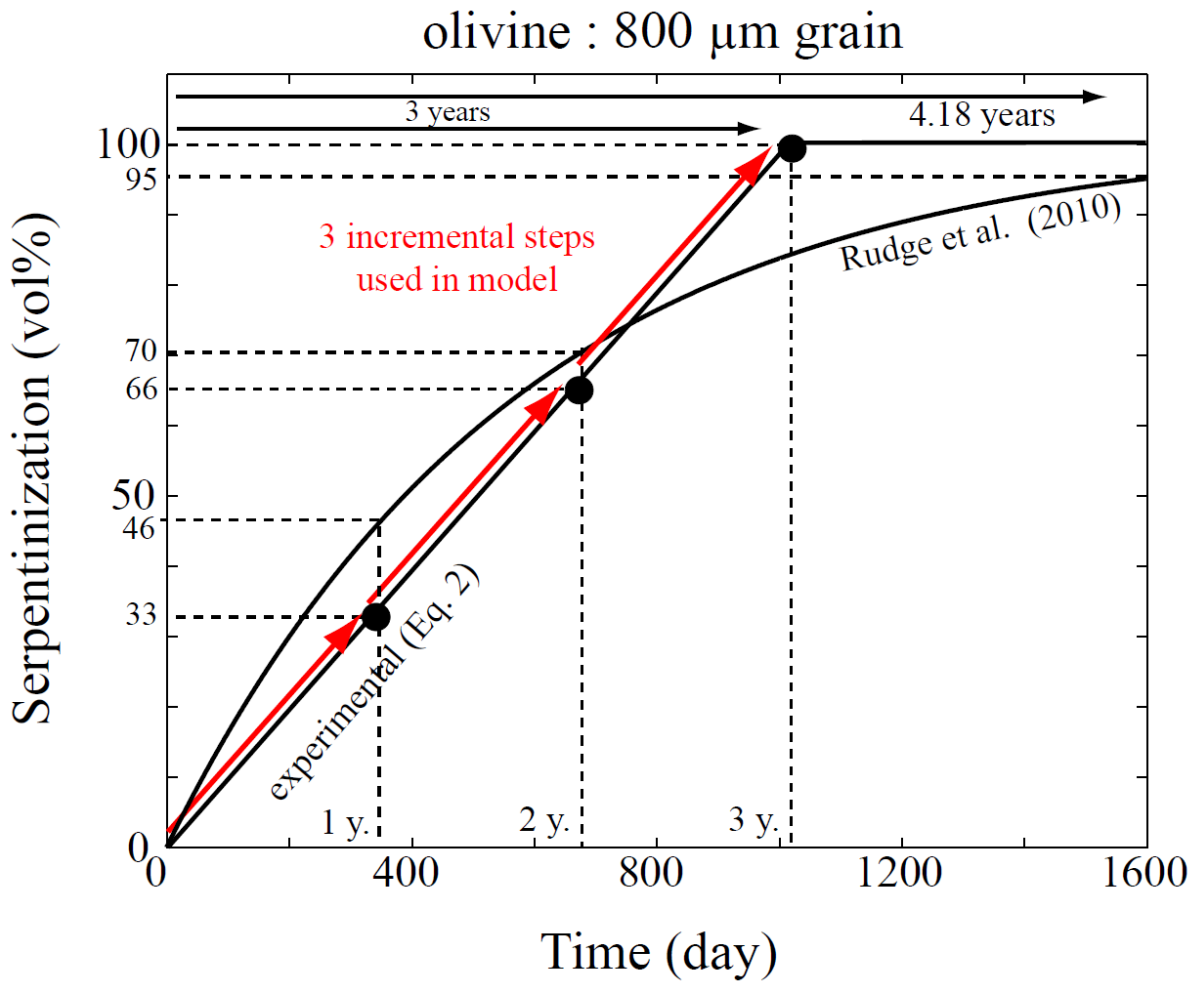


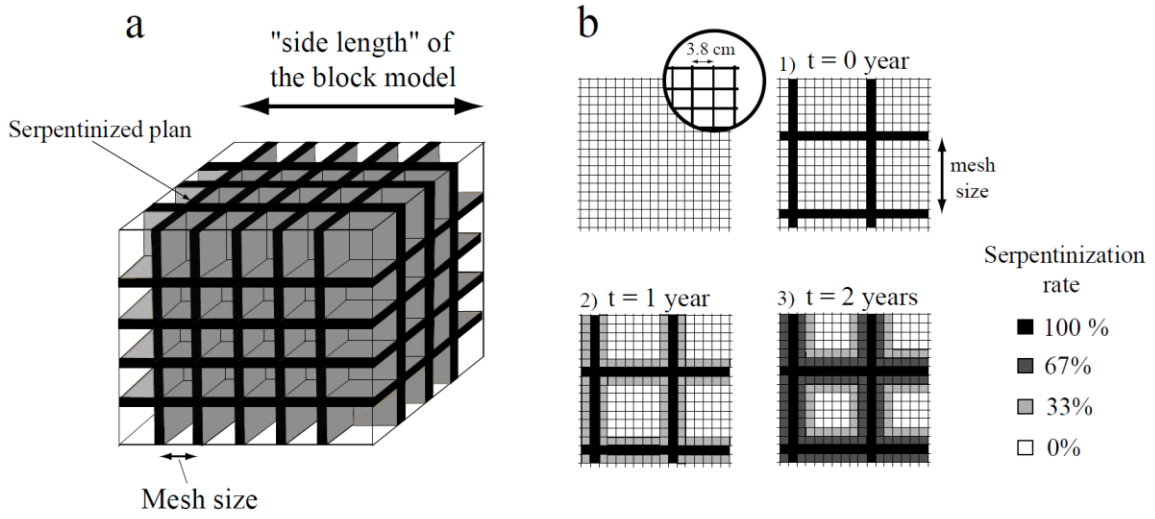
Figure C8: Numerical alteration of a 800 µm-size olivine grain using the relation defined by Rudge et al. (2010) (curve), and our experimental data (dotted line). For convenience, we used the linear trend defined in Eq. 2 with our experimental data.

The time required to serpentinize a 800 µm diameter olivine grain at 95 mol% is quite similar in both cases (4.18 years or 2.9 years). Serpentinization of natural olivine is therefore a very fast process, and the kinetic parameters derived from the experiments (Eq. C1 and C2) can be used to estimate the time required to serpentinize peridotite rocks in natural settings, which is the scope of the following section.

4. Modeling

Two numerical models were carried out in order to constrain the geometries and the size of the hydrothermal network of the natural hydrothermal site Rainbow. The two kinetic parameters derived from the experimental data (equations C1 and C2) at a micrometric scale were implemented in a metric or kilometric scale model and the amount of serpentine as well as the amount of hydrogen produced during the aqueous alteration of peridotite were estimated and compared with the present day flux of hydrogen measured at the hydrothermal vents of Rainbow (see appendix A). This flux of hydrogen measured at an interval of 10 years is constant (Charlou et al., 2002 ; Schmidt et al., 2007). Assuming that the flux of hydrogen at Rainbow is constant over longer periods, the volume of serpentine generated in hydrothermal network should increases linearly with time. The Rainbow site has been dated to be about 10,000 years old using the ^{230}Th/U measurement performed on the massive sulfide deposits collected around the active vents (Kuznetsov et al., 2006). The volume of serpentine produced during this period of 10000 years is $1.7.10^9$ m^3, (see figure CA in appendix A).

Estimation of the variation of the fracturation network with time at constant volume of peridotite: Model I – In the first simulation, the volume of serpentine produced over 10000 years, assuming that the present day flux of hydrogen is constant over time ($1.7.10^9$ m^3) was represented as a cube of 1200 m side-length a cubic volume (1200 m side length). This volume of initialy of fresh peridotite was assumed to be cut by a cubic mesh of fractures through which water can freely circulate (see Fig. C9a). The volume of serpentine generated with time was calculated for a variable averaging spacing between fractures.
The starting cube of pristine peridotite was discretized into elementary cubic volumes (called "voxels" in the following) having a side-length of 3.8 cm, which corresponds to the propagation distance of the serpentinization from the fractures toward the fresh peridotite in one year (Eq. C1). The serpentinization front moves thus at a rate of 1 voxel/year (see sketches in Fig. C9b). The amount of serpentine generated with time in the altered zone (in the voxels located at the moving serpentinization front) was assumed to by 33 vol% each year, as determined experimentally (see Eq. C2, and Figure C8). This increase of serpentine occurs thus in the three pixels that separate the fresh (white voxels in Fig. C9b,c) from the completely serpentinized peridotite (black voxels in Fig. C9b,c). The error introduced by neglecting the variation of grain size with time (use of Eq. C1) is depicted on Fig. C9c, which shows a snap shot of the modelled progress of serpentinization at 10 years. The calculation was made using either Eq. C2 (left) or the grain size dependant kinetic law of Rudge et al. (2010) (Fig. C9c right).



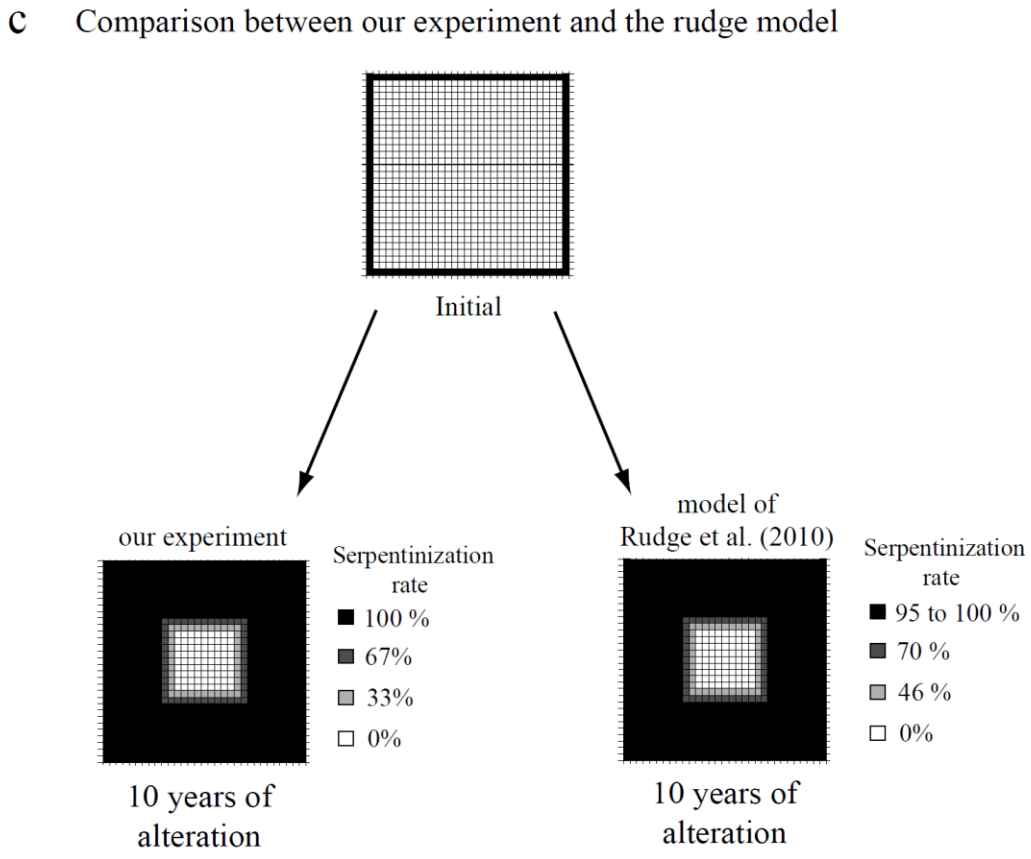


Figure C9: (a) Geometry of the first numerical model. Black plans correspond to the faults from which the altered front starts to move. (b) 2D-sketches representing the speed of the serpentinization front (1 pixel per increment) and the evolution of the serpentine concentration on each pixel (pixel color), as a function of the incremental step. (c) This figure shows the low differences between our model and the alteration inferred with the relation of Rudge et al. (2010).

The zone partially serpentinized obtained with the Rudge et al. (2010) equation is close to the linear trend, and the integrated volumes of serpentine calculated with both kinetic equations are therefore quite similar. As already discussed above, this comparison indicates that the error introduced by neglecting the influence of the grain-size variation onto the rate of serpentinzation (Eq. C2) is not significant at geological time and spatial scales. For reason of simplicity and to reduce the calculation time, Eq. (C2) was thus used in the following large-scale and –time modelling.

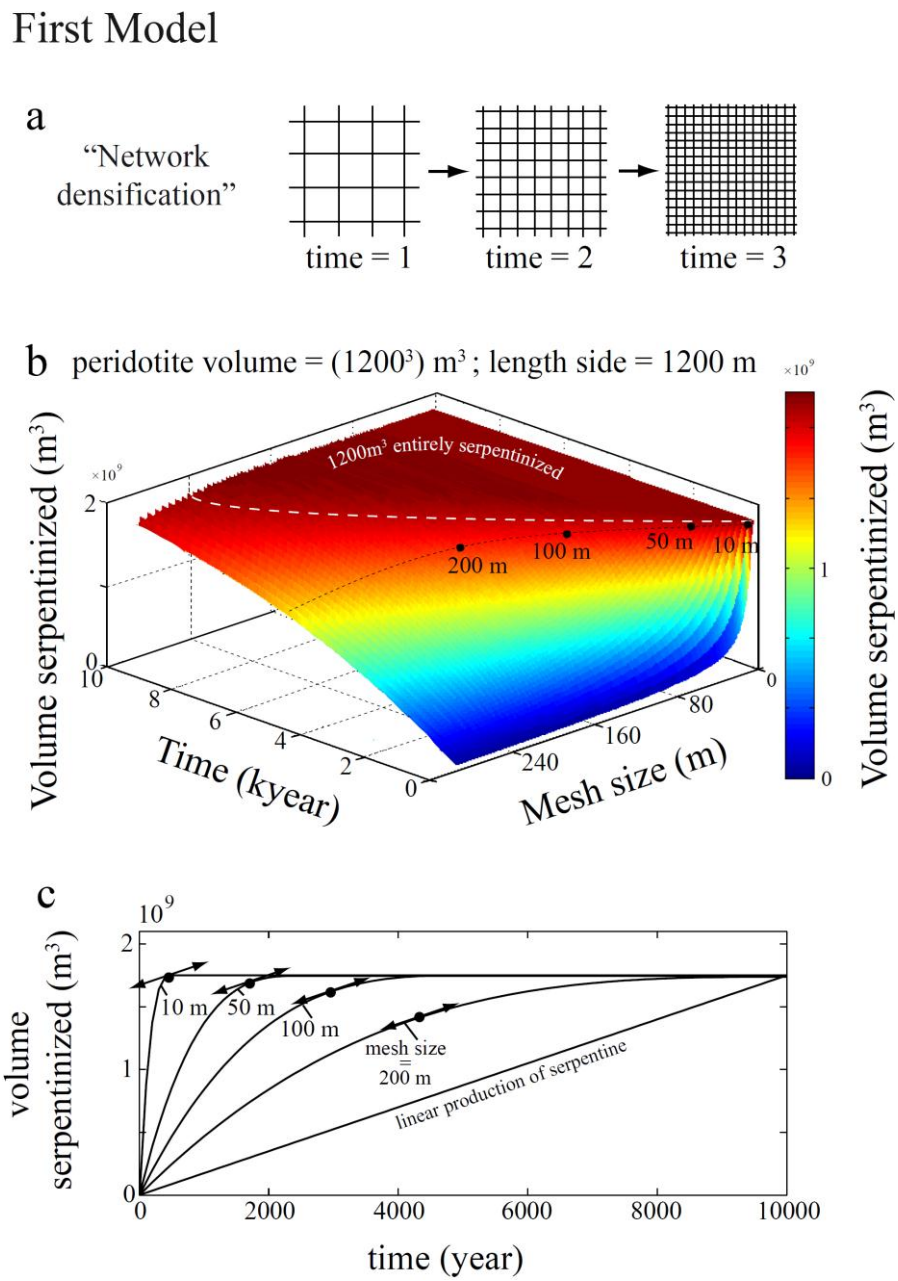


Figure C10: (a) Sketch representing the evolution of the hydrothermal network proposed in the first model. (b) 3D-diagram displaying the results as a colored surface corresponding to the serpentinized volume, calculated as a function of the time and the fault spacing. The curves represent the evolution of the volume inferred in Rainbow and Logatchev, and permit to define the fault spacing evolution with time.(c) Volume serpentinized as a function of time for different mesh size.

The evolution of the volume of serpentine with time for variable spacing between the faults ("mesh size") is depicted by the coloured surface in Fig. C10b, and the evolution at fixed mesh sizes (sections of the block diagram, Fig. C10) are shown in Fig. C10c. Whatever the mesh size considered, Fig. C10b,c shows that the rate of serpentinization decreases with time, which is due to the reduction of the surface of the serpentinization front (see e.g. Fig. C9c). The integrated surface of the serpentinization front is also proportional to the density of fractures, so that the time required to completely achieving serpentinization of the intial volume of fresh peridotite increases with the mesh size. Complete serpentinization is achieved after 9 000 and 200 years for initial mesh sizes of 240 and 10 m, respectively (Fig. C10b). Assuming that all the hydrogen produced during serpentinization is expelled at the hydrothermal vents, the outgoing flux of hydrogen is proportional to the time-derivative of serpentine production. The value of the flux of hydrogen deduced from present-day measurements (see Appendix A) is shown by the double arrows and by the black dashed line in Fig. C10b. For a constant mesh size of 240 m, this flux is calculated to decrease with time from $11.89.10^7$ mol/year at 2000 years to 0 at 10000 years. The present-day flux of hydrogen is obtained after 400 to 4300 years for mesh sizes ranging from 10 to 200 m. It can be also seen in Fig. C9 that the time required to serpentinize the considered initial volume of peridotite decreases rapidly with decreasing the mesh size. Lister et al. (1980) have shown that the establishment of hydrothermal circulation in the oceanic crust requires a dense fault network (fault spacing between 1 and 10 meters). According to Fig. C10, complete serpentinization of the 1200^3 m^3 initial volume of peridotite is achieved within 200 years, which is clearly unrealistic. It is therefore concluded from this first simulation that either 1) the rate or serpentinization at 300°C derived from the experimental data is greater than that in natural setting, 2) the temperature at which serpentinization occurs at Rainbow is either lower than 200°C or higher than 400°C; Marcaillou et al. (submitted) showed that at such conditions, the rate of serpentinization was significantly lower than at 300°C (temperature at which the Fig. C9 was computed), 3) the volume of peridotite affected by the hydrothermal network is not constant with time. The next simulation was aimed at studying this last possibility.

Estimation of the variation with time of the altered peridotite volume at constant fracturation network: Model II – The possible spatial expansion of the hydrothermal network with time was considered in a second simulation, which was conducted assuming 1) a constant fault spacing of 1 m and an infinite volume of fresh peridotite through which the hydrothermal network can freely spread, and 2) a constant rate of hydrogen production and therefore a linear increase of the total volume (V1) of serpentine generated with time (curve 4 in Fig. C11a).

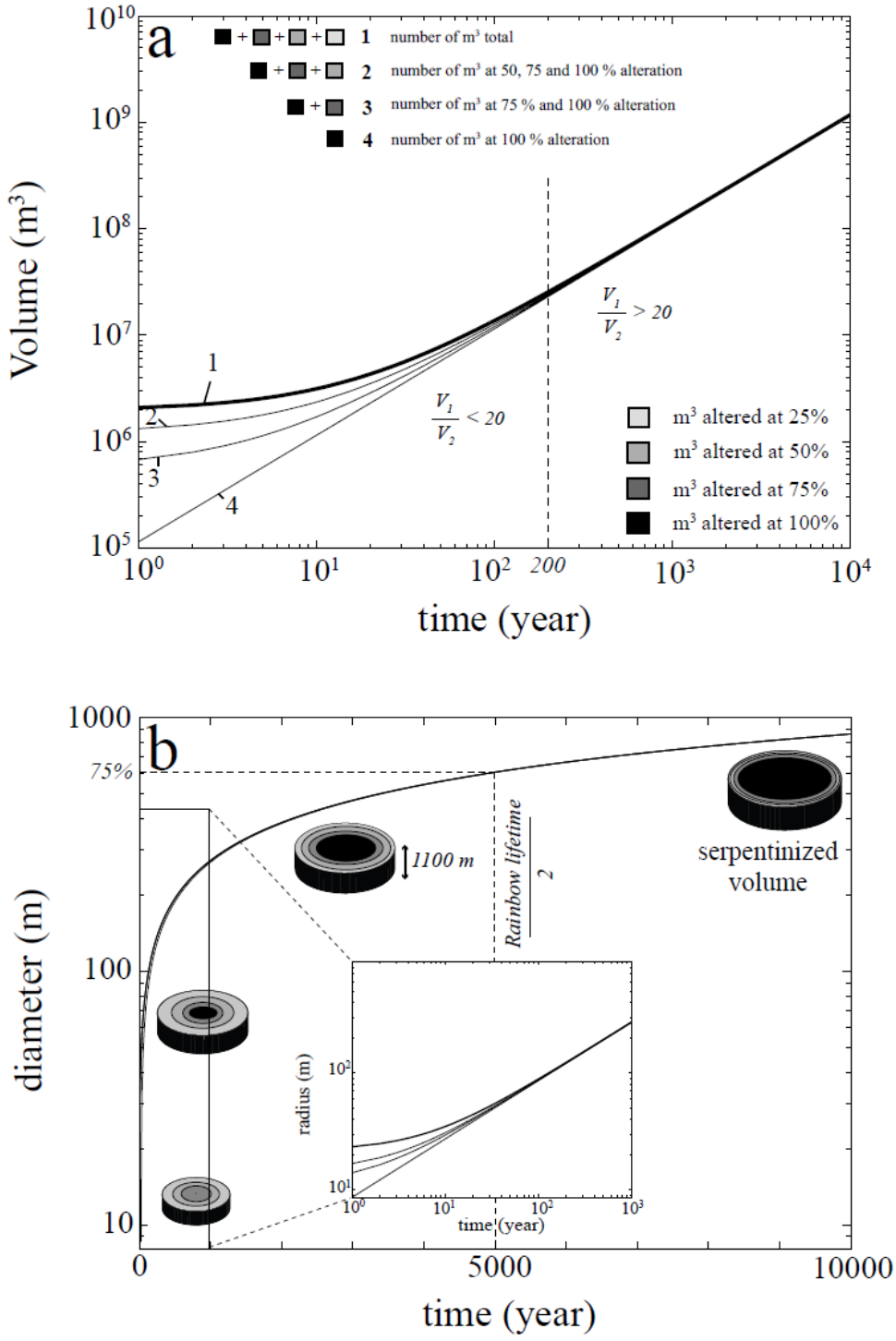


Figure C11: (a) Evolution of the hydrothermal network volume in 10 years. The bold curve corresponds to the sum of the entirely (V_1) and partially altered (V_2) volume. V_2 correspond to the number of m^3 being altered, at each moment, to ensure the linear production of hydrogen measured on active vents. (b) Radius, corresponding to a hydrothermal network having a cylindrical shape with a height of 600 m, plotted as a function of time (see text for explanations). The schematic cylinders symbolize the hydrothermal network in which the color represents the different alteration degree layers.

The rate of hydrogen production estimated from the present-day measurement of the flux of hydrogen expelled from the vents (Appendix A) is calculated to result from the progressive serpentinization of a constant volume of peridotite of $2.19.10^6$ m^3 at the front of the expanding serpentine body. This volume of partially serpentinized peridotite (V_2) was arbitrary split into three equal volumes containing 25 vol%, 50 vol%, and 75 vol% serpentine (see gray boxes on Figure C11a). The ratio V_1 /V_2 increases as a function of time (see the curves convergence in Fig. C11a) and after 200 years of alteration, V_2 represents only 1/20 of the volume entirely serpentinized (V_1). Additional assumptions were necessary to constrain the lateral size and shape of the hydrothermal network. Both experimental (Martin and Fyfe, 1970 ; Marcaillou et al., 2011) and numerical (McCollom et al., 2009 ; Rudge et al., 2010) studies have shown that the rate of serpentinization drop rapidely at temperature below 200°C and above 400°C. Considering an average crustal thickness of 4 km in the slow mid-ocean ridge (Minshull et al., 2006; Muller et al., 1999 ; Escartin and Cannat, 1999), and a basal temperature of 1300°C, the average vertical thermal gradient is about 330°C.km^{-1}. The 200-400°C zone were serpentinization is the most effective has therefore a thickness limited to 1100 m and is located at about 2 km depth (between 700 and 1300m). Assuming that serpentinsation is restricted to this level, and neglecting the advective-convective transport of heat by the hydrothermal circulation, the radial expansion of the serpentinization front leads to the formation of a cylindrical serpentinite body of radius evolving with time as shown in Fig. C11b. The diameter increases strongly from 0 to 400 m during the first 1000 years, and moderately aftwards. Calculation shows that the radius of the cylinder has reached 70% (620m) of this final size in 5000 years, the half-life time of Rainbow. After 10000 years of alteration, the hydrothermal network has a diameter close to 900 m, and the width of the partially altered volume (V_2), is less than 1 meter at the end of the simulation. The uncertainties associated with this value are certainly large, although difficult to estimate accurately. However, the calculated lateral extension of the hydrothermal network is in the range of that corresponding to the area covered by the smokers on the oceanic floor. It is therefore expected that the kinetic parameters constrained experimentally from short time duration experiments with a larger availability of water than in natural settings are not strongly overestimated.

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Conclusions

The experimental data obtained with starting fragments of peridotite provide, for the first time, a quantitative information about the rate of serpentinization of fresh compact peridotite under natural P-T conditions. The experimental data show that the serpentinization of compacted peridotite at 300°C, 300 bar is 12 times lower than that of powdered peridotite. From 30 to 84 days run duration with the rock fragments, the serpentinization front was found to propagate at a constant velocity of 4 cm.year^{-1}. This value is higher than the average spreading rate of low-spread mid-ocean ridges (~2 cm.year^{-1}). The hydrothermal alteration of natural peridotite is thus fast enough to serpentinize completely the volumes of ultramafic rocks generated at mid-ocean ridges.

The experimental data were used to constrain not only the velocity at which the serpentinization propagates, but also the volume of serpentine generated with time. These two parameters were used to model the evolution of the hydrothermal network volume in natural settings. The results suggest that the size of the hydrothermal network should increase with time. Neglecting the advective-convective transport of heat, and assuming that the propagation of the serpentinization front is not limited by the availability of water, the hydrothermal network at the Rainbow field is estimated to have a cylindrical shape with a 1100m vertical axis and a minimum diameter of about 1 km (see Fig. C12).

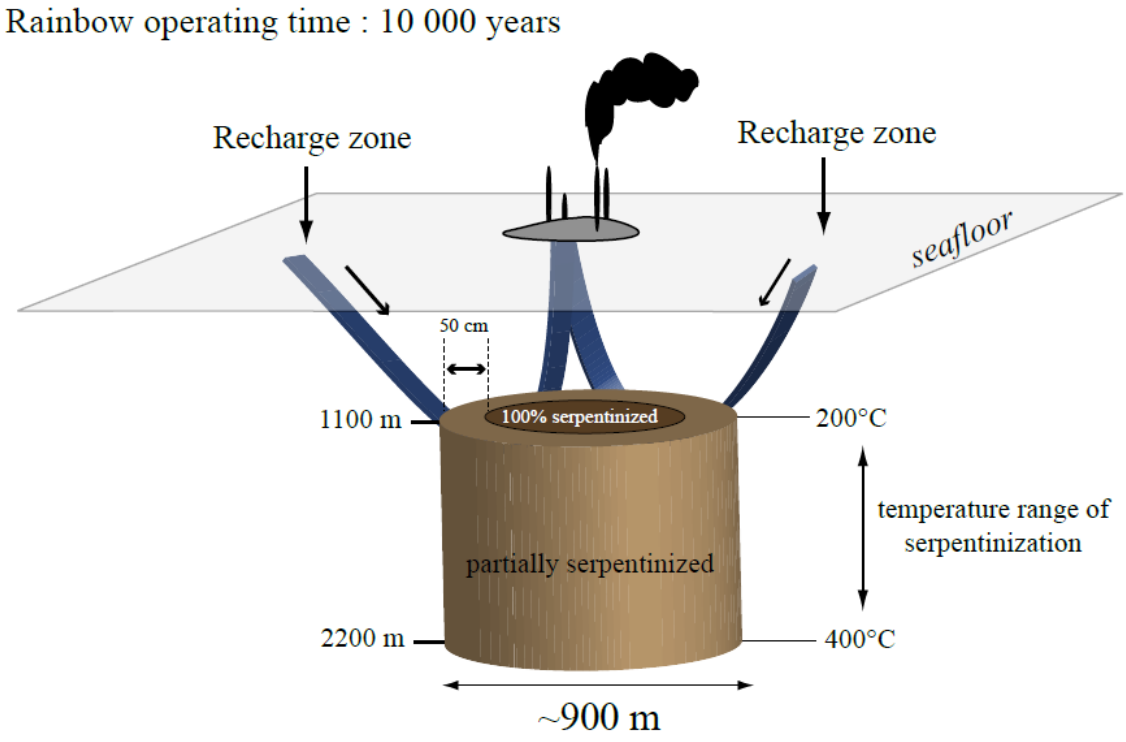

Figure C12: 3D-schema representing the Rainbow hydrothermal field nowadays. The network is represented as a green cylinder having a diameter of 1.8 km.

This calculation is constrained by the present day flux of hydrogen measured at the hydrothermal vents, and assuming a vertical temperature gradient of 175°C.km^{-1}. More work is also clearly needed to build more realistic models that consider the possible limitation of serpentinization by the availability of water, the volume expansion due to the formation of serpentinite, and the transport of heat associated with the fluid circulation, and the presence of structural discontinuties. However, an important conclusion of the present study is that the rate of serpentinization in nature is probably of the same order of magnitude as that derived from the experiments. This suggests that the availability of water is not the most important controlling parameter of serpentinization in nature.

Appendix A: Production of hydrogen in natural hydrothermal fields.

The experiment results of Marcaillou et al. (2011) showed that one mole of H_2 is produced during the alteration of ~0.003 m^3 fresh peridotite at 300°C and 300 bar. The volume of serpentine generated with time during the aqueous alteration of peridotite in natural settings can be calculated from the hydrogen discharge measured on Rainbow. This flux (in mol/s) is calculated as :

$$H_2(t) = N_{as} \cdot V_f \cdot \pi \cdot R^2 \cdot C_{H2} \quad (1)$$

where N_{as} is the number of active smokers on the hydrothermal site, V_f is the fluid velocity in $m.s^{-1}$, R is the radius of vent, and C_{H2} is the concentration of hydrogen in $mol.m^{-3}$. At Rainbow, ten major vents (N =10) release hot water with uniform and constant composition (Charlou et al., 2002; Marques et al., 2006). The measured concentrations of H_2 are close to 16 $mmol.L^{-1}$, the fluid velocity (V) is about 1.5 ± 0.5 $m.s^{-1}$ (Charlou, pers. com.) and the diameter of the vents is assumed to be 10 cm (R = 0.05m). The evolution of the serpentine volume with time is presented in the following Fig. CA.

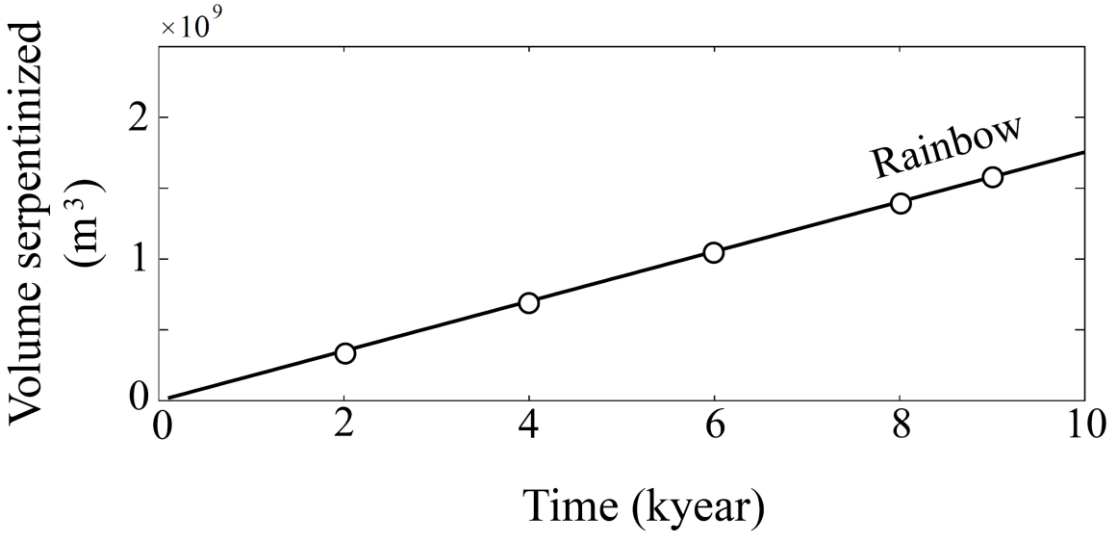

Figure CA: Linear evolution of the volume serpentinized with time

Appendix B: Size-dependant kinetic model for the olivine dissolution (see Fig. C8)

To constrain the serpentinization rate of a spherical grain of olivine, a first order-kinetic reaction was inferred. Considering the olivine dissolution as following:

$$1.5 \text{ olivine} + H_2O \leftrightarrow 1 \text{ serpentine} \quad (1)$$

the corresponding rate of reaction (*r*) is defined by the evolution of the olivine concentration with time:

$$r = \frac{-d(olivine)}{dt} = k[olivine] \quad (2)$$

where *olivine* is the olivine concentration in mol%, *t* is the time, and *k* is the rate constant. The integrated first-order rate law is:

$$\ln (\text{olivine}) = -k.t \text{ Û olivine} = \exp(-k.t) \quad (3)$$

An incremental step model was used to determine the alteration rate, and thus the evolution of the serpentine concentration during the alteration of a spherical grain of olivine having a diameter of 800 μm. For that, the concentration of olivine was estimated using the rate constant defined by Rudge et al. (2010), and defined as follow:

$$k = k_0 . \left(\frac{a_0}{a} \right)^2 \exp\left(-\alpha (T - T_0)^2 \right) \quad (4)$$

where $k_0 = 10^{-6}$ s^{-1}, a_0/a reflects the scaling due to the water/rock surface (with a_0 = 70 μm, and a is the grain size of olivine), a is a adjustable parameter equals to 2.09×10^{-4} °C^{-2}, T_0 = 260 °C is the temperature used in the Martin and Fyfe (1970), and T the experimental temperature (in °C). At each step of 1 day, the grain of olivine is partially altered and its size decreases. Therefore, the new diameter of the grain is defined in order to adjust the value of the rate constant *k*, which is function of the grain size (see Eq. 4) and consequently evolves during the alteration process. We obtained the following curve:

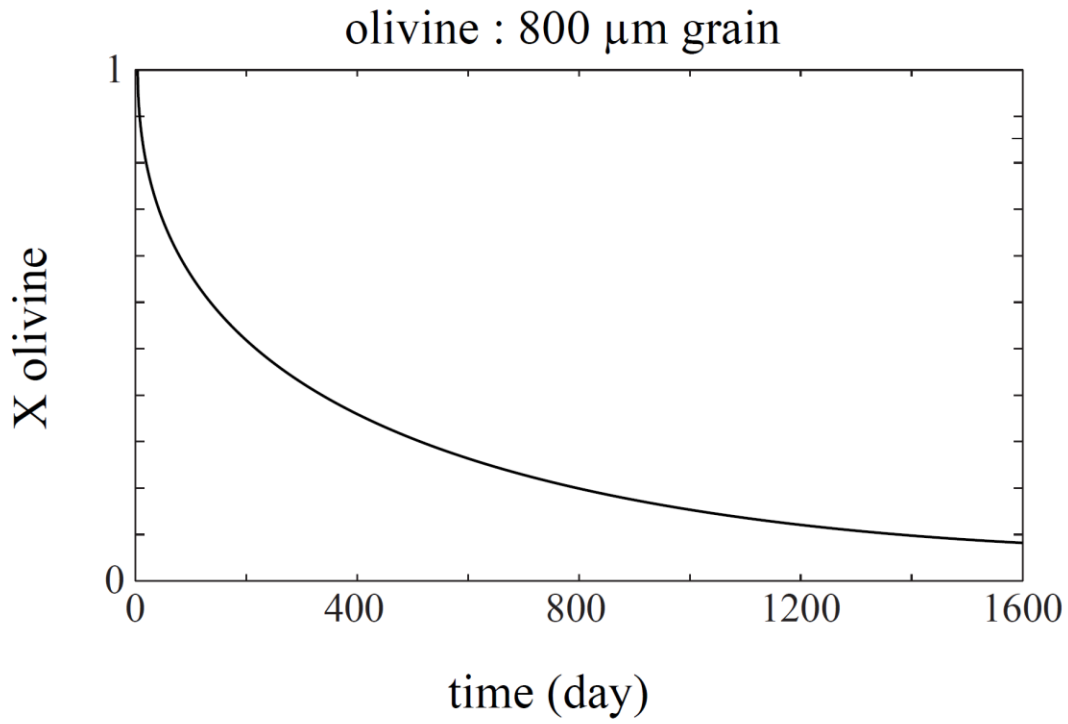

Figure CB: Evolution of the olivine molar fraction as a function of time.

Based on this resulting curve, the amount of olivine (in mol%) was firstly converted into serpentine using the stoichiometry inferred in equation 1. Finally, the mole number of serpentine was transformed into vol% using the molar volume (V_m) ratio between olivine and serpentine and equals to 1.2 (see equation below).

$$\frac{V_m(serp)}{V_m(ol)} = \frac{53}{44} \cong 1.2 \qquad (5)$$

Cet article présente la vitesse d'altération d'un fragment naturel de péridotite. Celle-ci est 12 fois inférieure aux vitesses calculées sur la même roche sous forme de poudre. Les données expérimentales montrent que la progression du front de serpentinisation ainsi que pourcentage de volume serpentinisé augmente linéairement avec le temps. Ces paramètres cinétiques nous permettent d'infirmer la possibilité d'une densification progressive d'un réseau hydrothermal de taille fixe alors qu'ils défendent plutôt l'extension d'un réseau ayant une densité de fracture constante au cours du temps. Il résulte que le réseau hydrothermal de Rainbow constitue un cylindre de 1100 m d'épaisseur et d'environ 2 km de diamètre.