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# Dissolution-precipitation processes governing the carbonation and silicification of the serpentinite sole of the New Caledonia Ophiolite

Marc Ulrich<sup>1,2,#,\*</sup>, Manuel Muñoz<sup>2</sup>, Stéphane Guillot<sup>2</sup>, Michel Cathelineau<sup>1</sup>, Christian Picard<sup>3</sup>, Benoit Quesnel<sup>4</sup>, Philippe Boulvais<sup>4</sup>, Clément Couteau<sup>5</sup>.

<sup>1</sup> Laboratoire Géoressources, CNRS, UMR 7566, Université de Lorraine, France.

<sup>2</sup> Institut des Sciences de la Terre, CNRS, UMR 5275, Université de Grenoble 1, France.

<sup>3</sup> Laboratoire Chrono-environnement, UMR 6249, Université de Franche-Comté, France.

<sup>4</sup> Géosciences Rennes, CNRS, UMR 6118, Université de Rennes 1, France.

<sup>5</sup> Service géologique, Koniambo Nickel SAS, Nouvelle Calédonie.

# present location: IPGS-EOST, UMR 7516, Université de Strasbourg, France

\* corresponding author: [mulrich@unistra.fr](mailto:mulrich@unistra.fr)

## ABSTRACT

The weathering of mantle peridotite tectonically exposed to the atmosphere leads commonly to natural carbonation processes. Extensive cryptocrystalline magnesite veins and stock-work are widespread in the serpentinite sole of the New Caledonia ophiolite. Silica is systematically associated with magnesite. It is commonly admitted that Mg and Si are released during the laterization of overlying peridotites. Thus the occurrence of these veins is generally attributed to a *per descensum* mechanism that involves the infiltration of meteoric waters enriched in dissolved atmospheric CO<sub>2</sub>. In this study we investigate serpentinite carbonation processes, and related silicification, based on a detailed petrographic and crystal-chemical study of serpentinites. The relationships between serpentine and alteration products are described using an original method for the analysis of  $\mu$ -XRF images performed at the centimeter scale.

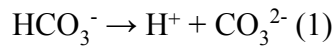
Our investigations highlight a carbonation mechanism, together with precipitation of amorphous silica and sepiolite, based on a dissolution-precipitation process. In contrast with the *per descensum* Mg/Si-enrichment model that is mainly concentrated in rock fractures, dissolution-precipitation process is much more pervasive. Thus, although the texture of rocks remains relatively preserved, this process extends more widely into the rock, and may represent a major part of total carbonation of the ophiolite.

*Keywords: Serpentine, magnesite, carbonation, silicification, New Caledonia ophiolite*

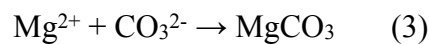
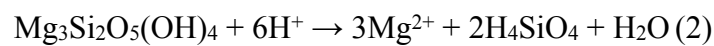
## 1 INTRODUCTION

2  
3 Carbon dioxide is currently one of the primary greenhouse gases having an impact on global  
4 warming. Therefore, numerous recent studies have focused on the potential of sequestration of CO<sub>2</sub>  
5 by mineral carbonation, either through *ex situ* (e.g. Bobicki *et al.*, 2011; Power *et al.*, 2011;  
6 Renforth *et al.*, 2011; Badlucan and Dlugogorski, 2013; Harrison *et al.*, 2013) or *in situ* processes  
7 (e.g. Cipolli *et al.*, 2004; Hansen *et al.*, 2005; Teir *et al.*, 2007; 2009; Andreani *et al.*, 2009; Rudge  
8 *et al.*, 2010; Kelemen *et al.*, 2011; Klein and Garrido, 2011). Among the various mineral species  
9 that may undergo carbonation reaction, Mg-bearing minerals (as well as Ca-carbonates) are of a  
10 great interest as they are very common at Earth surface and thus represent an important reservoir for  
11 CO<sub>2</sub>. In addition, magnesite (MgCO<sub>3</sub>) has a long term stability, contrarily to alkali carbonates,  
12 which are readily soluble in water (Lackner *et al.*, 1995). Basically, magnesite is formed by the  
13 reaction between a Mg-rich source and CO<sub>2</sub>-rich fluids (Bain, 1924) and can integrate variable  
14 amount of cations (mainly divalent, e.g. Ca and Fe) by substituting Mg in the crystal structure.  
15 Based on the study of numerous magnesite deposits, Abu-Jaber and Kimberley (1992b)  
16 distinguished vein-type and massive-type magnesite, the second type forming deeper than the  
17 former. Numerous other parameters play a role in magnesite formation, such as temperature, the  
18 origin of the components or the mechanisms of precipitation. The temperature of magnesite  
19 formation extends from ambient to ~400°C (Halls and Zhao, 1995; Wilson *et al.*, 2009; Klein and  
20 Garrido, 2011). The origin of CO<sub>2</sub> is variable as it may be related to either weathering (atmospheric  
21 CO<sub>2</sub>), metamorphic (deep seated CO<sub>2</sub>) or magmatic (magmatic CO<sub>2</sub>) sources (Abu-Jaber and  
22 Kimberley, 1992b). The source of magnesium is usually local at the outcrop scale but can also be  
23 distant, e.g. coming from the weathering of magnesian rocks at the Earth surface and transported  
24 downward by meteoric water infiltration (Podwojewski, 1995; Jurković *et al.*, 2012). Mechanisms  
25 of magnesite precipitation are also variable. Abu-Jaber and Kimberley (1992b) reported two main  
26 ways of magnesite precipitation: i) precipitation through a reaction that involves CO<sub>2</sub>-rich fluid and  
27 Mg-rich rock, or alternatively Mg-rich fluids and CO<sub>2</sub>-rich rock (*i.e.* the most common way to form  
28 magnesite); ii) the oversaturation of the fluid with respect to magnesite may be enhanced by the  
29 fluid evaporation and/or degassing (Dabitzias, 1980; Fallick *et al.*, 1991; Zedef *et al.*, 2000;  
30 Ghoneim *et al.*, 2003). In both cases, hydrated Mg-carbonate species may precipitate alternatively  
31 or in association to magnesite (e.g. Zedef *et al.*, 2000; Beinlich and Austrheim, 2012) Detailed  
32 studies of the precipitation mechanisms can thus provide major clues for the understanding of  
33 natural CO<sub>2</sub> sequestration.

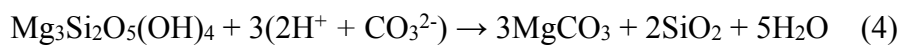
1 Among the various rocks that have the potential to react with CO<sub>2</sub>, ultramafic rocks, and  
 2 particularly serpentinites, are probably the most efficient feedstock material for long-time storage  
 3 through the formation of magnesite (Dabitzias, 1980; Jedrysek and Halas, 1990; Pohl, 1990; Fallick  
 4 *et al.*, 1991; Abu-Jaber and Kimberley, 1992b; Sherlock and Logan, 1995; Goff and Lackner, 1998;  
 5 Gerdemann *et al.*, 2003; Ghoneim *et al.*, 2003; Cipolli *et al.*, 2004; Schulze *et al.*, 2004; Hansen *et*  
 6 *al.*, 2005; Teir *et al.*, 2007, 2009; Kelemen and Matter, 2008; Rudge *et al.*, 2010; Klein and Garrido,  
 7 2011; Jurković *et al.*, 2012). Serpentine carbonation onsets by the dissolution of atmospheric CO<sub>2</sub>  
 8 into water, where CO<sub>2</sub> forms different species as a function of pH. At pH < 6.5, carbonic acid  
 9 (H<sub>2</sub>CO<sub>3</sub>) dominates, at pH between 6.5 and 10.5, bicarbonate (HCO<sub>3</sub><sup>-</sup>) dominates and at higher pH,  
 10 carbonate anion (CO<sub>3</sub><sup>2-</sup>) dominates. Serpentine dissolution and magnesite precipitation are also pH-  
 11 dependent (Klein and Langmuir, 1987; Guthrie *et al.*, 2001; Tneir *et al.*, 2007; Prigiobbe *et al.*,  
 12 2009; Teir *et al.*, 2009; Krevor and Lackner, 2011). Experimentally, Teir *et al.* (2007) have shown  
 13 that the best efficiency for serpentine to carbonate conversion is obtained in the pH range of 8-11,  
 14 with an optimum at pH 9. Roughly similar pH conditions were measured for the optimum  
 15 carbonation of olivine (Prigiobbe *et al.*, 2009). At pH > 8, bicarbonate starts to dissociate into H<sup>+</sup>  
 16 and CO<sub>3</sub><sup>2-</sup> ions:



21 Interaction between CO<sub>2</sub>-rich water and serpentine gives rise to the exchange of H<sup>+</sup> and Mg<sup>2+</sup>  
 22 cations on the mineral surface. This reaction produces silica and water, while free Mg<sup>2+</sup> cations  
 23 react with CO<sub>3</sub><sup>2-</sup> anions to form magnesite:



29 The overall reaction can be summarized as follow:



1  
2 Worldwide, carbonation of serpentinite commonly leads to the formation of magnesite  
3 deposits in association with ophiolitic bodies, *e.g.* in California (Bodenlos, 1950; Sherlock and  
4 Logan, 1995), Egypt (Ghoneim *et al.*, 2003), Greece (Dabitzias, 1980), Italy (Cipolli *et al.*, 2004),  
5 Norway (Beinlich *et al.*, 2012) or Oman (Kelemen and Matter, 2008). In New Caledonia, similar  
6 magnesite deposits have been described in the serpentine sole of the ophiolite, but few studies have  
7 focused on the origin of this magnesite (Glasser, 1904; Trescases, 1973; Ulrich, 2010; Quesnel *et*  
8 *al.*, 2013). Quesnel *et al.* (2013) propose that magnesite veins in the serpentinite sole formed  
9 tectonically, at temperatures between 40 and 80°C. On the basis of stable isotope analyses (O and  
10 C), these authors propose that the fluid from which magnesite formed was originally meteoric water  
11 and that the carbon source is mostly atmospheric, with a possible biogenic contribution. They also  
12 suggest that magnesium originated from the dissolution of the peridotite at the top of the ophiolite  
13 during laterization and was transferred down to the sole by the infiltration of meteoric waters under  
14 tectonically active conditions. The *per descensum* model is largely invoked to explain magnesite  
15 deposits in lateritic environments (Dabitzias, 1980; Pefrov *et al.*, 1980; Pohl, 1990; Abu-Jaber and  
16 Kimberley, 1992a; 1992b; Foster *et al.*, 2002; Jurković *et al.*, 2012; Oskierski *et al.*, 2012). It  
17 requires a well-drained system where meteoric waters, charged with atmospheric CO<sub>2</sub>, dissolve  
18 serpentine (and other Mg-silicates), a process that releases magnesium and silicon into solution.  
19 Meteoric waters then percolate downward thanks to a microfracturing permeability system, thus  
20 dissolving more magnesium. Within this frame, precipitation of magnesite is due to supersaturation  
21 of fluids, which are generated by the neutralization of carbonic acid by serpentine dissolution, as  
22 shown by reactions (2) and (3) (Bodenlos, 1950; Pohl, 1990; Fallick *et al.*, 1991; Abu-Jaber and  
23 Kimberley, 1992b; Giammar *et al.*, 2005; Kelemen *et al.*, 2011). Alternatively, the ultramafic pile  
24 may become a partially closed system, and therefore limit the exchange between atmospheric CO<sub>2</sub>  
25 and meteoric water (Jurković *et al.*, 2012). Progressive dissolution of serpentine during the fluid  
26 migration downwards consumes H<sup>+</sup> ions, as shown by reaction (3). As CO<sub>2</sub> is not freely available  
27 anymore, such consumption of H<sup>+</sup> ions causes the increase of pH, enhancing magnesite  
28 precipitation (Jurković *et al.*, 2012).

29 Considering the origin of magnesium as deriving from the laterization rises the question about  
30 the mechanism of magnesite precipitation in New Caledonia. In such a case, and similarly to  
31 magnesite deposits from Euboea (Greece, Boydell, 1921), magnesite formation may be the result of  
32 direct precipitation from the fluids without interacting with hosted rocks of the deposit site. This  
33 hypothesis was favored by the composition of New Caledonia waters passing through peridotites

1 and serpentinites (sampled in la Coulée river, Mont-Dore), showing that they are enriched in  
2 magnesium and  $\text{CO}_3^{2-}$  ions (Barnes *et al.*, 1978). Alternatively, field investigations highlight a close  
3 relationship between serpentinite, magnesite and silica, suggesting that the two latter phases may  
4 originate from the dissolution of the former. In this case, magnesite would precipitate by *in situ*  
5 replacement of the serpentine, using magnesium released during the serpentine dissolution. In this  
6 study we provide evidences of magnesite formation through such a process on the basis of mineral  
7 characterization using an original analytical method for the interpretation of micro-X-Ray  
8 Fluorescence ( $\mu$ -XRF) images. We particularly focus on the formation process of magnesite veins  
9 coupled to intense silicification observed in the serpentinite sole of the New Caledonia ophiolite.

## 11 1. GEOLOGICAL SETTINGS AND SAMPLE DESCRIPTIONS

13 New Caledonia is located in the SW Pacific, 2000 km east of the Australian coasts (Figure 1).  
14 It is composed of several islands that belong to the Norfolk ridge (La Grande Terre, Island of Pines,  
15 Belep Islands) and to the Loyalty ridge (Loyalty Islands). The main island, la Grande Terre, consists  
16 of a patchwork of terranes reflecting the geodynamic evolution of the SW Pacific region from late  
17 Permian to Eocene (*e.g.* Cluzel and Meffre, 2002; Cluzel *et al.*, 2001; 2012). Among these terranes,  
18 the ophiolite is the most prominent as it covers more than 25% of the island. The so-called  
19 Peridotite Nappe is composed of a large and continuous massif located south of the island and some  
20 isolated klippen widespread along the west coast (Figure 1). The ophiolite was formed between 83  
21 Ma with the opening of the South Loyalty Basin and its subsequent closing at 34 Ma, timing of its  
22 obduction on the Norfolk continental basement (Cluzel *et al.*, 2001; Crawford *et al.*, 2003; Schellart  
23 *et al.*, 2006; Whattam *et al.*, 2008; Whattam, 2009; Ulrich *et al.*, 2010; Cluzel *et al.*, 2012). Since its  
24 emergence, the uppermost part of the Peridotite Nappe has undergone an intense laterization. This  
25 led to the development of a thick laterite bed (up to 60 m thick; Sévin *et al.*, 2012) that owns ~30%  
26 of the world nickel resources. The whole ophiolite is formed of upper mantle rocks (mainly  
27 harzburgites) with minor cumulates (Prinzofher, 1981). Peridotites are highly serpentinitized,  
28 particularly at the base of the ophiolite which is made of a thick (up to 400 m thick, Audet, 2010;  
29 Ulrich *et al.*, 2010) and silicified serpentinite sole where large amount of magnesite veins have  
30 crystallized (Quesnel *et al.*, 2013).

31 Samples presented in this study were collected in the serpentinite sole of the Koniambo  
32 massif (Figure 1). Similar outcrops occur on the serpentinite sole from other peridotite massifs in  
33

1 New Caledonia (Ulrich, 2010). In the field, the whole sole is highly deformed, finely schistose and/  
2 or intensely brecciated, and has recorded multiple serpentinization events (Ulrich, 2010): Massive  
3 serpentinization, which is of a typical bottle-green color in the field (Figure 2), is cross-cutted by  
4 light-green colored serpentine veins. The latter is associated with black magnetite impregnations  
5 and micro-cracks filled by fibrous serpentine (chrysotile). Magnesite occurs as millimeter to multi-  
6 decimeter stock-work veins with a typical cauliflower-like texture, cross-cutting serpentinites  
7 (Figure 2). The magnesite is mainly snow-white colored, but can also appear greenish depending of  
8 the amount of intergrown serpentine. On the basis of structural observations, Quesnel *et al.* (2013)  
9 distinguished two types of veins. The first type of veins is observed along and/or within the margins  
10 of top to the SW-centimeter shallow dipping shear zones. The second type of veins corresponds to  
11 steeper veins occasionally crosscut by the low-dipping shear zones. Magnesite can also develop  
12 pervasively by precipitating in large and massive serpentine blocks (Figure 2 a, b, c). In this case,  
13 the magnesite seems to develop first at the expense of the light-green colored serpentine to  
14 progressively extend to bottle-green serpentine, a relationship that is not clear when magnesite fills  
15 the main shear zones, as described by Quesnel *et al.* (2013).

16

## 17 **2. ANALYTICAL METHODS**

18

### 19 1. X-Ray Diffraction

20

21 Analyzes were performed at the Institut des Sciences de la Terre (ISTerre, Grenoble, France)  
22 on sample powders obtained after the crushing of separated magnesite veins and serpentinite host  
23 rock mineral fractions. X-ray diffraction (XRD) patterns were recorded with a Bruker D5000  
24 powder diffractometer equipped with a Kevex Si(Li) solid state detector using  $\text{CuK}\alpha_{1+2}$  radiation.  
25 Intensities were recorded at  $0.02^\circ$   $2\theta$  step intervals from  $5$  to  $80^\circ$ , with a 6 seconds counting time  
26 per step. Size of the divergence slit was  $0.298^\circ$ .

27

### 28 2. Raman Spectroscopy

29

30 Raman spectroscopy measurements were performed at the Ecole Normale Supérieure de Lyon  
31 and at GéoRessources Nancy, France, in both cases using a Horiba Jobin-Yvon LabRam HR800  
32 spectrometer and a visible ionized argon laser source with a wavelength of 514 nm. Output laser  
33 power was 100 mW, and measurements were performed using an Olympus lens of x100 to focus the

1 laser beam onto an area that was 1  $\mu\text{m}$  in diameter. Analyzes were done on macroscopic samples  
2 and on thin sections. Spectra result from the average of 5 acquisitions of 10 s to 20 s to optimize the  
3 signal/noise ratio. Two regions of the Raman spectra were investigated: 150-1250  $\text{cm}^{-1}$  for structural  
4 bonding characterization and 2800-3900  $\text{cm}^{-1}$  for the characterization of the hydroxyl groups.

### 5 6 3. Micro-X-ray Fluorescence

7  
8 Micro-X-ray Fluorescence ( $\mu\text{-XRF}$ ) analyses were performed on a 5 mm-thick rock section  
9 (Figure 2d) using EDAX Eagle III spectrometer at ISTERre (Grenoble, France). The X-ray tube  
10 consists of a Rh anode operating at 250  $\mu\text{A}$  with an acceleration voltage of 40 kV. Polycapillary  
11 lenses were used to focus the X-ray beam down to 40  $\mu\text{m}$  full-width-at-half-maximum at the sample  
12 surface. An energy dispersive X-ray detector with resolution of 140 eV was used to measure  
13 fluorescence spectra. Chemical maps were recorded with a matrix of 256 x 200 pixels, a 40  $\mu\text{m}$  step  
14 interval in both directions, and a dwell time of 1 s per pixel. For each map, the grey-scale  
15 corresponds to the intensity of the  $\text{K}\alpha$ -lines of the different elements (Si, Mg, Fe, Al, Ni, Ti, Mn, Cr,  
16 Ca, K) calculated from the integration of a specified region of interest (ROI) of the energy-range of  
17 XRF spectra. Then, ROI maps (see electronic supplements, Figure S4) are used to calculate phase  
18 maps thanks to a new routine, specially developed Matlab<sup>©</sup>-based code, following the same  
19 approach than that successfully applied first to the computing of mineral-phase maps from  
20 hyperspectral  $\mu\text{-XANES}$  mapping (Muñoz *et al.*, 2008). In the case of hyperspectral  $\mu\text{-XRF}$  maps,  
21 the phase map calculation consists first of determining pure mineral phases that are expected to be  
22 present in the sample, in order to create standard spectra (or “pure” spectra). Then for each pixel of  
23 the map, a linear combination of the different standard spectra is performed in order to fit each  
24 single spectrum. Results provide quantitative phase maps showing the distribution of minerals  
25 previously identified in the sample (*e.g.*, based on XRD and/or Raman analyses). This approach is  
26 particularly useful to highlight relationships between minerals, especially for the characterization of  
27 finely-divided mineral assemblages, *i.e.* when the beam is larger than grain size (such as here,  
28 typically below 1 micron). Concentration maps (in wt.%) are finally recalculated on the basis of  
29 phase distribution maps considering the chemical composition of standards (Table 1)

## 30 31 4. RESULTS

### 32 33 1. Mineralogy and chemical compositions



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*a. Bulk mineralogical compositions*

Figure 3 shows the X-ray diffraction patterns obtained on separated fractions of serpentinite and magnesite. The serpentinite mainly consists of serpentine with minor amount of magnetite and chromite. Serpentine occurs as lizardite and chrysotile. The occurrence of chrysotile is consistent with the presence of fibrous serpentine in microcracks as described above. Despite a careful separation, small peaks of magnesite and silica are present in the diffraction pattern of the serpentinite, suggesting that both minerals also occur at the micrometer scale within the hosted rock.

XRD pattern of magnesite powder shows that the carbonate exhibits its most characteristic reflections at the following  $d$  values (in Å, arranged according to decreasing intensities): 2.74, 2.10, 1.70, 2.50, and 1.94 (Figure 3). In addition, the diffraction pattern shows that magnesite systematically integrates small amounts of sepiolite ( $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6(\text{H}_2\text{O})$ ), a mineral that is frequently described in association with carbonate in ultramafic environments (*e.g.* Birsoy, 2002; Yalıçın and Bozkaya, 2004; Boschetti and Toscani, 2008). On the basis on this XRD pattern, magnesite is the only carbonate to crystallize. Neither dolomite nor calcite are formed, contrarily to numerous magnesite deposits previously described in the literature (Griffis, 1972; Dabitzias, 1980; Jedrysek and Halas, 1990; Fallick *et al.*, 1991; Abu-Jaber and Kimberley, 1992b; Lugli *et al.*, 2000; Zedef *et al.*, 2000; Ghoneim *et al.*, 2003; Jurković *et al.*, 2012).

*b. Optical microscopy*

Figure 4 shows the typical mineralogical textures of carbonated serpentinites composing the sole of the New Caledonia ophiolite. In thin section, the serpentinite does not exhibit any relic of primary minerals (*i.e.* olivine and pyroxene). However, the habits of grains and original textures of primary minerals (*e.g.* cleavage planes of orthopyroxene) have been preserved (typical pseudomorphic “mesh” texture, Figure 4a, b) and indicate that the parent rock was a harzburgite. As highlighted by XRD analyzes, opaque minerals associated with the serpentine are small grains of magnetite and chromite disseminated in the mesh. In these rocks, magnesite occurs as finely disseminate grains (*i.e.* cryptocrystalline texture) that developed both at the rim and in cracks affecting serpentine grains (Figure 4b, d). These grains progressively aggregate to form larger zones with a typical granular texture (Figure 4a-c). The sepiolite, identified by XRD and optical microscopy, occurs as brown fibers interstitially to the magnesite nodules (Figure 4c). Silica also occurs close to magnesite. Microscopic observations show that the nature of the silica is variable: it

1 occurs as an amorphous solid (gel-like) surrounding magnesite aggregates and serpentine grains in  
2 area where magnesite dominates (Figure 4a, c, d). Where serpentine is dominant, silica consists of  
3 crystalline to fine grains, forming vugs with a typical colloform texture propagating in the  
4 serpentine mesh (Figure 4e, f). In this case, the nature of silica ranges from amorphous-like near the  
5 rim of the vug to quartz-like at the center (Figure 4c, e, f).

6

### 7 *c. Raman spectroscopy*

8 Raman analyses were performed to further identify minerals that compose the serpentinite.  
9 This technique is complementary to XRD, since it is particularly efficient to distinguish among the  
10 different varieties of serpentine (*e.g.* Lemaire, 2000; Auzende *et al.*, 2004) as well as silica  
11 polymorphs (*e.g.* Götze *et al.*, 1998; Pop *et al.*, 2004). Figure 5 shows Raman spectra collected on  
12 carbonated serpentinites. Results show that lizardite is the dominant serpentine variety that occurs  
13 as individual grains and in the mesh, and corresponds to the bottle-green colored serpentine  
14 described in the macroscopic observations. Chrysotile (not shown in Figure 5) has also been  
15 detected, as already highlighted by XRD. In addition, light green serpentine was identified as  
16 polygonal serpentine. It shows quite similar patterns to those of the lizardite at low wavenumbers,  
17 but strongly differs at high wavenumbers (from 3500 to 3800  $\text{cm}^{-1}$ , corresponding to OH group),  
18 where the polygonal serpentine is characterized by a large peak composed by two bands centered at  
19 3689 and 3700  $\text{cm}^{-1}$  (*e.g.* Lemaire, 2000; Auzende *et al.*, 2004).

20 The Raman spectrum of magnesite is characterized by four distinct bands located at 209, 327,  
21 737 and 1094  $\text{cm}^{-1}$  (Figure 5), consistently with the work of Krishnamurti (1956). The lack of bands  
22 at 3448 and 3648  $\text{cm}^{-1}$  (*i.e.*, in the OH region; typical of hydromagnesite) shows that magnesite is  
23 anhydrous.

24 Silica polymorphs are clearly identified using Raman spectroscopy. Vug rims consist of opal-  
25 CT (Silica #1, Figure 4e) while brown coronas (Silica #2, Figure 4e) and white fine grains (Silica  
26 #3, Figure 4e) inside of the vugs are identified as chalcedony (Figure 5). Although significantly  
27 different in microscopic observations (Figure 4e, f), both chalcedonies display very similar Raman  
28 spectra, except on the intensity of the band located at 501  $\text{cm}^{-1}$  which is significantly higher in the  
29 white chalcedony (electronic supplements, Figure S1). Notice that in all silica polymorphs, the large  
30 bands observed between 3100 and 3900  $\text{cm}^{-1}$  indicate the presence of molecular water.

31

### 32 *d. XRF mapping*

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1 The elemental distribution, expressed in weight percent, in a typical serpentinite texture  
2 surrounded by magnesite is shown in Figure 6. On the basis of chemical measurements, it was not  
3 possible to discriminate lizardite from polygonal serpentine, both having very similar compositions.  
4 Therefore, we only refer to serpentine in the followings, focusing on the nature of processes that  
5 preferentially affect the serpentine grains or the mesh. The distribution maps of MgO and SiO<sub>2</sub>  
6 highlight serpentine grains (s) as well as mesh texture (m). The chemical composition of these  
7 grains is consistent with the stoichiometry of serpentine minerals, with about 43 wt.% for both MgO  
8 +Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. However, SiO<sub>2</sub> concentration in the mesh is significantly higher, and can reach up  
9 to 65 wt.%. To better understand such differences in chemical compositions, we calculated the  
10 phase distribution maps according to the minerals that are expected to be present in this sample  
11 (Figure 7 and electronic supplements, Figure S4). Phase distribution reveals that the central zone of  
12 the mapped area mainly consists of serpentine minerals. The amount of serpentine is at least 50 %  
13 in the mesh and close to 100 % in grains. Silica distribution is relatively homogeneous in the mesh,  
14 with about 30 % silica, but shows peculiarities close to the magnesite, where the silica content  
15 reaches about 100 %. In contrast, the amount of silica in serpentine grains is well below 5 %.  
16 Finally, the calculation of phase distribution maps was obtained with about 20 % of magnesite in  
17 the serpentinite texture (*i.e.* the central area).

18 Figure 8 shows density correlation diagrams between serpentine, magnesite and silica based  
19 on the phase distribution maps for the two regions delimited by squares in Figure 7. These diagrams  
20 statistically illustrate the description made above on the phase maps and reveal two distinct  
21 processes. In the region 1, the diagrams show a clear anticorrelation between silica and serpentine,  
22 corroborating that a great part of the pixels of this region corresponds to "silicified serpentine". At  
23 the opposite, the relationships between magnesite and serpentine on one hand and those between  
24 silica and magnesite on the other hand are less straightforward. To better understand these two  
25 diagrams, the region 2 (dashed square in Figure 7) was delimited around a heterogeneous serpentine  
26 grain that appears partially altered (Figure 9). This alteration occurs around fractures in the grain  
27 and is expressed by a lighter color of the serpentine in microscopic view. Considering this grain, a  
28 statistical analysis shows that silica and magnesite are correlated to each other, whereas they are  
29 both anticorrelated to serpentine (Figure 8, region 2). This point is particularly interesting since the  
30 phase maps clearly highlight here a process of replacement of serpentine by an assemblage of  
31 magnesite and silica. Even if silica and serpentine are anticorrelated in both regions, carbonation  
32 and silicification processes do not follow rigorously the same trend. On the basis of our specific  
33 treatment of the XRF maps, we demonstrate here that the serpentinite is affected by two distinct

1 weathering processes: while the mesh texture is mainly affected by a silicification process, the  
2 serpentine grains are mainly affected by the crystallization of a magnesite + amorphous silica  
3 assemblage.

4

## 5 **5. DISCUSSION**

6

7 Serpentinite carbonation in New Caledonia has a supergene origin, following a *per descensum*  
8 model (Glasser, 1904; Trescases, 1973; Ulrich, 2010; Quesnel *et al.*, 2013). The atmospheric carbon  
9 dioxide is first dissolved in meteoric water. The CO<sub>2</sub>-enriched fluids then circulate through the  
10 lateritic cover, dissolve the residual Mg-rich minerals before driving to the precipitation of  
11 magnesite in fractures and to a porosity reduction in the serpentinite, within the serpentinite sole.  
12 This carbonation process leads to the formation of clusters of magnesite, potentially very large, and  
13 usually very localized to the serpentine rich fractures or volumes. Although this process is most  
14 easily observed in the field, our results show that the serpentine dissolution leads to the local  
15 crystallization of magnesite and silica. This diffuse process is potentially the main mechanism of  
16 carbonation of the serpentinite sole.

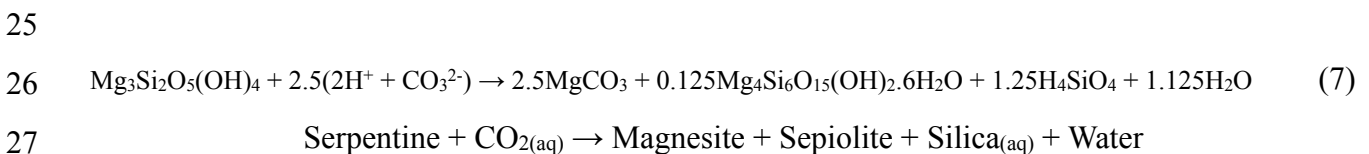
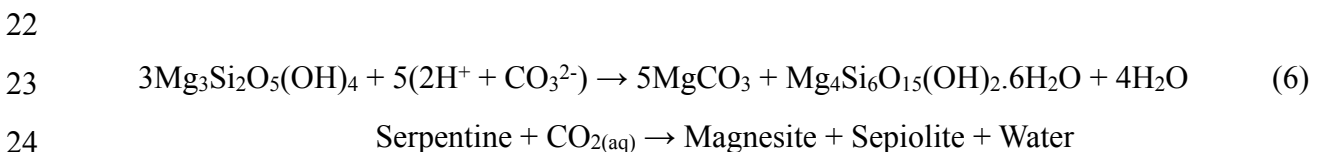
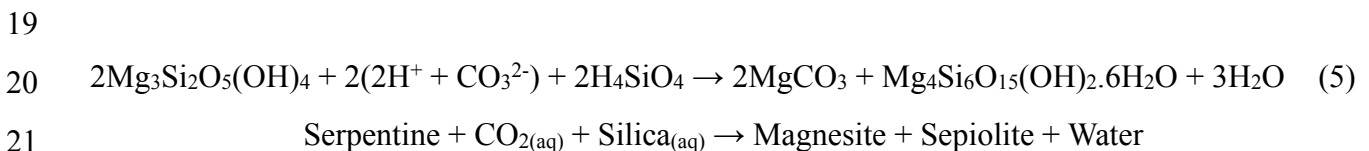
17

### 18 1. Carbonation after serpentine dissolution

19

20 On the basis of our results of our mineralogical investigations, several features provide  
21 evidence that magnesite precipitation occurs through serpentine dissolution. First, the development  
22 of magnesite along the edges of adjacent serpentine grains is a characteristic of carbonation by *in*  
23 *situ* replacement of the serpentine (Figures 4b, 4d and 9). When serpentine grains are preserved,  
24 carbonation is limited to the rims, the core remaining unaffected. At the opposite, the dissolution  
25 and replacement of the serpentine are more efficient in case of fractured grains (Figure 9). This  
26 observation is consistent with experimental studies showing that intense grain fracturing is required  
27 to ensure complete carbonation (*e.g.* Haug *et al.*, 2011; Kelemen *et al.*, 2011; Hövelmann *et al.*,  
28 2012; van Noort *et al.*, 2013). Another way to illustrate the progressive serpentine carbonation is  
29 given by Figure S2 (in electronic supplements). Here, the RGB map (for Red, Green, Blue, see the  
30 figure caption for more details) shows that magnesite is ubiquitous, formed by the replacement of  
31 the serpentine grains, and that only a few of the latter are preserved from the carbonation process. In  
32 addition, considering the stoichiometry and the molar volumes of the mineral species involved in  
33 reaction (4), volumes of magnesite and silica produced by the dissolution of 1 mole of serpentine

1 (108 cm<sup>3</sup>) are respectively 85 cm<sup>3</sup> and 58 cm<sup>3</sup> ( $V_{\text{Mgs}}/V_{\text{Silica}} \sim 1.45$ ), leading to a volume increase of  
 2 about 30 %. Statistics calculated on the serpentine grain presented in Figure 9 (corresponding to the  
 3 region 2, Figure 7) show that the assemblage consists of about 62 vol.% of serpentine, 21 vol.% of  
 4 magnesite and 15 vol.% of silica ( $V_{\text{Mgs}}/V_{\text{Silica}} \sim 1.4$ ; Figure 8). This assemblage compares well with  
 5 the result of dissolution of 38 vol.% of serpentine, which leads to the formation of ~22 vol.% of  
 6 magnesite and ~15 vol.% of silica. These estimates testify that results given in the phase maps are  
 7 in good agreement with the stoichiometry of reaction (4). Second, carbonation by serpentine  
 8 dissolution is also evidenced by the precipitation of an amorphous silica layer at the grain rims  
 9 (Figure 4d). This observation is consistent with the previous studies that systematically reported the  
 10 formation of a Si-rich layer after Mg-bearing mineral breakdown (*e.g.* Luce *et al.*, 1972; Lin and  
 11 Clemency, 1981; Guthrie *et al.*, 2001; Schulze *et al.*, 2004; Giammar *et al.*, 2005; Bearat *et al.*,  
 12 2006; Sipilä *et al.*, 2008; Andreani *et al.*, 2009; Daval *et al.*, 2011; King *et al.*, 2011, Hövelmann *et al.*,  
 13 *et al.*, 2011; 2012). Third, sepiolite, which is described in our samples in association with magnesite  
 14 (Figures 3 and 4c), also formed subsequently to the dissolution of serpentine (*e.g.* Jones and Galàn,  
 15 1988; Birsoy, 2002; Yalçın and Bozkaya, 2004; Andreani *et al.*, 2009). Similar occurrences of  
 16 sepiolite have been reported during natural (Yalçın and Bozkaya, 2004) and experimental  
 17 (Andreani *et al.*, 2009) carbonation of Mg-bearing minerals (serpentine and olivine). Actually,  
 18 sepiolite may form in different ways:



28  
 29 All these reactions contribute to form magnesite, but they differ as reactions (5) and (6) conserve all  
 30 Mg and Si in solids and are characterized by a volume gain (~60% and ~30%, respectively) while  
 31 reaction (7) is balanced on volume. In addition, Eq. (5) consumes silica while Eq. (7) produces it.  
 32 Only on the basis of cm-scale maps, it is difficult to estimate which reaction occurred: in our sample,  
 33 sepiolite represents less than 1 vol.% (see electronic supplements, Figure S4). Among the reactions

1 written above, Eq. (7) is the one that produces the smallest amount of sepiolite, regarding the  
2 amount of magnesite that stoichiometrically precipitates. In contrast, Birsoy (2002) demonstrated  
3 that sepiolite formation is much more favored in the presence of Si-rich solution. In that case,  
4 sepiolite in our sample may derive from Eq. (5).

5 The fact that some serpentine grains are only partially transformed into magnesite indicates  
6 that the carbonation process was not completed. The reason why the reaction does not go to  
7 completion may be due to (1) silica precipitation, (2) pH increase and/or (3) porosity decrease.  
8 Numerous studies proposed that the formation of a Si-rich layer at the rims of serpentine grain  
9 during the first steps of dissolution might inhibit further Mg diffusion, potentially retarding or even  
10 stopping the process of carbonation (Gerdemann *et al.*, 2003; Schulze *et al.*, 2004; Alexander *et al.*,  
11 2007; Daval *et al.*, 2011). Although Si-rich layer effectively reduces the accessibility of fluids to the  
12 reactive surface of minerals, recent investigations demonstrate that some permeability is maintained  
13 as carbonation remains active even after its development (Béarat *et al.*, 2006; Andreani *et al.*, 2009;  
14 Hövelmann *et al.*, 2012). Thus, it is not obvious that precipitation of Si-rich layer led the serpentine  
15 carbonation to stop. Alternatively, following reaction (4), the dissolution of serpentine consumes 2  
16 moles of  $H^+$  for 1 mole of  $CO_3^{2-}$ , leading to a progressive increase of fluid pH. According to Barnes  
17 *et al.* (1978), fluids reacting with serpentinite in New Caledonia have pH ranging from 9 to 11. At  
18 pH 9,  $HCO_3^-$  dominates over  $CO_3^{2-}$ , making the serpentine dissolution possible following reactions  
19 (1) and (2). At pH 10.5,  $CO_3^{2-}$  species become dominant and at pH 10.8,  $HCO_3^-$  represent less than  
20 20% of the carbonate species in the fluid. In these conditions, magnesite precipitation is favored,  
21 but serpentine dissolution is scarce due to the lack of  $H^+$  ions (*e.g.* Teir *et al.*, 2007). Thus, intensive  
22 exchange between  $H^+$  ions and  $Mg^{2+}$  cations on the serpentine surface leads to a progressive  
23 increase of pH that may inhibit further serpentine dissolution and subsequent carbonation. There is  
24 no evidence to argue against such process in New Caledonia, but it requires that atmospheric  $CO_2$  is  
25 not freely available and thus a roughly closed system (Jurković *et al.*, 2012). A third explanation  
26 may account for the inhibition of carbonation. Hövelmann *et al.* (2012) recently investigated the  
27 microstructure and porosity evolution as a function of carbonation reaction progress in natural  
28 peridotite. On the basis of their experimental results, they reported that a carbonation extend of ~10  
29 % leads to a closure of 50 % of the initial porosity. They demonstrated that magnesite precipitation  
30 in fracture pore space reduces the permeability and progressively stops the fluid pathway,  
31 preventing further reaction between the fluid and the silicate surface and ultimately ends the  
32 carbonation process. Contrarily to serpentinization, which is able to propagate through a reaction-  
33

1 induced fracturing mechanism (*e.g.* Plümpner *et al.*, 2012), carbonation is self-limited as the reaction  
2 will be inhibited due to magnesite growing that ultimately clogs the system. This implies that no  
3 volume gain occurs at the rock-scale (Beinlich *et al.*, 2012). Numerous studies highlight the  
4 necessity of active fracturing to ensure complete carbonation (*e.g.*, Kelemen and Matter, 2008;  
5 Kelemen *et al.*, 2011; Boschi *et al.*, 2012). In our samples, no evidence of carbonation-induced  
6 fracturing has been observed so far, even if Quesnel *et al.* (2013) show the syn-kinematic character  
7 of magnesite veins at the outcrop scale. At the millimetric scale, volume gain associated with  
8 reaction (4) may have inhibited the complete carbonation of serpentinite by clogging the reacting  
9 zone. Such a process may prevent the infiltration of additional fluids, resulting in the partial  
10 carbonation of serpentine grains as illustrated by Figure 7 (see also electronic supplements, Figure  
11 S2).

## 12 13 2. Redox conditions during magnesite precipitation

14  
15 The behavior of iron during carbonation has been poorly investigated. Such information  
16 would be indicative of redox conditions during magnesite precipitation. In serpentinite, iron is  
17 mainly hosted by iron oxides (magnetite, Fe<sub>3</sub>O<sub>4</sub>) surrounding serpentine grains or disseminated in  
18 the mesh texture (see electronic supplement, Figure S5). Iron content in serpentine is ~2 wt.%  
19 (expressed as FeO, Table 1). It substitutes Mg<sup>2+</sup> cations in octahedral sites (O'Hanley, 1996). During  
20 serpentine dissolution, iron is released from the mineral structure and may subsequently form Fe-Si-  
21 rich layer that progressively evolves into magnetite at the interface between serpentine and aqueous  
22 fluid (Fallick *et al.*, 1991; Alexander *et al.*, 2007; Andreani *et al.*, 2009, Saldi *et al.*, 2013).  
23 Alternatively, it may precipitate as siderite (FeCO<sub>3</sub>) under rather high *p*CO<sub>2</sub> and specific pH range  
24 from 5.5 to 7.5 (Ohmoto *et al.*, 2004) or be integrated in magnesite by substituting Mg<sup>2+</sup> cations  
25 (Abu-Jaber and Kimberley, 1992b; Hansen *et al.*, 2005). In each of these minerals, iron oxidation is  
26 expected to differ according to oxidizing conditions: it is mostly oxidized in magnetite (*i.e.* 2/3 of  
27 iron is ferric iron) while it is in ferrous state in siderite or magnesite. In our sample, XRF analyzes  
28 show that the iron content in magnesite is very low (Table 1), suggesting that its integration into the  
29 structure of the magnesite was very scarce. In addition, we never identified siderite in our samples  
30 so far. As stated above, siderite precipitates at pH conditions that are significantly lower than those  
31 of New Caledonia waters, so it is likely that pH was too high to make siderite precipitate. Magnetite  
32 is ubiquitous in our sample. Therefore, discriminating magnetite grains related to prior  
33 serpentinization events to those potentially derived from carbonation is not obvious. However,

1 microscopic observations show that numerous magnetite grains have precipitated inside of partially  
2 carbonated serpentine grains (Figures 4d and 9) while magnetite related to serpentinization  
3 generally forms outside of serpentine grains. Schematic representation in Figure 9 highlights the  
4 systematic association of magnetite with cracks in the serpentine grain. According to Andreani *et al.*  
5 (2009), such grain fracturing may be considered as zones of localized fluid flow that favor the  
6 precipitation of magnetite during the first step of mineral dissolution. In contrast, their experiments  
7 show that carbonation initiates in domains of reduced fluid flow zones (fractures of a smaller size)  
8 where chemical gradient are small and thus facilitate local supersaturation, high pH and more  
9 reducing conditions. These results indicate that magnetite associated with the carbonation process  
10 may be used as a proxy to estimate the fluid flow rate at the serpentine grain scale: Fractures filled  
11 by magnetite correspond to high fluid flow zones characterized by more oxidizing conditions. In  
12 these regions, dissolution occurs but not magnesite precipitation (Andréani *et al.*, 2009).  
13 Magnesium migrates to zones of reduced fluid flow, corresponding to regions dominated by  
14 magnesite or partially carbonated serpentine (Figures 9. 10). In these areas magnesite precipitates  
15 due to local supersaturation under more reducing conditions. This underlies that redox gradients  
16 occur even at grain scale.

17

### 18 3. Serpentine mesh silicification

19

#### 20 a. Silica mobilization and precipitation

21 Intense silicification of the serpentine mesh was revealed during this study based on XRF  
22 measurements and Raman spectroscopy (Figures 6-8, electronic supplements, Figures S2 and S3).  
23 For instance, the region 1 (Figure 7) is composed of 62 vol.% of serpentine, 24 vol.% of silica and 7  
24 vol.% of magnesite in average. The precipitation of 7 vol.% of magnesite consumes 12 vol.% of  
25 serpentine and forms 5 vol.% of silica, on the basis of reaction (4). Such excess of silica necessarily  
26 involves a contribution of silica from outside of the region 1. Phase maps show that pure silica  
27 mainly occurs in gaps between magnesite aggregates (left-side of the map, Figure 7 and electronic  
28 supplements, Figure S2). However, when aggregates agglomerate subsequently to magnesite  
29 growth (right-side of the map, Figure 7 and electronic supplements, Figure S2), silica is expelled  
30 from the magnesite. Numerous experimental studies indicate the progressive migration of silica  
31 rather than being rejected from the growing magnesite (Schulze *et al.*, 2004; Hövelmann *et al.*,  
32 2011; 2012). As stated above, the first steps of serpentine dissolution release silica that immediately  
33 precipitates as a Si-rich layer. As carbonation reaction proceeds, the released silicon may feed the



1 growth of the Si-rich layer, but Hövelmann *et al.* (2012) reported that such inward growth is  
2 limited. This limitation is mainly associated with pH increase of fluid during the carbonation  
3 process. At pH>9, magnesite precipitates while silica is solubilized and is therefore able to migrate  
4 away from the solid-fluid interface. Occurrence of water within silica is demonstrated by the Raman  
5 spectrum measured in the region of high frequencies (Figure 5), which exhibits a typical spectrum  
6 of molecular water. As illustrated by XRF mapping, fluids enriched in silica subsequently to  
7 serpentine dissolution, propagates in the serpentine meshwork. Similar observations have been  
8 reported in serpentinites from the Oman and the Ligurian ophiolites (Stanger, 1985; Boschi *et al.*,  
9 2009; Lacinska and Styles, 2012). According to Lacinska and Styles (2012), the well-preserved  
10 mesh texture (as observed in our samples) induces a combination of iso-volumetric processes of  
11 slow rate dissolution of the mesh serpentine and immediate local precipitation of silica. They also  
12 argue that precipitation of silica is favored at near-neutral pH conditions. Such conditions differ  
13 from those we assume in our system (high alkali pH). However, Williams and Crerar (1985)  
14 attributed the precipitation of amorphous silica phases in nature due to the formation of dense  
15 colloids in supersaturate alkaline aqueous solutions. In addition, progressive dissolution of silica  
16 causes pH of the solution to drop (Williams and Crerar, 1985; Williams *et al.*, 1985). Following  
17 these observations, we infer that such process may favor the dissolution of the serpentine mesh and  
18 the subsequent grain-by-grain replacement by amorphous silica phases, as postulated by Lacinska  
19 and Styles (2012). Such a process involves the removal of substantial amount of magnesium. As  
20 shown above, serpentine grain carbonation occurs stoichiometrically, *i.e.* magnesium released after  
21 serpentine grain dissolution, then immediately precipitates as magnesite. Thus, it is likely that the  
22 magnesium released during serpentine mesh silicification migrates out of the reaction zone. This  
23 assumption is consistent with the study of Boschi *et al.* (2009) that reported similar magnesium  
24 mobilization after serpentine dissolution and silica precipitation.

25

#### 26 *b. Silica evolution*

27 Raman spectroscopy shows that silica formed in response to serpentine carbonation  
28 crystallizes as opal-CT and chalcedony (Figure 5). Such silica polymorphs are commonly described  
29 in association with magnesite and are consistent with formation at low temperature conditions  
30 (Boydell, 1921; Bodenlos, 1950; Dabitzias, 1980; Pohl, 1990; Abu-Jaber and Kimberley, 1992b;  
31 Klein and Garrido, 2011). According to Lacinska and Styles (2012), the formation of opal-CT  
32 indicates precipitation from supersaturated fluids. Williams *et al.* (1985) and Williams and Crerar  
33 (1985) show that the precipitation of silica polymorphs is driven by multiple steps of dissolution-

1 precipitation. Systematically, studies made on the silica diagenesis report that saturated silica  
2 solutions do not form opal-CT directly, but follow a sequential crystallization with first the  
3 precipitation of amorphous opal-A (Graetsch *et al.*, 1985; Williams *et al.*, 1985; Williams and  
4 Crerar, 1985; Heaney, 1993; Lacinska and Styles, 2012). Opal-A then evolves by means of  
5 dissolution–precipitation with concurrent ordering of the structure and removal of water, forming a  
6 pathway as follow: opal-A (amorphous) → opal-CT (cristobalite-tridymite assemblage)→  
7 chalcedony → quartz. According to Williams *et al.* (1985), the relationship between solubility and  
8 surface area or particle size is sufficient to explain such evolution. In our samples, only opal-CT and  
9 chalcedony have been identified so far. One possible explanation to account for the absence of opal-  
10 A is the complete replacement by opal-CT. The association with magnesite supports this hypothesis,  
11 since carbonates are thought to enhance the formation of opal-CT (Williams and Crerar, 1985).  
12 Quartz has never been described associated with serpentinite in New Caledonia, so it is likely that  
13 the transition chalcedony to quartz does not occur. This reaction is very slow and is more likely to  
14 occur in a closed system, from the precipitation of fluids undersaturated in silica with respect to  
15 opal-A, opal-CT or chalcedony (Lund, 1960 and references therein; Williams *et al.*, 1985; Williams  
16 and Crerar, 1985). In our samples, vugs containing chalcedony are systematically characterized by  
17 the presence of a hole on its center (Figure 4). Similar observations were reported by Lund (1960)  
18 from silicified corals where both chalcedony and quartz precipitated. This author concluded that the  
19 hole served as a conduit for the continuous circulation of dissolved silica, resulting in the  
20 precipitation of chalcedony. At the opposite, when no hole was observed, chalcedony was  
21 completely replaced by quartz.

22 As an example, the concurrent reordering that occurs during the diagenetic pathway of silica  
23 is illustrated by the behavior of chalcedony (Figures 4 and electronic supplement, Figure S1).  
24 Chalcedony, as many of the microcrystalline SiO<sub>2</sub> varieties, consists of an intimately intergrowth of  
25  $\alpha$ -quartz and moganite. Moganite is a silica polymorph that typically contains up to 3 wt.% of water  
26 which is not a constituent of the structure. Using Raman spectroscopy, Pop *et al.* (2004) showed  
27 that during the opal-CT to chalcedony transition, moganite starts growing after  $\alpha$ -quartz and  
28 preferentially in the most crystallized areas. It can be used as a proxy to evaluate the ordering of the  
29 chalcedony during its transition from opal CT to quartz (Götze *et al.*, 1998; Rodgers and Cressey,  
30 2001; Pop *et al.*, 2004). In Figure 4c, both silica #2 and silica #3 have been identified as chalcedony  
31 but differ in microscopic observation by their colors. In Raman spectroscopy, silica #2 and silica #3  
32 almost display the same patterns, except the intensity of the band at 501 cm<sup>-1</sup> (moganite) that is  
33 higher in the white chalcedony (electronic supplement, Figure S1). The moganite content (in wt.%)

1 of chalcedony can be calculated using the Raman band integral ratios  $I_{(501)}/I_{(465)}$  (*i.e.* moganite/  
2 quartz) and applying the calibration curve proposed by Götze *et al.* (1998). We find that both  
3 chalcedonies are dominated by moganite, which represents 77 wt.% in brown chalcedony (silica #2,  
4 Figure 4c) and 81 wt.% in white chalcedony. The enrichment of moganite traduces the progressive  
5 ordering of chalcedony which ultimately transforms in quartz given sufficient time (Williams and  
6 Crerar, 1985; Heaney and Post, 1992; Rodgers and Cressey, 2001; Lynne *et al.*, 2007).

#### 7 8 4. Coupled carbonation-silicification in dissolution-precipitation processes: a summary 9

10 Based on our results and those from previous experimental studies, we infer that serpentine  
11 carbonation occurred due to the circulation of high pH meteoric waters dissolving the serpentine.  
12 Serpentine dissolution started at grain boundaries and in large grain fractures that correspond to  
13 regions where the fluid flow is the highest (Figure 10a). In these regions, intensive exchanges  
14 between  $H^+$  and  $Mg^{2+}$  ions led to the development of a Si-rich layer and the precipitation of  
15 magnetite at the mineral/water interface (Figure 10b). In contrast, magnesite precipitation was not  
16 favored in these zones of high fluid flow, which are characterized by strong chemical gradients and  
17 local oxidizing conditions (Andreani *et al.*, 2009). Released magnesium therefore migrated to  
18 regions of reduced fluid flow, where magnesite nucleated at the expense of serpentine surfaces by a  
19 process of dissolution-precipitation due to local supersaturation and more reducing conditions  
20 (Figure 10b-c). Here, the growth of magnesite was mainly fed by magnesium coming from the  
21 dissolution of adjacent serpentine grain. Potentially, distal contributions may have occurred (*i.e.*  
22 coming from the laterization, Barnes *et al.*, 1978), since magnesite incorporate calcium while this  
23 element is not concentrated in serpentine (Table 1). Silica released during the carbonation process  
24 may first have precipitated *in situ* as amorphous silica (opal A/CT), but progressive pH increase  
25 during the reaction facilitates the silicon solubilization and subsequent migration away from the  
26 fluid-solid interface (Figure 13c; Schulze *et al.*, 2004; Andreani *et al.*, 2009; Hövelmann *et al.*,  
27 2011; 2012). Silica was then able to propagate in the serpentine mesh, silicifying the latter by  
28 precipitating first as an amorphous gel that progressively orders its crystalline structure to  
29 ultimately evolve as quartz if given sufficient time (Figure 10c; Williams and Crerar, 1985; Heaney  
30 and Post, 1992; Rodgers and Cressey, 2001; Lynne *et al.*, 2007). Magnesium leached during the  
31 serpentine mesh carbonation migrated out from its original reacting zone and potentially fed larger  
32 magnesite deposits in syn-tectonic fractures, as previously proposed by Boschi *et al.* (2009) in the  
33 Ligurian ophiolite. Carbonation process ended when the overall serpentine was converted into an

1 assemblage of magnesite + silica or, alternatively, when magnesite precipitation induced closure of  
2 the initial porosity (Figure 10d, Hövelmann *et al.*, 2012).

3 In agreement with recent studies from Andreani *et al.* (2009), Boschi *et al.* (2009), or  
4 Hövelmann *et al.* (2011; 2012), our study demonstrates the importance of active fracturing in the  
5 idea of *in situ* CO<sub>2</sub> sequestration. Although the volume extend expected during serpentine  
6 carbonation may lead to the system clogging, serpentine mesh silicification involves substantial  
7 removal of magnesium. This magnesium may migrate out of the reaction zone and subsequently  
8 precipitates as massive magnesite veins along the main structural discontinuities such as those  
9 described in New Caledonia by Quesnel *et al.* (2013). As previously underlined by Boschi *et al.*  
10 (2009), such a process may be considered as an alternative, efficient way for CO<sub>2</sub> sequestration.

11

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1 **Figure captions**

2

3 **Figure 1:** Localization of the main ophiolitic occurrences composing the Peridotite Nappe.  
4 Simplified geological map of the Koniambo massif is modified from Maurizot *et al.* (2002).

5

6 **Figure 2: a, b, c)** Snow-white colored magnesite veins crystallized in massive serpentinite  
7 blocs, Koniambo massif. Magnesite show a typical cauliflower texture and is closely associated  
8 with silica veins (in brown). **d)** Typical sample of carbonated serpentinite. Orange dashed line  
9 square localizes the mapped area by  $\mu$ -XRF presented in Figures 6 to 8 and in Figures S2 and S3.

10

11 **Figure 3:** Typical XRD patterns of serpentinite and magnesite. Liz: Lizardite; Chr: Chromite;  
12 Opl: Opal; Mgs: Magnesite; Mgt: Magnetite; Ctl: Chrysotile. Numbers upon the magnesite peaks  
13 correspond to  $d$  values, given in Å.

14

15 **Figure 4: a)** Microphotography under polarized light illustrating the development of  
16 magnesite and silica in serpentinite. **b)** Microphotography under crossed-polarized light showing  
17 the development of magnesite along the rims of serpentine grains (indicated by the red arrows).  
18 Notice that the serpentinization also affects the orthopyroxene **c)** Magnesite grain aggregates  
19 surrounded by colloform amorphous silica gel. Associated brown and fibrous mineral corresponds  
20 to sepiolite (observation under polarized light). **d)** Nucleation of magnesite grain on serpentine  
21 surface surrounded by colloform amorphous silica gel. Black dots inside of the serpentine grain  
22 correspond to magnetite (observation under crossed-polarized light). **e)** Microtextures of a silica  
23 vein under polarized light (mesh: serpentine mesh; #1: opal-CT, #2 and #3: Chalcedony;  
24 identifications made by raman spectroscopy, see Figure 5). **e)** Same as e) under crossed-polarized  
25 light. Mineral abbreviations: Mgs: magnesite; Mgt: Magnetite; Opx: Orthopyroxene; Sep: sepiolite;  
26 Srp: serpentine

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28 **Figure 5:** Typical Raman spectra observed for serpentine (lizardite and polygonal),  
29 chalcedony, opal-CT and magnesite composing the serpentinite sole of the New Caledonia  
30 ophiolite.

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1 **Figure 6:** Quantitative chemical maps of MgO, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> (in wt.%) calculated on the  
2 basis of  $\mu$ -XRF measurements (EDAX Eagle III). Complete procedure for the map calculation is  
3 detailed in the text.

4  
5 **Figure 7:** Spatial repartition and quantification of mineral phases (in %) calculated on each  
6 pixel of the mapped area (Figure 2d), based on  $\mu$ -XRF measurements (EDAX Eagle III). Square-  
7 delimited regions correspond to areas used to construct correlation diagrams in Figure 8.

8  
9 **Figure 8:** Correlation diagrams (represented as density fields) between serpentine, magnesite  
10 and silica based on the phase distribution maps for the two square-delimited regions in Figure 8.  $n$   
11 corresponds to the total number of pixels composing each region. Colorbar values correspond to the  
12 number of pixels in one grid cell of a size of 5% by 5%.

13  
14 **Figure 9:** Microphotography under polarized light and schematic representation of the  
15 partially carbonated serpentine grain (corresponding to the Region 2 in Figure 7).

16  
17 **Figure 10:** Schematic sketch of coupled carbonation-silicification in dissolution-precipitation  
18 processes. **a)** High pH meteoric waters (yellow arrows) percolating in serpentinite porosity start to  
19 dissolve the serpentine. **b)** In zones of high fluid flow (see the text for more details), dissolution of  
20 the serpentine surface releases Mg<sup>2+</sup> cations (white arrows) that migrate to zones of reduced fluid  
21 flow, leaving behind a Si-rich layer. Iron released during this dissolution step immediately  
22 precipitates as magnetite due to local oxidizing conditions favored by the constant renewal of water  
23 that characterizes zones of high fluid flow (Andreani *et al.*, 2009). **c)** Magnesite precipitates at the  
24 expense of serpentine surface in zones of reduced fluid flow due to local supersaturation and more  
25 reducing conditions. Released silica may precipitate as amorphous silica interstitially to magnesite  
26 aggregates, but increasing pH as the carbonation proceeds leads to its solubilization and subsequent  
27 migration in the serpentine mesh (orange dashed arrows). **d)** Silica, in aqueous form, propagates in  
28 the serpentine mesh and finally precipitates in amorphous opal A subsequently evolving to opal CT,  
29 chalcedony and ultimately quartz. Complete serpentine replacement in a magnesite+silica  
30 assemblage may occur. Alternatively, the growing of magnesite may lead to the closure of initial  
31 porosity, preventing additional fluid circulations and thus ending the carbonation process before  
32 going to completion (Hövelmann *et al.*, 2012).

1 **Table**

2

3 **Table 1:** *In situ* concentration measurements by  $\mu$ -XRF for serpentine, magnesite, silica,  
4 sepiolite, magnetite and chromite used for the calculation of quantitative maps shown in Figure 6  
5 (see also electronic supplements, Figure S6).

6

7	Elements	Serpentine	Magnesite	Silica	Magnetite	Sepiolite	Chromite
8	MgO	40.25	46.84	-	-	24.72	12.34
9	Al <sub>2</sub> O <sub>3</sub>	0.41	-	-	-	0.46	23.22
10	SiO <sub>2</sub>	43.60	0.39	100.00	-	62.66	0.08
11	K <sub>2</sub> O	-	-	-	-	0.01	0.01
12	CaO	-	0.54	-	-	0.2	0.07
13	TiO <sub>2</sub>	0.01	-	-	-	0.02	-
14	Cr <sub>2</sub> O <sub>3</sub>	0.02	-	-	-	0.02	48.20
15	MnO	0.03	-	-	-	0.67	0.20
16	FeO	2.51	0.02	-	100.00	0.55	15.82
17	NiO	0.17	-	-	-	0.11	0.06
18	CO <sub>2</sub>	-	52.21	-	-	-	-
19	H <sub>2</sub> O	13.00	-	-	-	10.58	-
20	<b>Total</b>	100.00	100.00	100.00	100.00	100.00	100.00

18

19 **Supplementary figure captions**

20

21 **Figure S1:** Raman spectra of brown chalcedony (Silica #2, Figure 4) and white chalcedony  
22 (Silica #3, Figure 4). Both only differ by the intensity of the moganite band (501) which is  
23 significantly higher in the white chalcedony.

24

25 **Figure S2:** RGB (for Red-Green-Blue) map calculated by the superposition of the three phase  
26 maps shown in Figure 7. One color is attributed to each phase (Red: Magnesite; Green: Serpentine;  
27 Blue: Silica), in order to highlight the relationship between mineral phases. Pixels characterized by  
28 a mix of green and blue show the progressive silicification of the serpentine mesh. Greenish to  
29 brownish pixels (mix of red and green) correspond to partially carbonated serpentine grains.

30

31 **Figure S3:** Progressive silicification of the serpentine mesh illustrated by Raman  
32 spectroscopy.

33

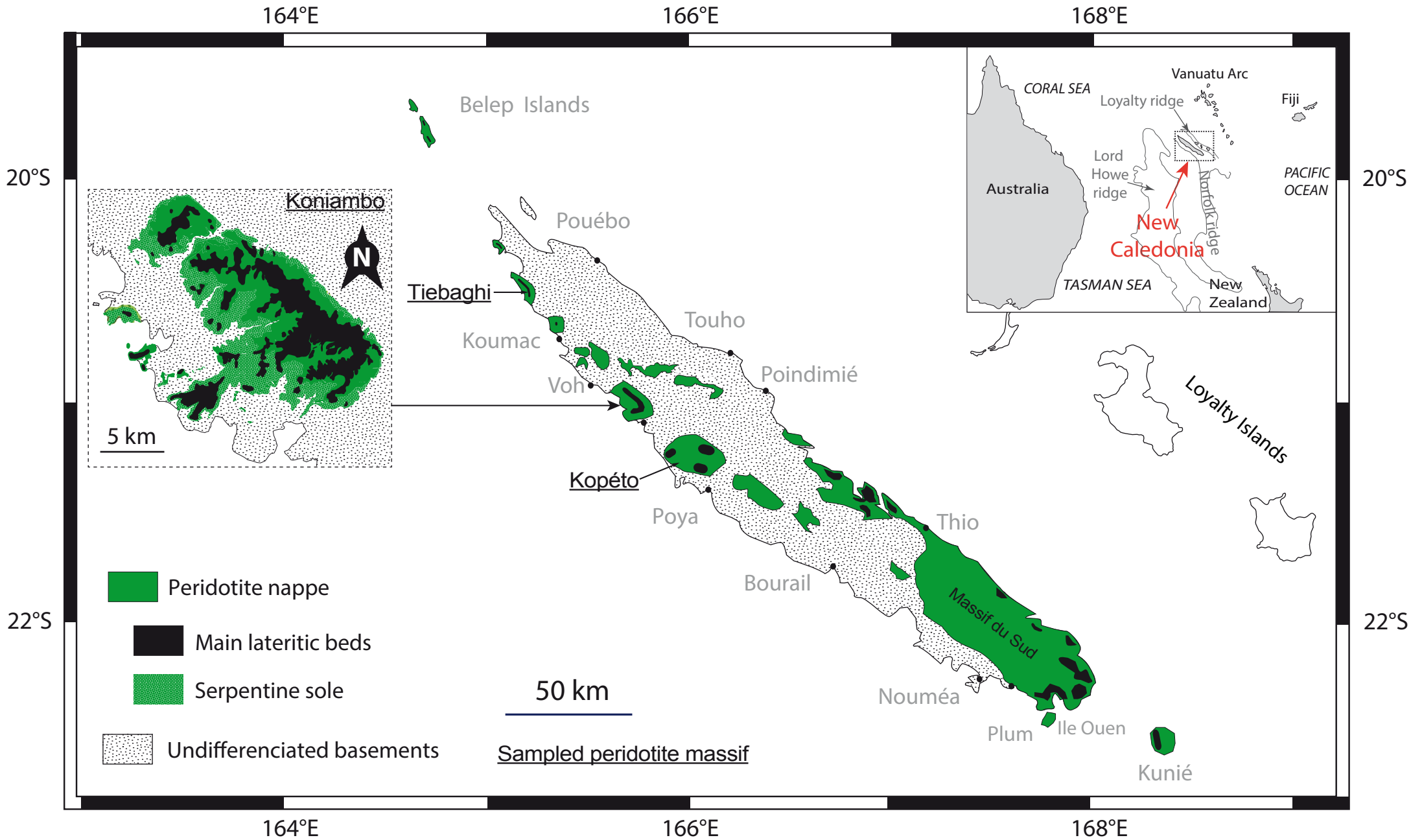


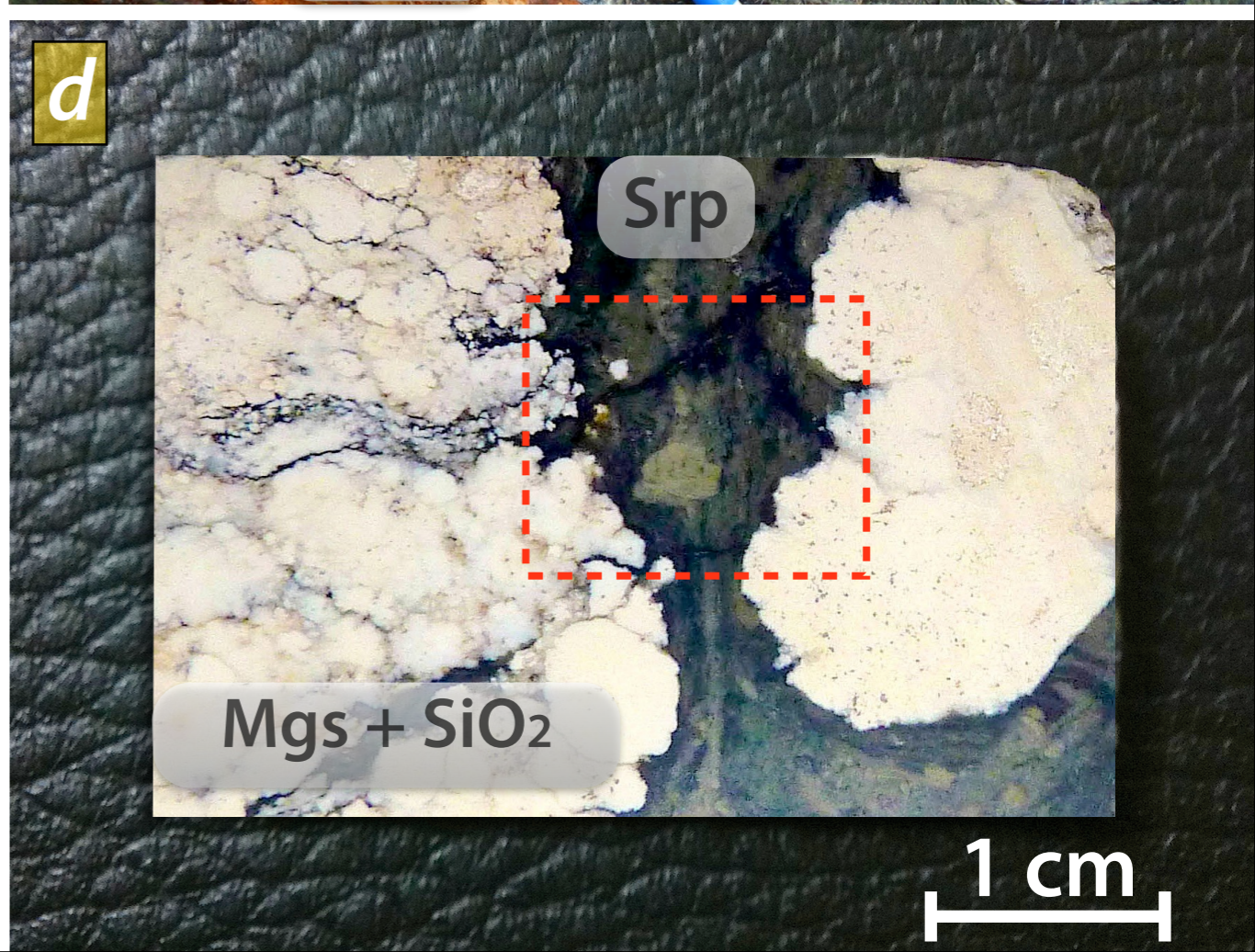
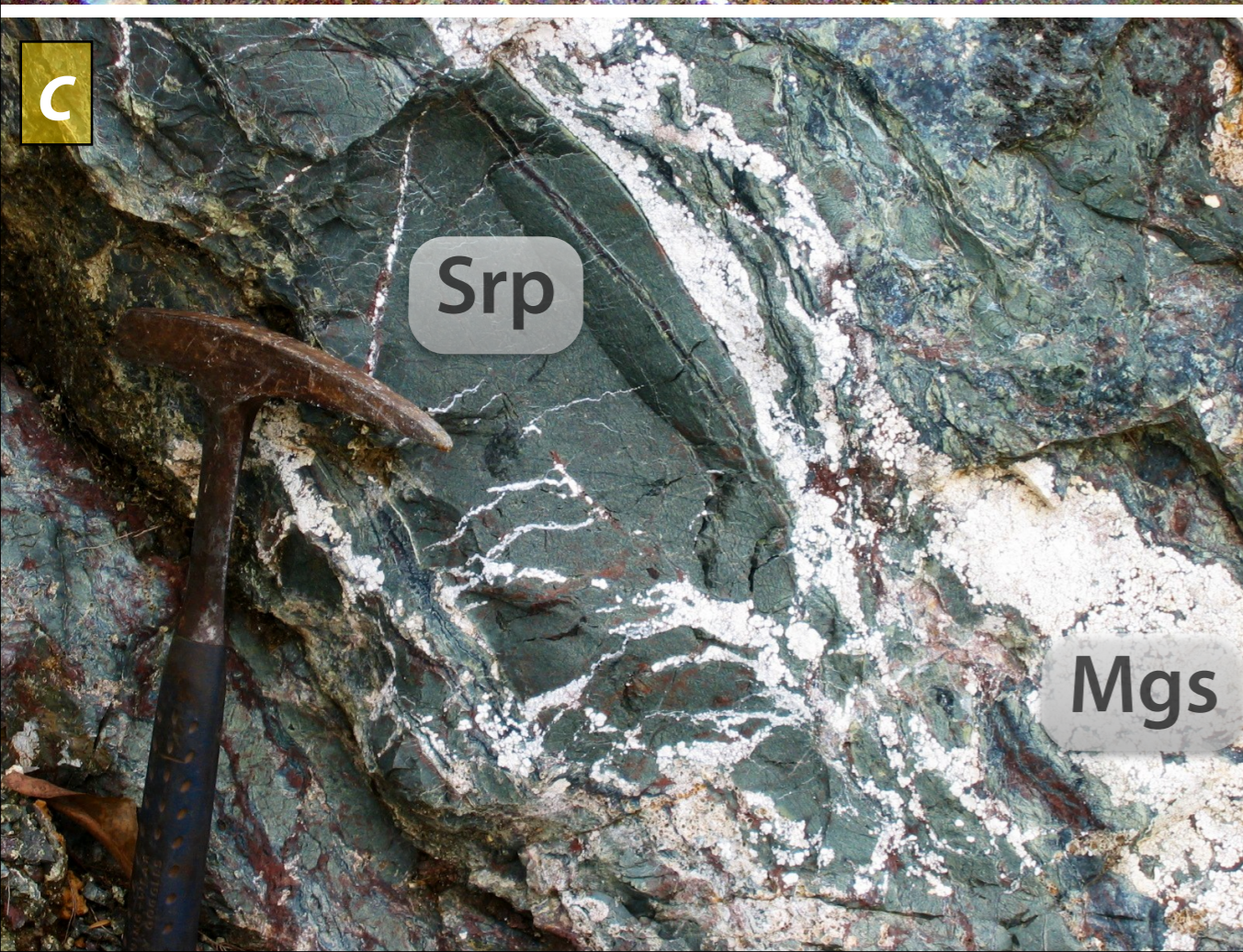
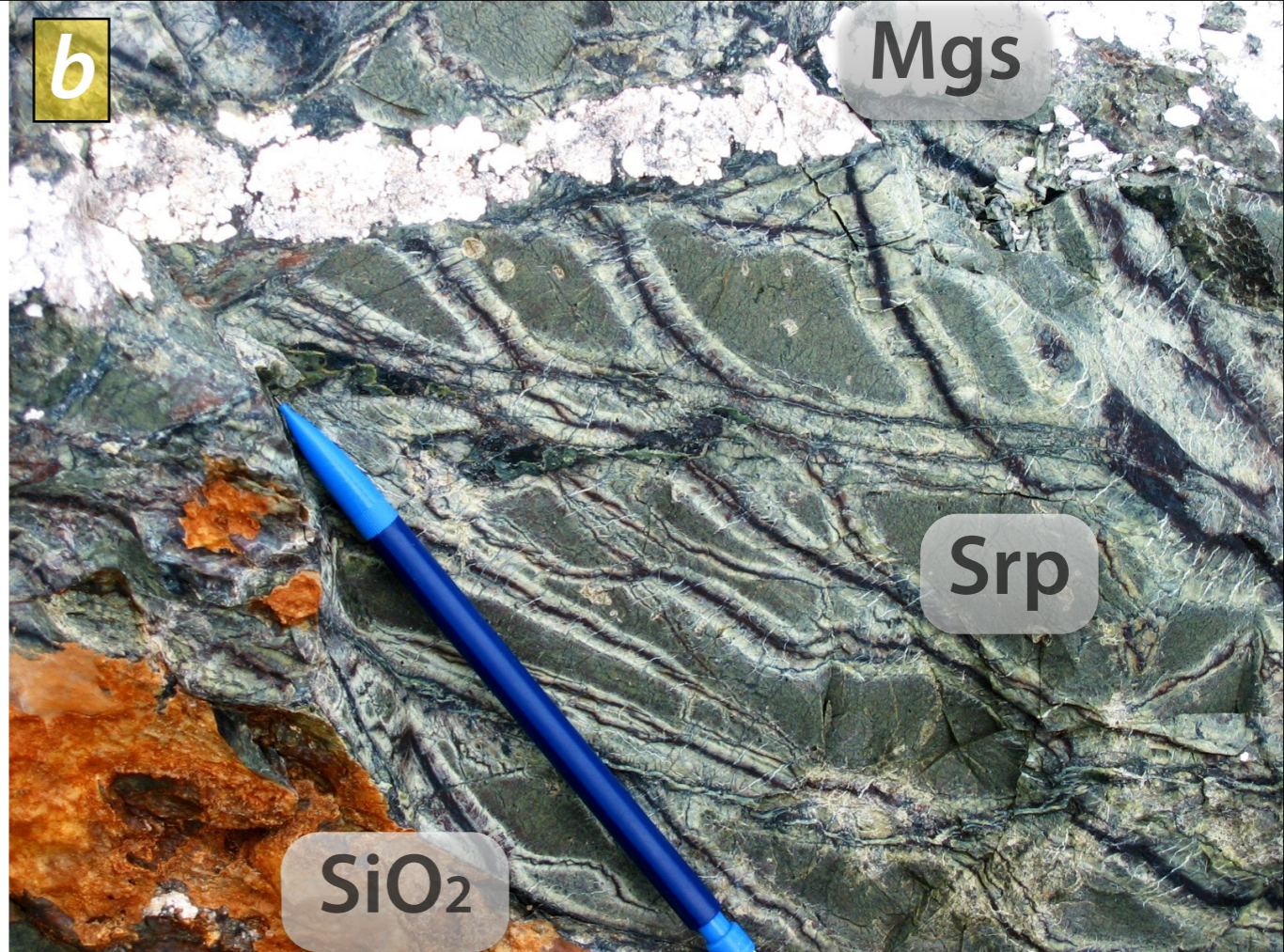
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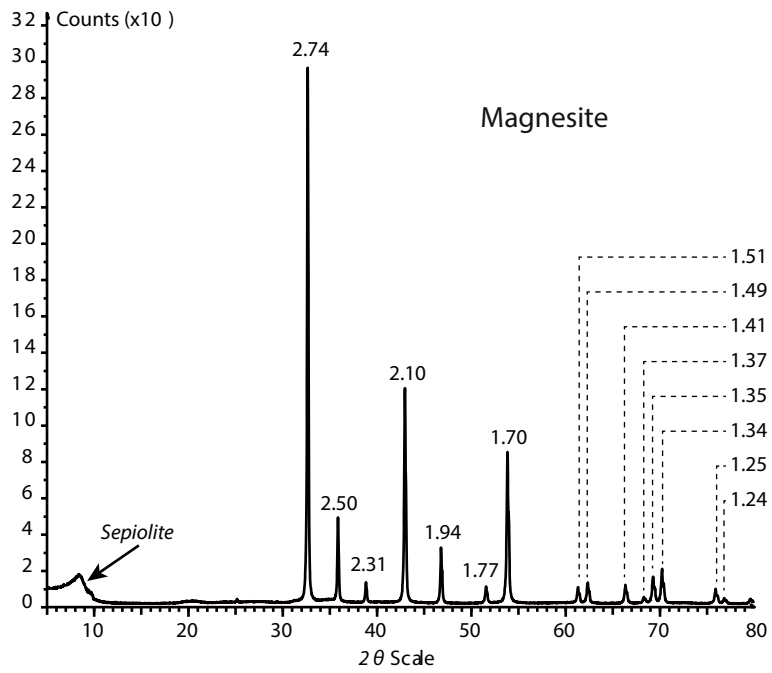
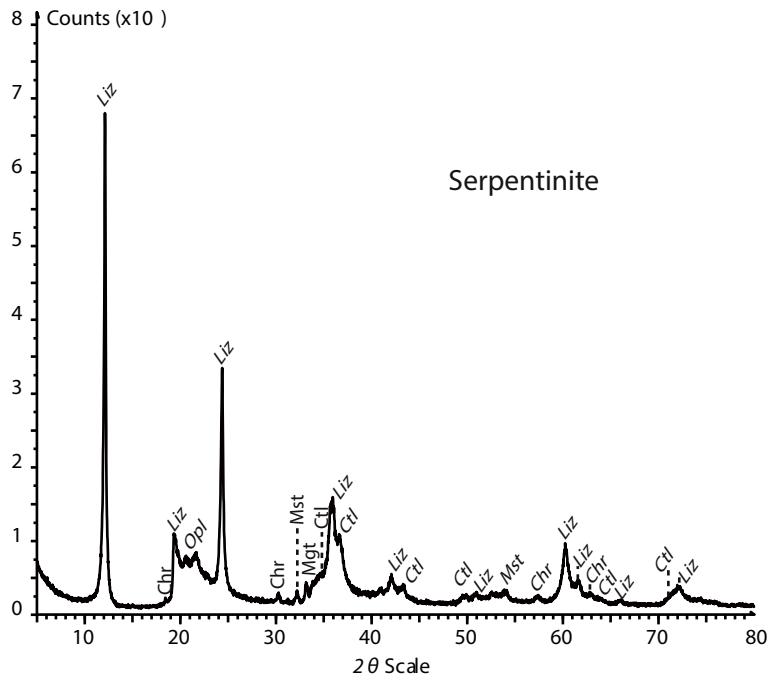
**Figure S4:**  $\mu$ -XRF maps of elemental concentrations based on ROI (region of interest) measurement at element K-edge. These maps correspond to raw data used for the calculation of mineral phase maps (in %) shown in Figure 6 and Figure S5, and quantitative maps shown in Figure 6 and Figure S6.

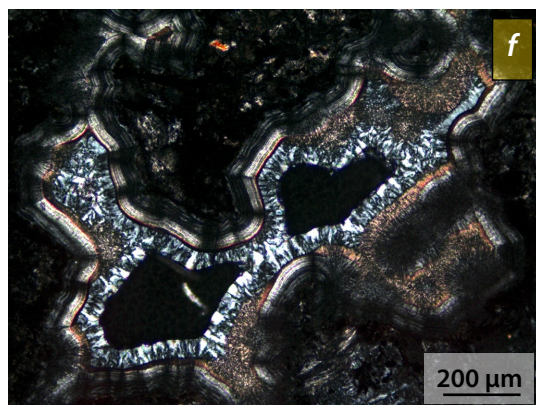
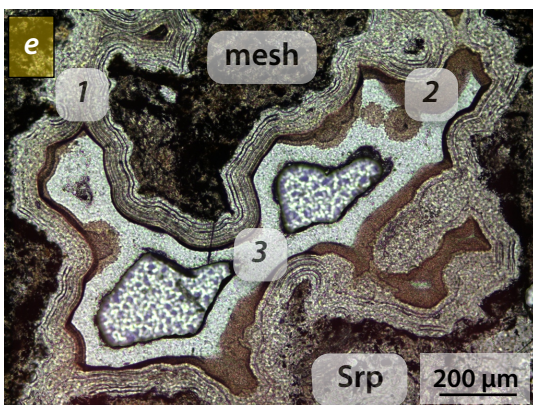
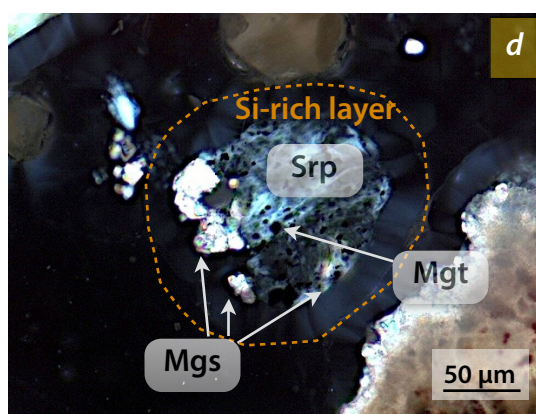
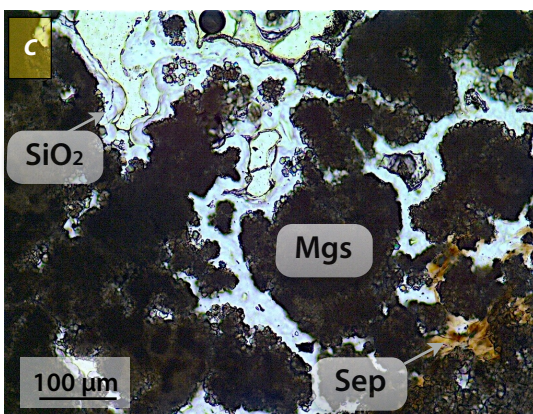
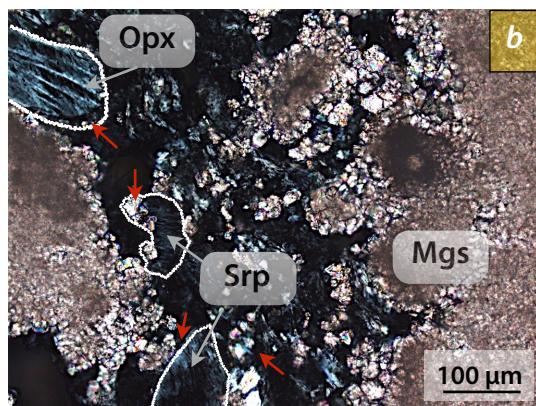
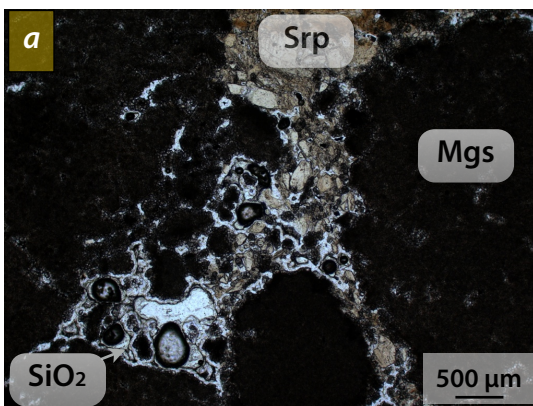
**Figure S5:** Maps of mineral phases calculated on the basis of  $\mu$ -XRF measurements (EDAX Eagle III). The «Total» map corresponds to the sum of phase maps and is used to verify the consistency of the calculation (each pixel of the map have to be close to 100 %).

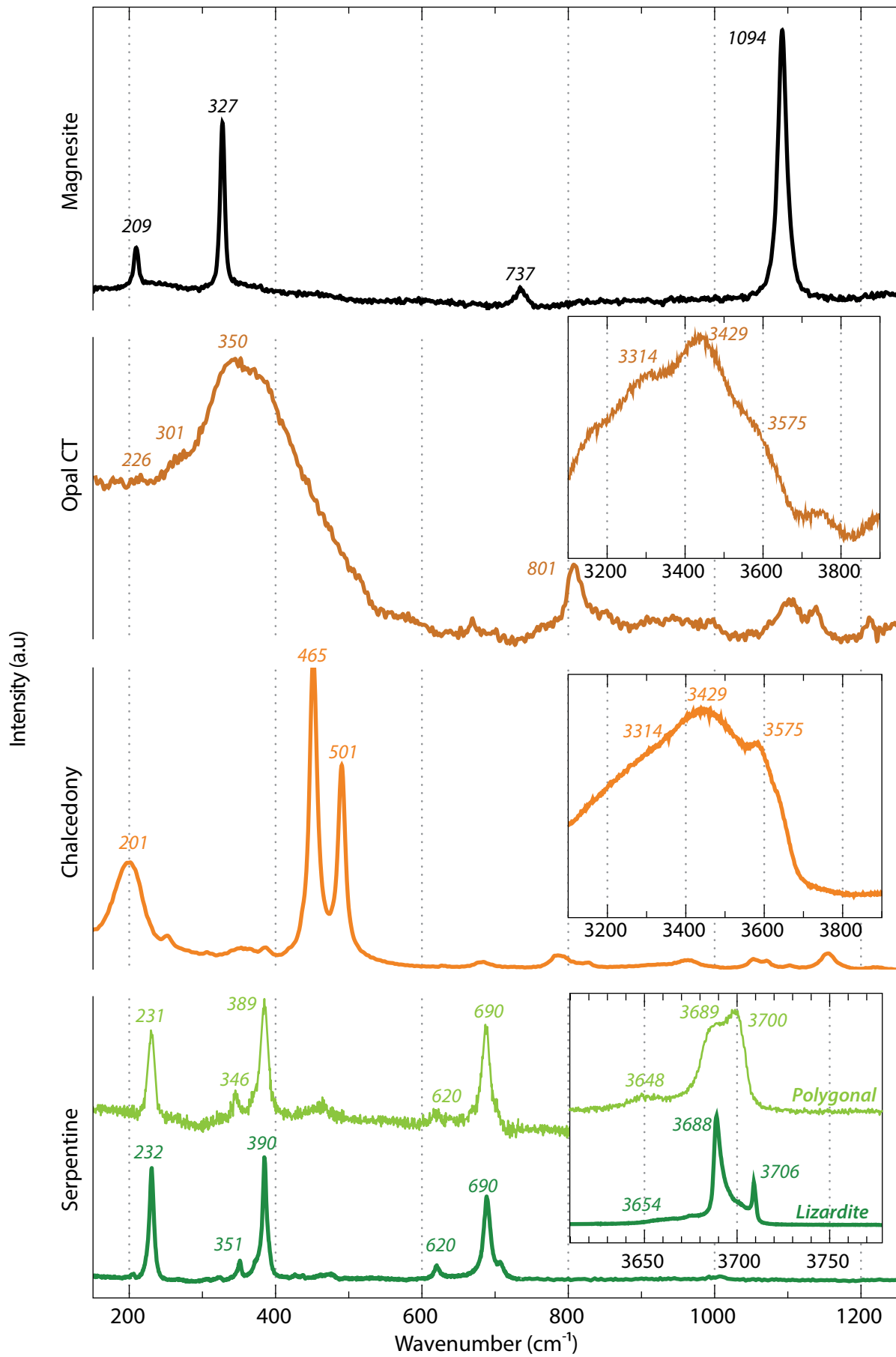
**Figure S6:** Quantitative maps (in wt.%) calculated on the basis of  $\mu$ -XRF measurements (EDAX Eagle III). The «Total» map corresponds to the sum of quantitative maps. Map of H<sub>2</sub>O +CO<sub>2</sub>, elements that cannot be measured by  $\mu$ -XRF, is calculated by subtracting the Total map to 100.

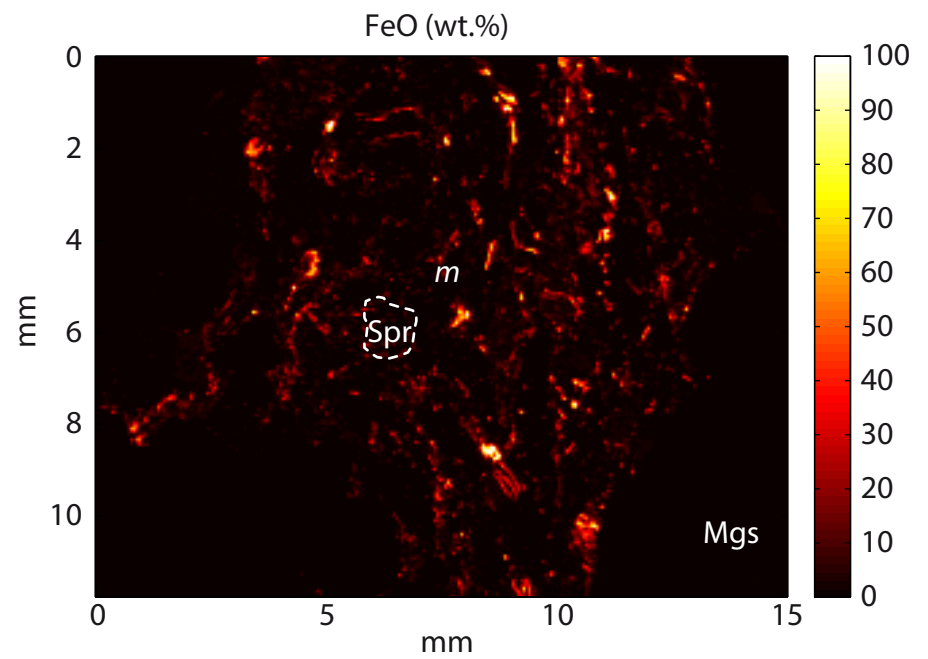
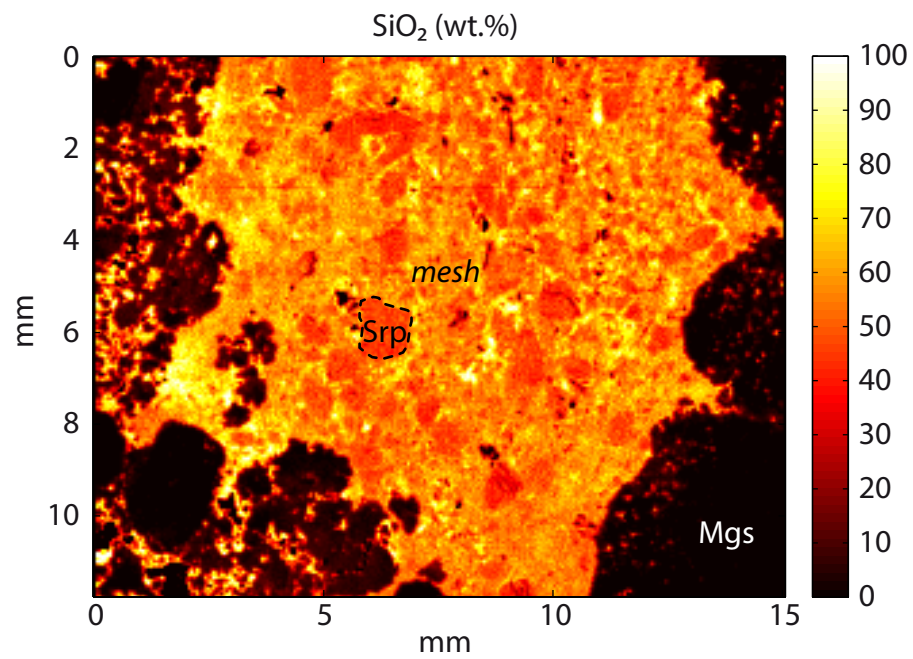
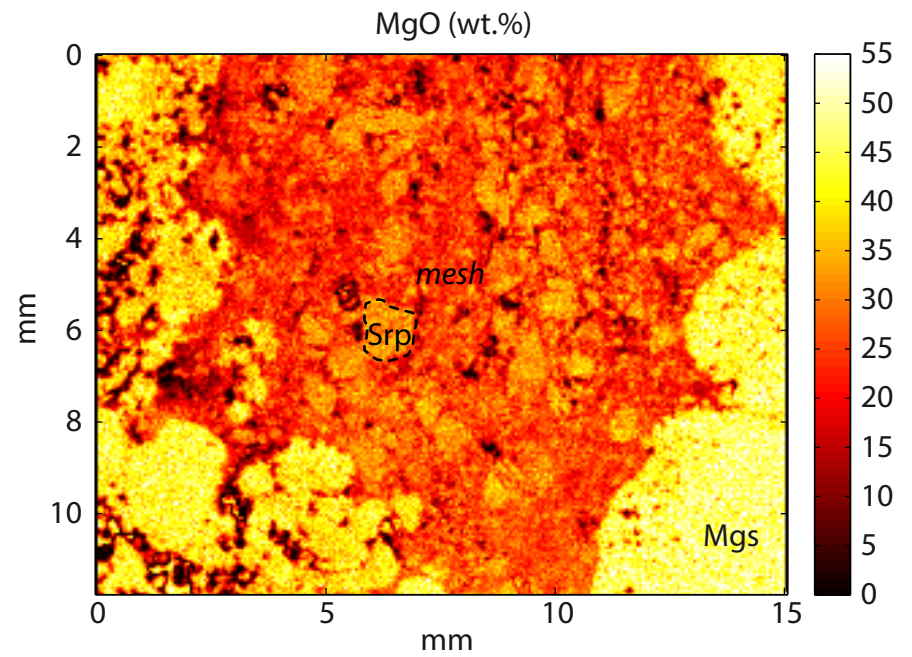
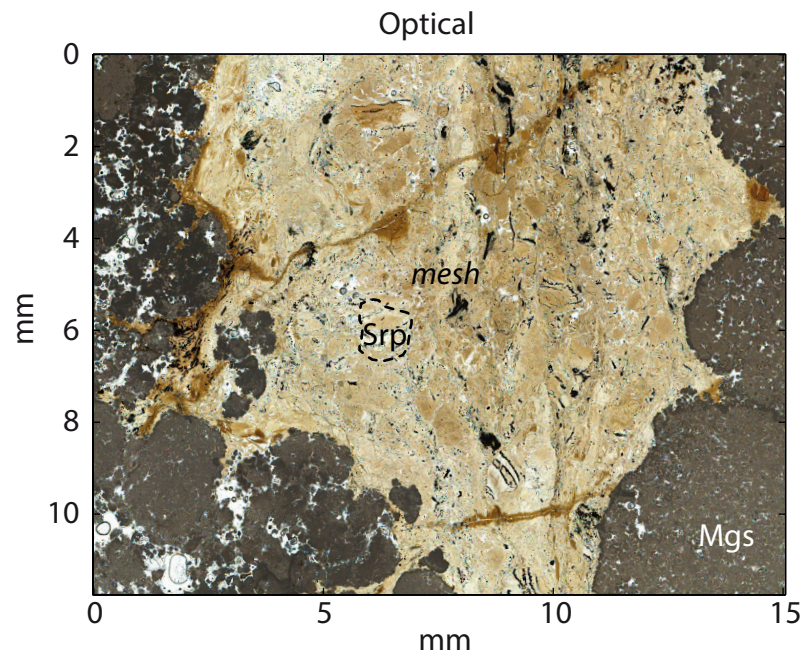


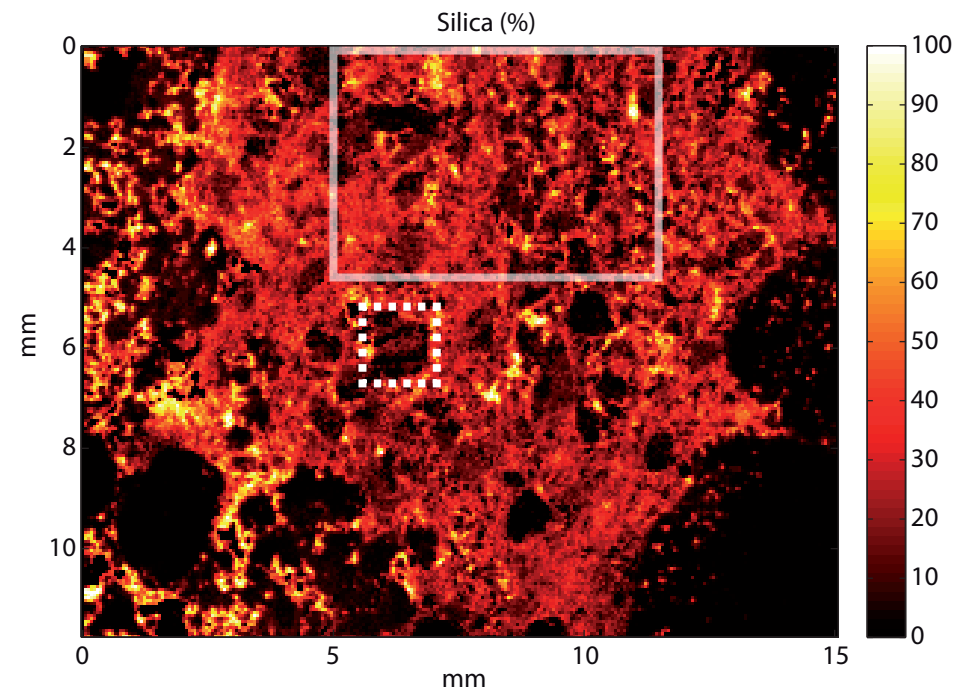
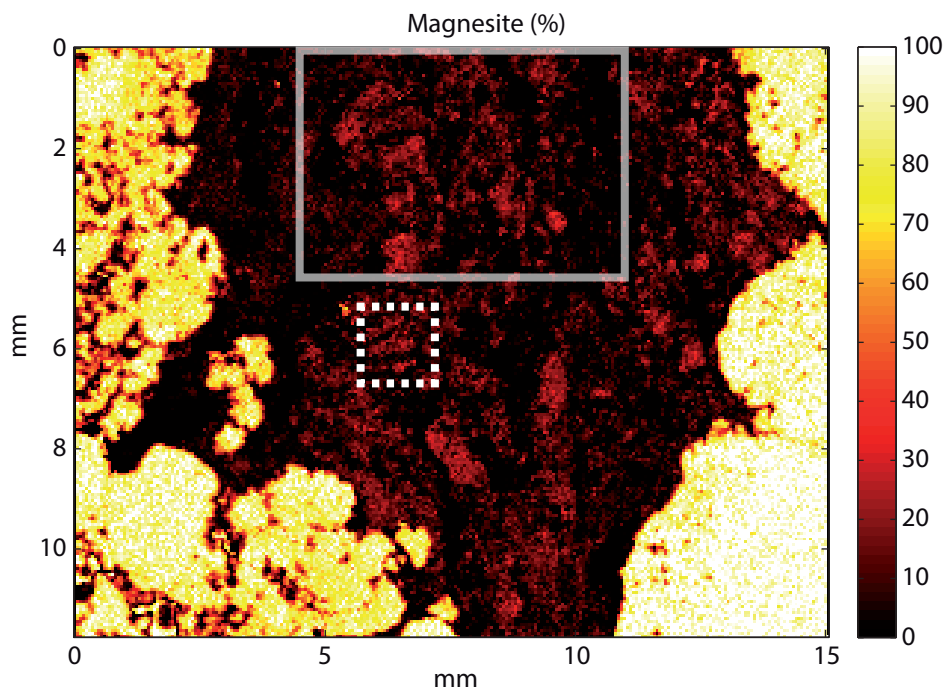
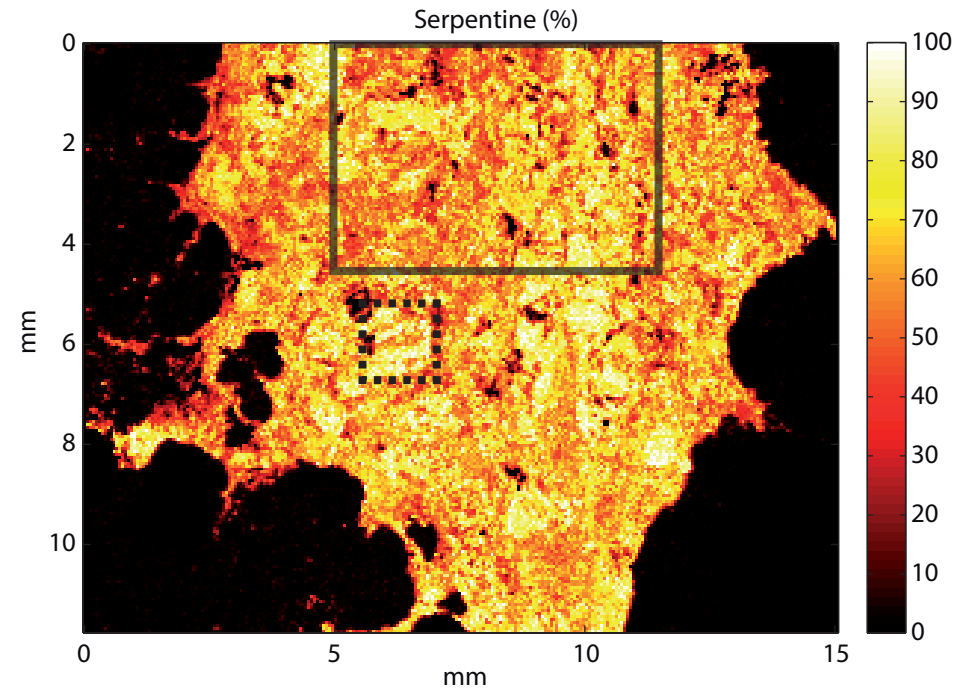
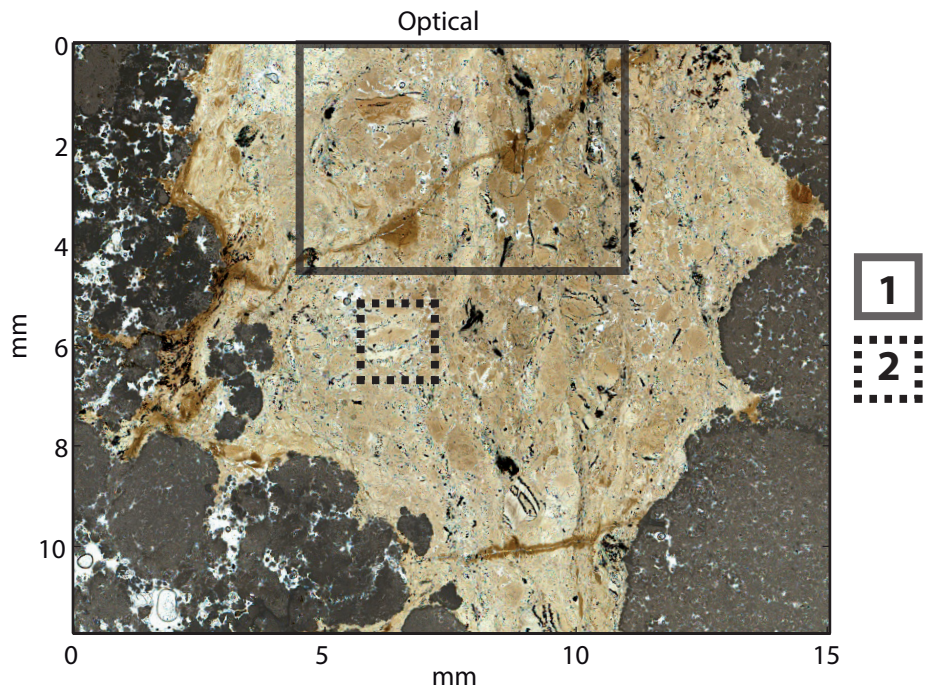






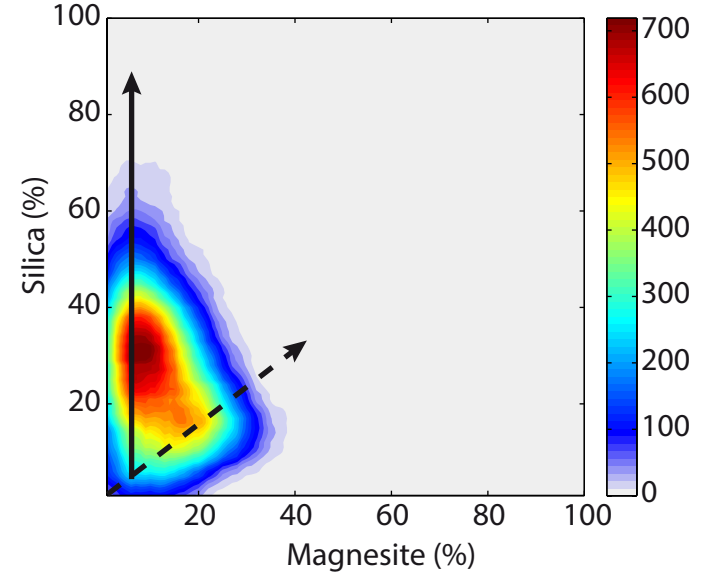
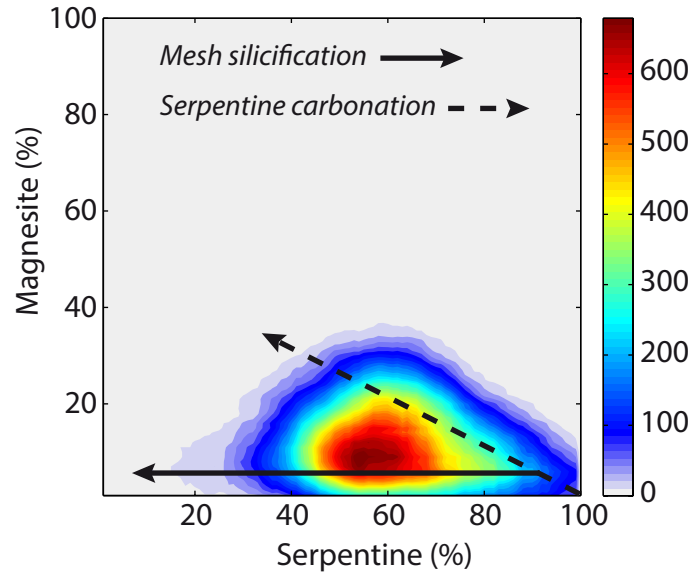
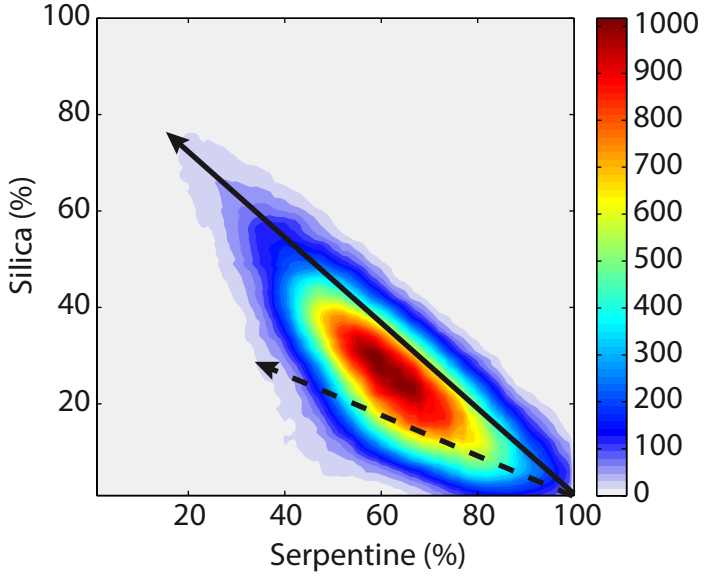




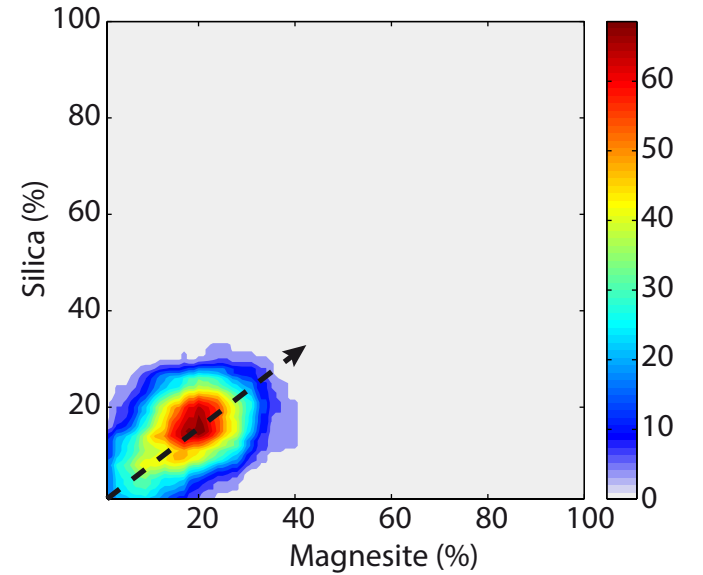
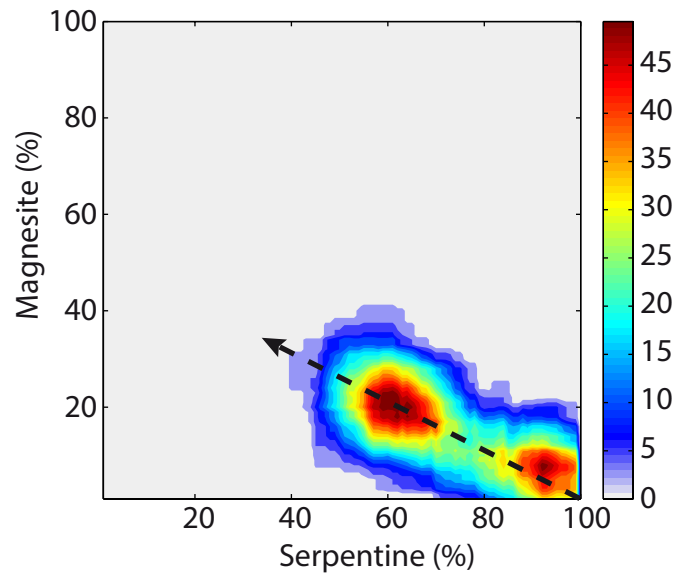
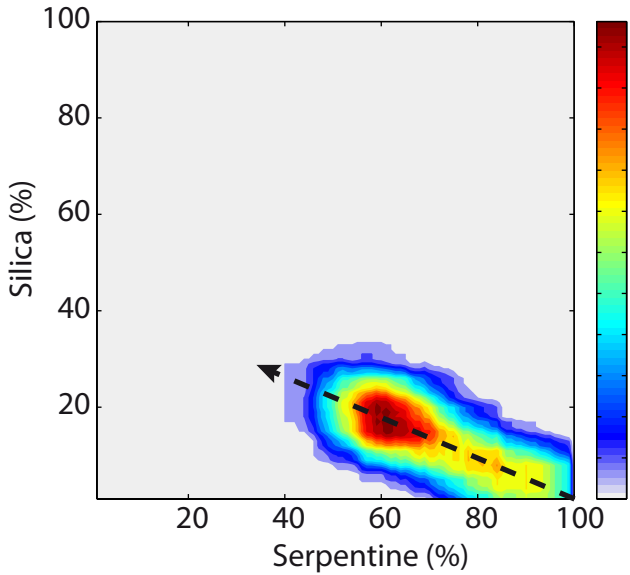


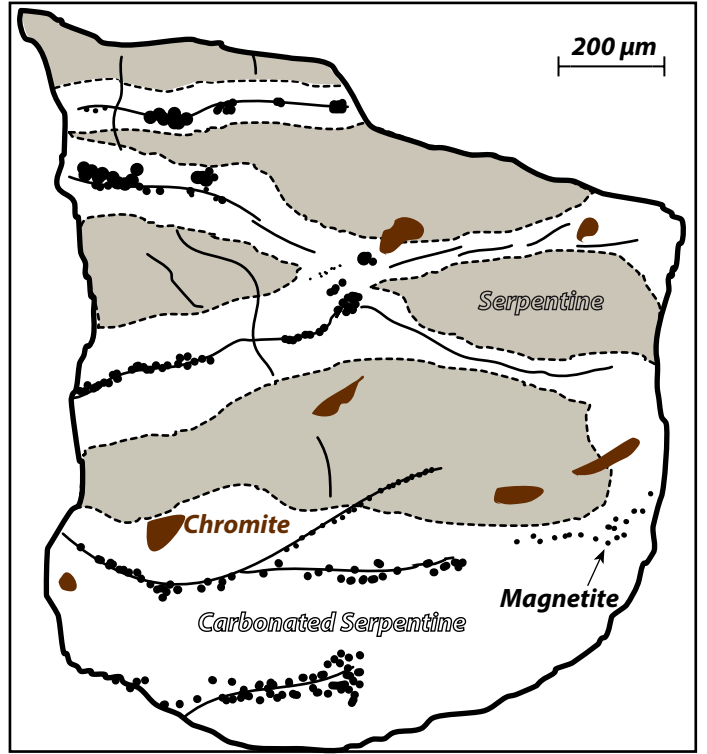


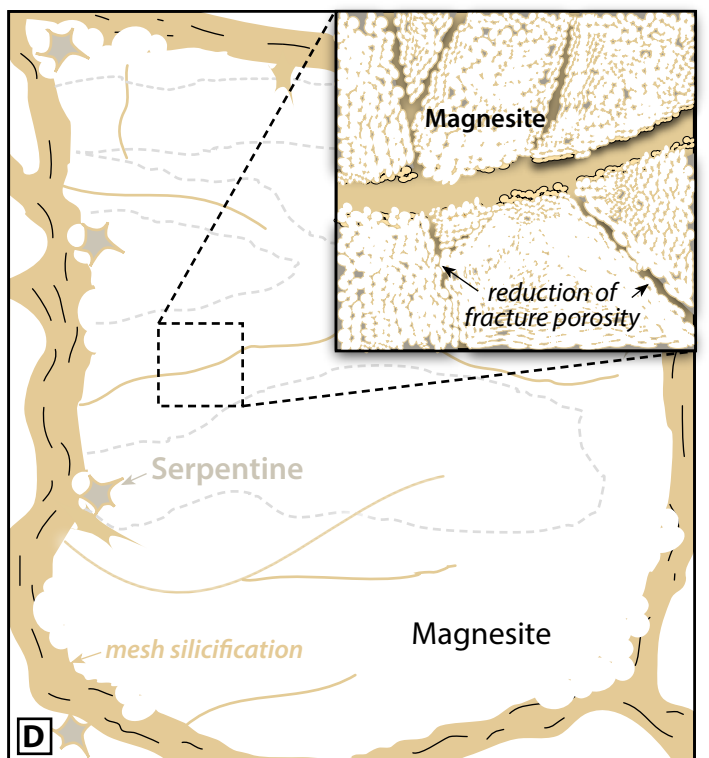
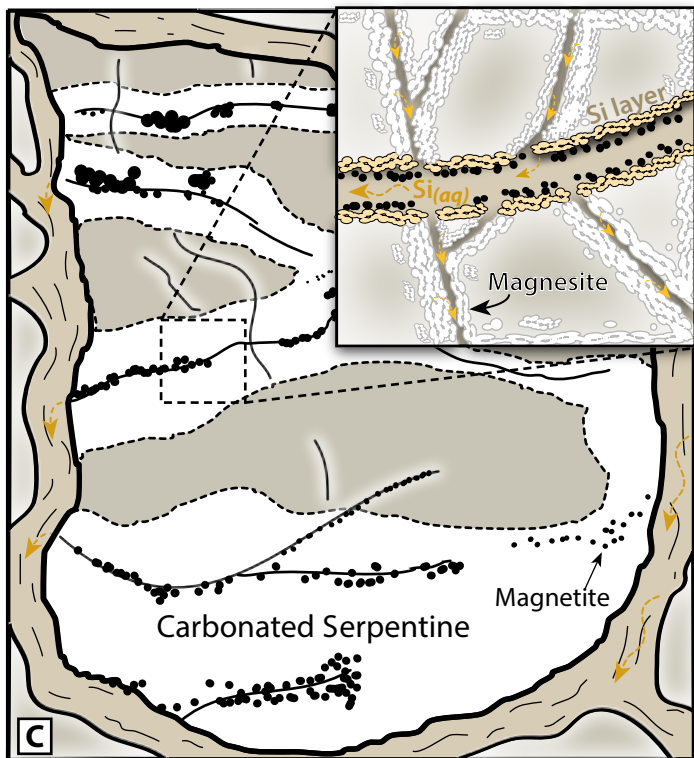
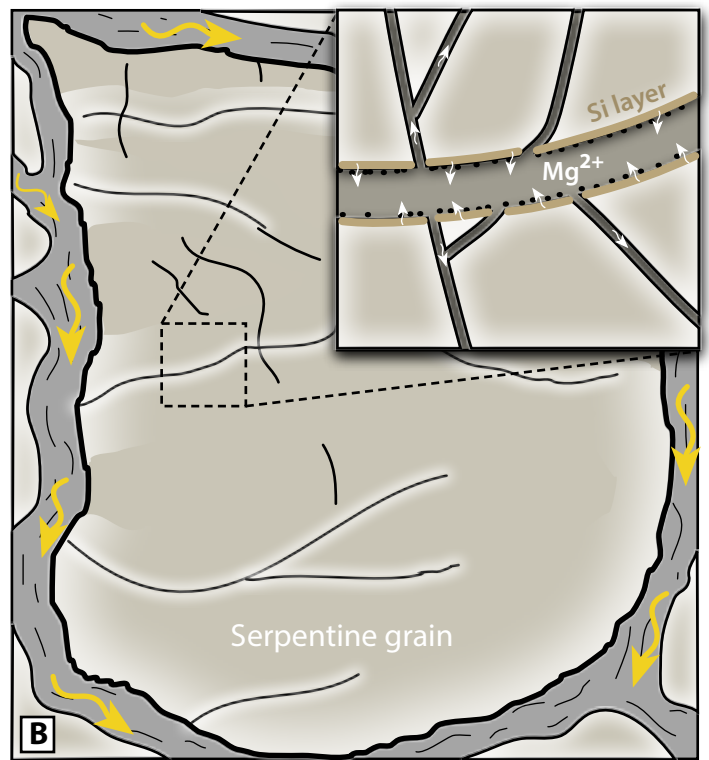
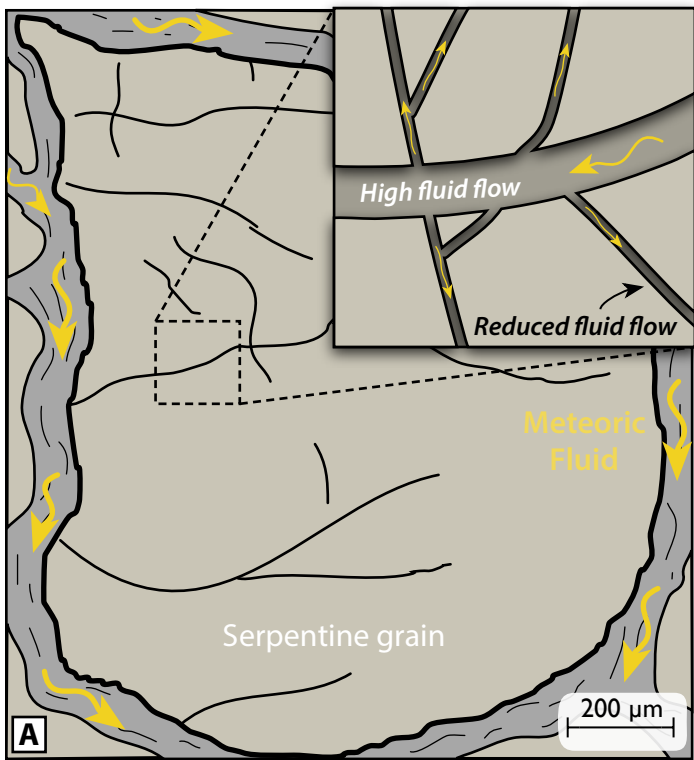
**Region 1 (n = 9200)**

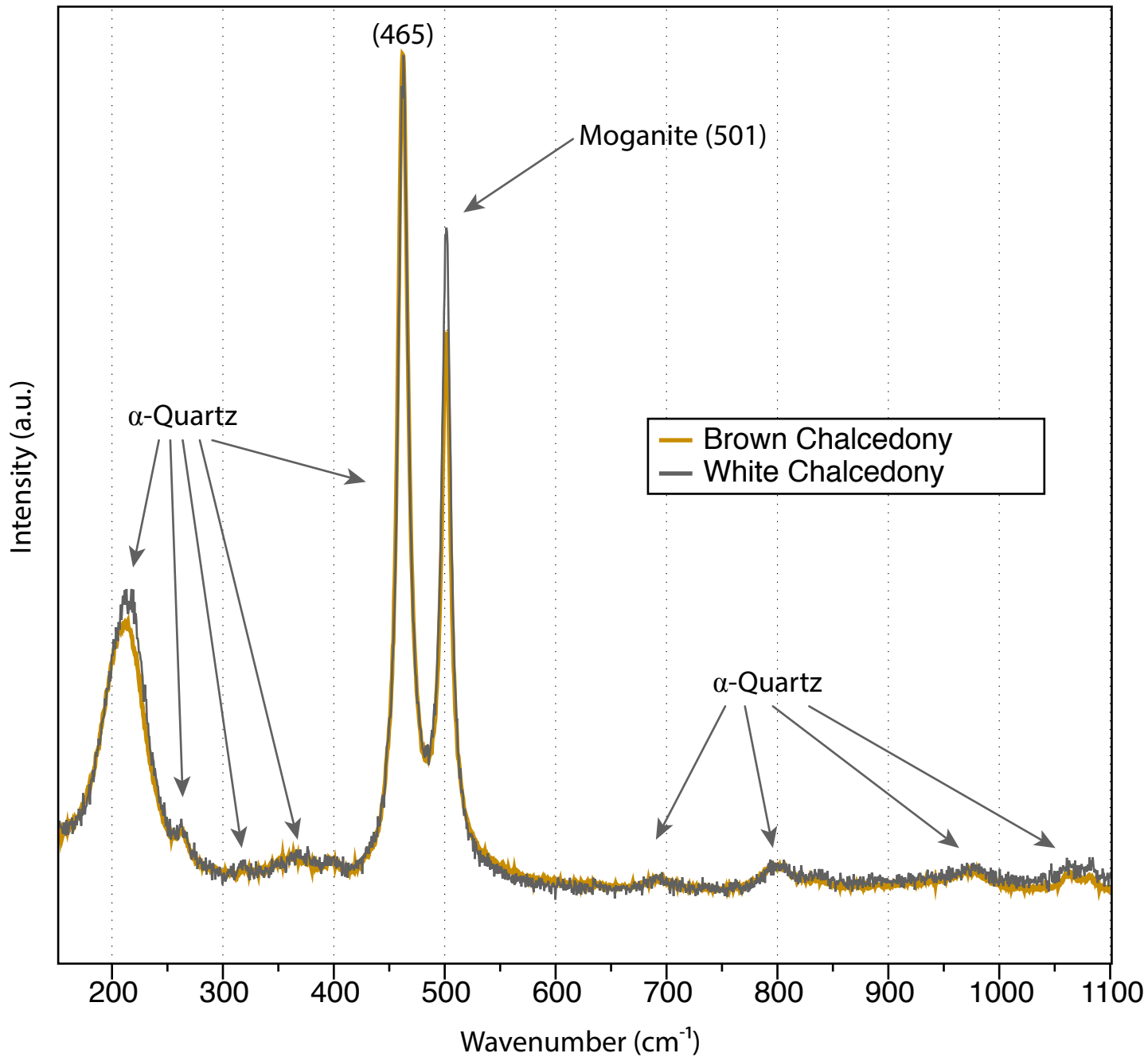


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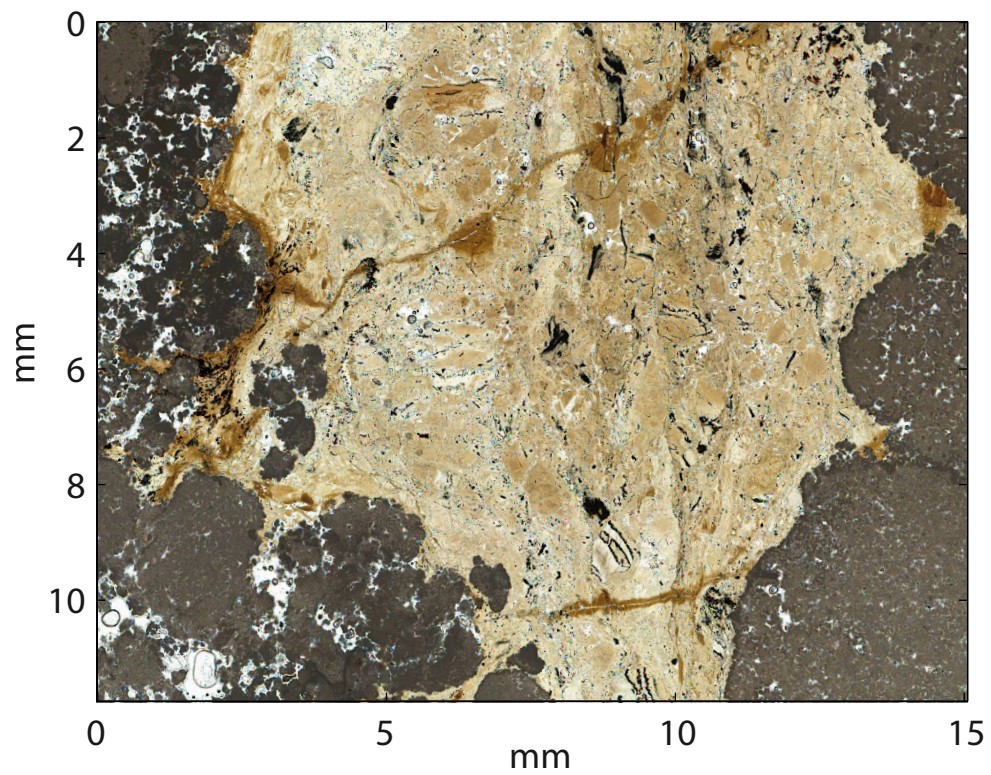








Optical



RGB : Magnesite/Serpentine/Silica

