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# 1 Mineralizations and transition metal mobility driven by organic carbon during

| 2 | low-temp | erature | serpentii | nization |
|---|----------|---------|-----------|----------|
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#### 17

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- 20 *Keywords*:
- 21 serpentinization
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- 23 organic carbon
- 24 metal mobility
- 25 organomineralization
- 26 supergene ore formation
- 27
- 28 Abbreviations:

- 29 bast: bastite
- 30 C-XANES: X-ray absorption near edge structure at the carbon K-edge
- 31 EDXS: energy dispersive X-ray spectrometry
- 32 EMPA: electron microprobe analysis
- 33 EPS: extracellular polymeric substances
- 34 Fe-ox: iron oxide
- 35 FIB: focused ion beam
- 36 H-adr: andraditic hydrogarnet
- 37 HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy
- 38 HR-TEM: high resolution transmission electron microscopy
- 39 pol-spt: polygonal and polyhedral serpentine
- 40 SAED: selected area electron diffraction
- 41 SEM: scanning electron microscopy
- 42 spl: spinel
- 43 spt: serpentine
- 44 STEM: scanning transmission electron microscopy
- 45 STXM: scanning transmission X-ray microscopy
- 46 TEM: transmission electron microscopy
- 47

## 48 ABSTRACT

Serpentinization is known to provide substantial amounts of energy in the form of molecular 49 hydrogen along with a suite of abiotic organic compounds of low molecular weight (mainly as short 50 chain alkanes and carboxylic acids), all sustaining the development of microbial ecosystems in the 51 mantle-derived crust. The latter have a cryptoendolithic life style and are responsible for (i) the 52 local formation of biomass and of organic metabolic byproducts and (ii) the production of 53 54 extracellular polymeric substances which organize the community in the form of a biofilm at the surface of the rock-forming minerals. In accordance, whatever their origin, organic compounds can 55 be diverse and widespread in the shallow oceanic crust where they undergo hydrothermal 56 degradation and remobilization through fluid circulations. Here we show that organic carbon is 57 directly involved in low temperature serpentinization reactions (< 200°C). Fine scale investigations 58 of microbial niches hosted in serpentinites from the Mid-Atlantic ridge were performed using 59 scanning and transmission electron microscopy along with scanning transmission X-ray 60 61 microscopy. They suggest that organic films generated at mineral surfaces as a consequence of rock colonization may influence the nature and structure of the serpentinization products as well as the 62 mobility and speciation of transition metals as the reaction progresses. This likely constitutes an 63 efficient yet poorly considered mechanism in active serpentinizing systems with possible 64 implications for ore formation associated with the alteration of ophiolitic massifs and subsurface 65 storage. 66

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#### 68 **1. Introduction**

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It was long assumed that the net flux of most hydrothermally-derived metals to the ocean was negligible because abundant polymetallic particulate phases, predominantly in the form of Fesulfides and Fe-oxyhydroxides, form when vent fluids discharge at the seafloor (German et al., 1991; Mottl and McConachy, 1990). Nonetheless, the importance of hydrothermally-derived metals for ocean biogeochemistry has been revisited during the last two decades. Enrichments in dissolved

iron compared to predicted solubility values were reported in non-buoyant hydrothermal plumes, 75 suggesting that a fraction of metals escapes from precipitation (Field and Sherrell, 2000; Resing et 76 al., 2015; Statham et al., 2005). Organic compounds were shown to bind and stabilize dissolved 77 metals (Bennet et al., 2008; Hawkes et al., 2013; Sander and Koschinsky, 2011; Toner et al., 2009) 78 or solid sulfur and iron particles (Fitzsimmons et al., 2017; Klevenz et al., 2011; Lau and Hsu-Kim, 79 2008), overall facilitating their long-range oceanic transport (Fitzsimmons et al., 2017; Sander and 80 Koschinsky, 2011; Sands et al., 2012; Wu et al., 2011). Organic-metal complexation reduces the 81 reactivity of the metallic species and prevents metal redox changes, precipitation or scavenging into 82 or onto particulate phases (Bennett et al., 2008). Therefore, it significantly increases dissolved metal 83 concentrations in hydrothermal fluids and associated fluxes of metals to the global ocean (Resing et 84 al., 2015; Sander and Koschinsky, 2011). Although iron has been one of the most investigated 85 metals due to its role as a limiting nutrient (Bennet et al., 2008; Boyd and Ellwood, 2010; Sander 86 and Koschinsky, 2011; Toner et al., 2009), hydrothermally-derived chromium, copper, and 87 88 manganese have also been shown to be transported to the non-buoyant hydrothermal plume and across oceans as complexes stabilized with organic ligands (Fitzsimmons et al., 2017; Resing et al., 89 2015; Sander et al., 2007). 90

91 While their compositions and sources are not fully determined, these metal-stabilizing organic complexes are postulated to form from organic ligands available in excess in the plume 92 93 source regions (Bennett et al., 2008, 2011). In addition to the small fraction of thermally-reworked marine dissolved and particulate organic matter that outlived hydrothermal circulation (Hawkes et 94 95 al., 2015; Rossel et al., 2017) and organic compounds mobilized during hydrothermal alteration of 96 organic carbon-rich sediments (e.g., Kawka and Simoneit, 1987), these plume enrichments in organic matter were postulated to derive from (i) chemosynthetic microbial activities occurring at or 97 close to vents (Lang et al., 2006), (ii) hydrothermal degradation of vent-hosted biological material 98 99 (Simoneit et al., 2004) and (iii) abiotic hydrothermal synthesis (Konn et al., 2015 and references therein). All these processes form a large diversity of organic compounds pervasively entrained into 100 buoyant hydrothermal plumes through chimney venting or diffuse flow. However, life is not limited 101

to ocean, sediment or seafloor hydrothermal vent ecosystems and both the ultramafic and mafic 102 oceanic subseafloors were also recognized as potentially-large microbial habitats (Mason et al., 103 2010; Ménez et al., 2012; Santelli et al., 2008). In particular, the serpentinization of mantle-derived 104 rocks is known to provide substantial amounts of molecular hydrogen through the reduction of 105 water coupled to the oxidation of ferrous iron-bearing minerals. This in turn favors the formation of 106 organic compounds such as short chain alkanes and carboxylic acids. Together with molecular 107 hydrogen, these organic compounds provide, despite the alkaline pHs associated with 108 serpentinization reactions, valuable energy sources for the development of cryptoendolithic 109 microbial ecosystems in the mantle-derived crust (Schrenk et al., 2013). These ecosystems can 110 locally form biomass and organic metabolic byproducts along with extracellular polymeric 111 112 substances (EPS) allowing to organize the community in the form of a biofilm at the surface of the rock-forming minerals. Abiotic organic synthesis and biological metabolic activities thus coexist in 113 these environments, the complex interplay between both pathways during the multistage 114 hydrothermal alteration of the oceanic crust being however far from being understood. In 115 accordance, organic compounds can be diverse in origin and nature and pervasively present in the 116 shallow oceanic crust where they undergo hydrothermal degradation and remobilization through 117 fluid circulations (Pasini et al., 2013). Serpentinization reactions also affect redox-sensitive 118 transition metals resulting in the formation of oxides, sulfides, native elements and alloys, 119 depending on the chemical and physical conditions of the system. Organic complexation may also 120 impact the fate of metals at depth in the oceanic lithosphere and play a role during fluid-rock 121 interactions that has never been considered yet. 122 Ménez et al. (2012) provided evidence for cobalt enrichments associated with the presence 123

Menez et al. (2012) provided evidence for cobart enfrictments associated with the presence
 of carbon-rich phases in a serpentinite from the equatorial Mid-Atlantic Ridge (MAR). These
 organic phases were inherited, at least partly, from the presence of former ecosystems identified
 through remnants of complex organic molecules. The organic phases were also suggested to
 mediate the formation of polygonal and polyhedral serpentines (pol-spt) precipitating in the cavities
 of andraditic hydrogarnets (H-adr). Overall, this suggested a potential role of organic compounds in

the regulation of elemental fluxes in the serpentinizing oceanic lithosphere. Here, we further 129 investigate the occurrences of polyhedral and polygonal serpentine along with organic-metal 130 associations in this MAR serpentinite by using a suite of high-resolution techniques, which includes 131 electron microprobe analysis (EMPA), scanning and transmission electron microscopies (SEM and 132 TEM) coupled with energy dispersive X-ray spectrometry (EDXS), scanning transmission electron 133 microscopy (STEM), and scanning transmission X-ray microscopy (STXM) associated with X-ray 134 absorption near edge structure at the carbon K-edge (C-XANES). The spatially-resolved 135 characterization of transition metals and organic carbon down to the nanometer scale highlights (i) 136 the involvement of an organic gel in the formation of pol-spt, (ii) a differential distribution of 137 metals depending on the nature of the associated organic phases and (iii) the precipitation of 138 139 nanometer-sized metallic oxides within the organic phases.

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## 141 **2. Material and methods**

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## 143 2.1. Geological setting

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The studied rock was dredged during the joint Russian-Italian cruise S22 (R/V Akademik 145 Nikolaj Strakhov) in the vicinity of the Sierra Leone area, a magma starved, slow-spreading region 146 of the equatorial MAR at 5-7° N (Figs. 1a-b). The non-transform Sierra Leone fault is located 147 between the Bogdanov and the Strakhov fracture zones (7°10' N and 4° N, respectively). The rift 148 zone is morphologically characterized by isolated basins, tectonically separated by transverse uplifts 149 150 (3000-2100 meters below seafloor) made up by outcrops of tectonized and altered deep-seated gabbros and mantle rocks (Peyve et al., 2003; Sharkov et al., 2012). Sample S2232-17 was collected 151 on one of the most elevated blocks during the dredge haul S2232, which was carried out on an 152 unsedimented ridge flanks of crust aged < 1 My (dredging interval: 6°08.9' N-33°25.4' W-6°09.1' 153 N-33°25.4' from 2250 to 2000 meters below seafloor). About 200 kg of variably serpentinized 154 peridotites were recovered during this haul (Peive et al., 2003). 155

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## 157 2.2. Sample petrography

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The studied rock corresponds to a fully serpentinized peridotite similar to rocks usually 159 found in serpentinized mantle along Mid-Ocean ridges. Primary mineralogy has been tentatively 160 inferred on the basis of the isomorphic mineral substitution. Prior to serpentinization, the rock 161 primarily consisted in olivine + orthopyroxene + clinopyroxene + chromian-aluminous spinel 162 revealing a spinel field equilibrated harzburgite (with theoretical modal clinopyroxene < 1%). Only 163 few relics of those primary minerals can be found. They include clinopyroxenes, partially-preserved 164 chromite cores derived from the chromian-aluminous spinel and rare olivine kernels (Pasini, 2013). 165 As shown in Fig. 1c, the high temperature (> 200°C; Klein et al., 2014) hydrated paragenesis is 166 composed of lizardite and magnetite, both after olivine, forming a characteristic mesh texture. 167 Serpentine after olivine is also found around spinel remnants. Fine-grained lizardite, commonly 168 defined as bastite, pseudomorphically replaces orthopyroxene. Chains or clusters of subhedral 169 microgeode-like and raditic hydrogarnets (10-40 µm in size) are crystallized in, or very close to, the 170 bastitized orthopyroxene along exsolution lamellae or microfractures (Fig. 1d). They are locally 171 stretched or, alternatively, coalesce with one another and are often associated with iron oxides. H-172 adr are commonly found in serpentinites and usually grow over bastite under high pH and high Ca<sup>2+</sup> 173 activity, low O<sub>2</sub> fugacity, low silica activity and temperature below 200°C (Frost and Beard, 2007 174 and references therein; Plümper et al., 2014). Late serpentine veins of millimeter widths crosscut 175 the whole rock, attesting for several stages of serpentinization (Fig. 1c). 176

177

178 2.3. Sample preparation

179

Conventional petrographic thin sections were prepared for EMPA. SEM observations were
 performed on both silicon carbide-polished and unpolished, resin-free chips of sawn rock. TEM and
 STXM require electron and X-ray transparent samples, respectively, i.e., measuring at least less

than ~100 nm in thickness. For this purpose, ultrathin focused ion beam (FIB) sections were milled 183 using the FIB dual beam facility FEI Strata DB 235 operating at the IEMN (Lille, France). Resin-184 free chips were beforehand coated with gold in order to reinforce the protection of the surface and 185 limit ion implantation into the samples. Regions of interest were covered with a platinum strap and 186 then excavated from both side of the Pt strap using a 30 kV Ga<sup>+</sup> beam, emitted from a Ga liquid 187 metal ion source operating at 7 to 1 nA. Further thinning to few tens of nanometers was obtained 188 with a glancing angle beam at low current (~100 pA). FIB foils have been repeatedly used to study 189 organic compounds within rocks with limited damages (e.g., Bassim et al., 2012; Benzerara et al., 190 2005; Bernard et al., 2009; Lepot et al., 2009). 191

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193 2.4. Electron microscopy

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SEM observations were performed on Au-coated, polished and unpolished, resin-free chips 195 using a Zeiss SUPRA 55 VP field emission microscope (Service Commun de Microscopie 196 Electronique à Balayage, UPMC, Paris, France). Beam accelerating voltage ranged between 15 kV 197 (for backscattered electron images, microanalyses and chemical maps) and 1 kV (for high resolution 198 secondary electron images). Images were collected using secondary electron detectors (Everhart-199 Thornley or InLens) and a backscattered electron detector (AsB). EDXS analyses were carried out 200 with a PGT Sahara spectrometer. Chemical maps were acquired and processed using the Spirit<sup>®</sup> 201 software. Spectra were fitted at each hyperspectral map point to produce elemental distributions. 202 203 TEM observations, high resolution-transmission electron microscopy (HR-TEM) and 204 selected area electron diffraction (SAED) were performed on ultrathin FIB sections using JEOL 2100 microscopes operating at an accelerating voltage of 200 kV (IMPMC, Paris, France and 205 Centro Interdipartimentale Grandi Strumenti, Modena, Italy). Both microscopes are equipped with a 206 207 LaB<sub>6</sub> filament. EDXS analyses were performed using a JEOL detector at IMPMC and an Oxford INCA 100 detector at CIGS. 208

209 TEM images and STEM maps were also acquired on ultrathin FIB sections using a JEOL

| 210 | 2100F microscope equipped with a field effect gun and operating at 200 kV (IMPMC, Paris,                |
|-----|---|
| 211 | France). High-angle annular dark-field (HAADF)-STEM was used with a focused electron beam of            |
| 212 | ~1 nm for Z-contrast imaging (Z referring to the atomic number). STEM-EDXS analyses were                |
| 213 | performed using a JEOL detector equipped with an ultrathin window allowing the detection of low-        |
| 214 | Z elements.   |
| 215 | When necessary, SEM and TEM images were further processed with the ImageJ software                      |
| 216 | (Schneider et al., 2012) for contrast and brightness adjustment.  |
| 217 |   |
| 218 | 2.5. Electron microprobe analysis   |
| 219 |   |
| 220 | EMPA were performed on carbon-coated petrographic thin sections using the Cameca                        |
| 221 | SXFive installed at CAMPARIS (Université Pierre et Marie Curie, Paris, France). Operating               |
| 222 | conditions were 10 kV and ~10 nA. Analyses were acquired in punctual mode.                              |
| 223 |   |
| 224 | 2.6. Synchrotron-based scanning transmission X-ray microscopy   |
| 225 |   |
| 226 | STXM and associated C-XANES analyses were performed at the branch line 5.3.2.2                          |
| 227 | (STXM Polymer beamline; Kilcoyne et al., 2003) of the Advanced Light Source (Lawrence                   |
| 228 | Berkeley National Laboratory, USA). A zone plate was used to monochromatize and focus the X-            |
| 229 | ray beam produced by the synchrotron radiation to a spot size of $\sim 25$ nm. The ultrathin FIB foils  |
| 230 | were scanned in the x-y directions at fixed photon energy to produce 2D images. The x-y plane           |
| 231 | refers to the plane perpendicular to the incident X-ray beam direction. The transmitted X-rays were     |
| 232 | detected a few hundreds of microns behind the sample. Energy calibration was carried out using the      |
| 233 | well-resolved peak of gaseous CO <sub>2</sub> at 294.96 eV. Carbon speciation maps with a 90 nm spatial |
| 234 | resolution were acquired under He atmosphere by collecting image stacks over the energy range           |
| 235 | 275-340 eV with a theoretical energy resolution of ~0.1 eV. Counting time was 1 ms per image.           |
| 236 | The image contrast results from differential absorption of X-rays, which depends on the chemical        |

composition of the sample. Images stacks were aligned using two dimensional cross correlation and
processed using STACKLab, a Matlab<sup>©</sup> STXM data analysis script collection. This routine was also
used to process energy-filtered images and extract XANES spectra at the carbon K-edge in order to
document the bonding environment of carbon for the pixels of interest.

241

242 **3. Results** 

243

3.1. Polyhedral and polygonal serpentine formation from hydrogarnet dissolution mediated by an
organic gel

246

Euhedral dissolution pits are often found as piercing the surface of the andraditic 247 hydrogarnets present in the S2232-17 serpentinite as shown by SEM (Fig. 2a) also highlighting 248 large cavities inside H-adr (Supplementary Fig. 1). This suggests that dissolution process affected 249 the hydrogarnets, as also proposed by Ménez et al. (2012). EMPA provided for H-adr a mean 250 formula of Ca<sub>2.71</sub>(Fe<sub>1.61</sub><sup>3+</sup>, Ti<sub>0.01</sub>, Al<sub>0.17</sub>, Cr<sub>0.03</sub>, Mg<sub>0.02</sub>)(Si<sub>2.92</sub>O<sub>10.93</sub>)(OH)<sub>1.07</sub> (Supplementary Table 1). 251 252 Pits and cavities are filled by polyhedral serpentine spheroids and polygonal serpentine rods (polspt), both showing a wide size range (few tens to 1,000 nm - mean 350 nm; Fig. 2c). Pol-spt show 253 an enrichment in Cr (mean 1.18±0.89 wt.%) and to a lesser extent in Al (mean 4.32±2.53 wt.%) and 254 255 Fe (mean 4.96±0.91 wt.%,) in comparison with the high temperature serpentines (i.e., the bastite, the mesh serpentine and the serpentine contouring spinels) (Fig. 3, Supplementary Fig. 2 and 256 Supplementary Table 1). Conversely, the pol-spt display low concentrations in cobalt (0.07±0.12 257 wt.%) and manganese  $(0.06\pm0.08 \text{ wt.}\%)$  while nickel reaches concentrations similar to what was 258 found for the four other types of serpentine (0.22±0.25 wt.%). When numerous, pol-spt appear to 259 fracture the H-adr crystals (Fig. 2b). This peculiar type of serpentine is also visible around the 260 hydrogarnets, filling various-sized voids around the H-adr spheroids (Figs. 2a, c and e), with a clear 261 indentation of the spheroids within the surrounding fine-grained bastite (Fig. 2f). H-adr crystals and 262 263 part of the bastite were progressively replaced by pol-spt that also spread inside the surrounding

remaining bastite through tiny veins (Figs. 2g-h).

The identification of pol-spt serpentines was confirmed by TEM and SAED (Figs. 4 and 265 5d). As described in literature (Baronnet and Devouard, 1996, 2005; Baronnet et al., 2007; 266 Andreani et al., 2008; Cressey et al., 2008, 2010), polyhedral serpentine is composed of triangular 267 facets made of lizardite basal planes showing lateral continuity from one sector to another and 268 forming tiny "onion like" geodesic spheroids (Fig. 4). The core of the spheroids usually hosts a 269 270 small fibre contoured by the triangular facets. Given that the geodesic spheroids have the simplest formulation as icosahedra, the inner cavity is possibly defined by this geometric limit. Polygonal 271 serpentine crystallizes as tiny fibres composed of concentric lizardite layers wrapped around the 272 fibre axis and made of 15 or 30 sectors (Fig. 5d). The fifteen-sector fibres are the smallest (< 400 273 nm - mean 350 nm), whereas the thirty-sector ones are larger (up to 1,000 nm - mean 610 nm). 274 SEM and TEM analyses highlight a close connection between pol-spt and H-adr (Figs. 5a-275 b). The globular topography of the H-adr inner cavities where pol-spt grew suggests local 276 277 transformation of H-adr into spherical and coalescent pol-spt (Fig. 5a). TEM analyses of FIB foils milled on H-adr grains also show that the pol-spt enclosed in the branched and elongated 278 dissolution cavities are embedded in a carbon-rich phase also covering the H-adr walls (Figs. 5b, d-279 g). This is in agreement with SEM observations collected on resin-free chips showing the presence 280 of carbon veils within the H-adr cavities (Fig. 5c). The organic film has a gel-like appearance and 281 does not show any structure or atomic organization using HR-TEM. It presents very low wetting 282 angles with respect to the phyllosilicate and the hydrogarnet (Figs. 5b and d). TEM-EDXS analyses 283 highlight the presence of Mg, Si and to a lesser extent, Ca and Fe in the gel (Fig. 5e), likely 284 285 responsible for the brightness of the fluffy phase observed by HAADF-STEM (Figs. 5f-g). The organic nature of the carbon gel was further demonstrated by STXM coupled with C-XANES 286 spectroscopy. As displayed in Fig. 6e, the C-XANES spectrum of the carbon gel shows a major 287 288 peak at 288.6 eV, characteristic of carboxylic functional groups (Cody et al., 1998; Benzerara et al., 2004; Bernard et al., 2009). STXM mapping shows that this organic phase is spectroscopically 289 homogeneous (Figs. 6d-e). 290

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Carbon-rich areas are also found as large patches in H-adr inner cracks and fractures nearby 294 iron oxides which precipitated concomitantly with H-adr (Fig. 7a). These carbon-rich patches are 295 296 associated with a complex intergrowth of late stage serpentines including pol-spt among numerous nanometric to micrometric fibrous chrysotile-like aggregates (Figs. 7 and 8a). These felt-like 297 298 organic matter accumulations are associated with enrichments in transition metals, notably cobalt 299 (Fig. 8c; Ménez et al., 2012) but also manganese (Fig. 8b) and to a lesser extent iron and nickel (Figs. 9e-h, 10 and 11). These metals are strictly confined to the H-adr filling material and not 300 dispersed in the host groundmass although some metal-rich nanophases can also be suspected in the 301 bastite and the mesh serpentine, based on EMPA (Supplementary Fig. 2 and Supplementary Table 302 1). With the exception of Fe, none of those elements were detected in the carbon gel embedding the 303 304 pol-spt previously described in the branched and elongated dissolution cavities (Figs. 5 and 6). The felt presents an organic C-rich component with variable texture and porosity, finely 305 intermingled with various amounts of micro- to nano-crystallites. As an illustration, Fig. 9d (or 306 307 Supplementary Fig. 3 for an enlarged version of Fig. 9d) shows that polyhedral serpentine geodesic spheroids and polygonal serpentines are embedded in a foamy carbon gel presenting a vesicular 308 texture with gradients in the size of the vesicles. The foamy appearance can be a primary character 309 310 or alternatively can have been induced by degassing of a light fraction or by cavitation under vacuum during measurements. The significant decompression experienced during the recovery from 311 312 the seafloor can also be invoked. Variations of the texture seem however to be correlated with the presence/absence of transition metals, the gel texture being locally more massive when the carbon 313 and metal contents are respectively lower and higher (Fig. 9). The foamy C-bearing gel is 314 associated with the presence of Co and minor Mn, Ni, and Fe (Figs. 9d, g and 11). In contrast, Fig. 315

316 9b shows a dense carbon-bearing phase spotted by subnanometric electron-dense phases that were

317 identified as well-crystallized Co-oxides (Figs. 10a-b and 11), likely responsible for the enrichment

in Co shown in Fig. 8c. In this area, Mn, Ni and Fe are also present in the C-phase but at lower 318 concentrations (Figs. 9e-f and 11). Similarly, a compact carbon-poor and likely more crystalline 319 matrix displaying high Mn concentrations was identified in the upper part of Fig. 9d 320 (Supplementary Fig. 3), based on STEM-EDXS mapping (Fig. 9h). In this area, pol-spt spheroids 321 322 are locally surrounded by well-crystallized Mn/Fe crusts measuring about 50 nm in thickness (Figs. 10c-d and 11). The surrounding C-bearing matrix also presents high Mn, and to a lesser extent Fe, 323 Co and Ni concentrations (Figs. 9h and 10e-h). This is confirmed by the relatively high brightness 324 of the corresponding area by HAADF-STEM (Fig. 9h). In some locations, abundant nanometer-325 sized rods of Fe-(oxyhydr)oxides were also found among the tiny fibres of magnesium silicates 326 within the carbon gel (e.g., Fig. 9g). Overall, transition metals appear to be associated with the 327 carbon-bearing phase but selectively enriched in two domains characterized by high and low carbon 328 concentrations for the Co-rich and Mn-Fe(-Ni) enriched areas, respectively. 329 Energy-filtered STXM images and associated C-XANES spectra collected in the same areas 330 show that these chemically-heterogeneous organic carbon micro-domains display distinguishable 331 signatures (Fig. 12). Similarly to what has been found for the carbon gel embedding pol-spt in the 332 branched and elongated dissolution cavities (Fig. 6), the Mn-enriched regions display mainly 333 absorption features of carboxylic functional groups at 288.6 eV along with the presence at a lower 334 amount of aliphatic carbon at 287.7 eV (Cody et al., 1998; Benzerara et al., 2004; Bernard et al., 335 2009). A peak at 290.4 eV was also observed. According to Chan et al. (2009), it can be indicative 336 of carboxyl groups binding iron and possibly other metals. Compared to the Mn-enriched area, the 337 Co-rich foamy region shows increased and decreased levels in aliphatics and carboxyl functional 338

groups, respectively, plus minor aromatic or olefinic carbon at 285.1 eV.

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341 **4. Discussion and implications** 

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As hypothesized by Ménez et al. (2012), textural relationships provide evidence that both Hadr dissolution and bastite resorption came along with the crystallization of polygonal and

polyhedral serpentine around the andraditic hydrogarnets and within their dissolution cavities (Figs.
2 and 5a-b). The pol-spt genetic link with Cr-rich hydrogarnets is also supported by EMPA showing
enrichment of the pol-spt in Cr and to a lesser extent in Al and Fe in comparison with the hightemperatures serpentines (Fig. 3 and Supplementary Fig. 2). These elements could have been
inherited from both the parent H-adr and the bastite, this latter being likely the source of Mg for the
precipitation of pol-spt (Supplementary Fig. 2).

Dissolution has selectively affected the crystal cores and progressed radially toward the 351 grain rims (e.g., Figs. 5c and 7c and Supplementary Fig. 1). This process led to the formation of 352 large inner cavities interpreted by Ménez et al. (2012) as the result of a cryptoendolithic microbial 353 activity. Note that the origin of the organics found in these rocks is not discussed in the present 354 paper and readers are referred to Ménez et al. (2012) and Pasini et al. (2013) and to the extensive 355 discussions on organics' systematics that can be found within. Dissolution cavities provided the 356 open space required for polyhedral serpentine to form (Andreani et al., 2008), along with the 357 appropriate temperature conditions. Indeed, while the mesh serpentine, the bastite, and the 358 serpentine contouring spinels are representative of the static replacement of the high temperature 359 paragenesis during the first stages of serpentinization (> 200°C; Klein et al., 2014), the pol-spt are 360 instead representative of crystallization occurring after complete hydration of the host pyroxene. 361 Moreover, as discussed by Ménez et al. (2012), their precipitation after H-adr, which forms below 362 200°C (Frost and Beard, 2007; Plümper et al., 2014) attests for low-temperature conditions in 363 agreement with Andreani et al. (2008). These authors also suggest a general enrichment in trivalent 364 cations as a stabilizing factor for pol-spt nucleation. This requirement is met here when considering 365 366 the aluminum and chromium concentrations in pol-spt, as measured by EMPA (Supplementary Fig. 2 and Supplementary Table 1). For iron, while pol-spt display with the vein spt the highest 367 concentrations, we did not succeed in determining the ferric iron content of pol-spt based on EMPA 368 (Pasini, 2013). Nonetheless, as H-adr iron is solely in the form of Fe(III), it may suggest that at least 369 a fraction of the pol-spt iron is present as Fe(III). 370

371 In our study, we observe that polyhedral and polygonal serpentines crystallized together in

spatially-restricted areas, hence suggesting that they likely derive from the same process. Polygonalserpentine has been viewed by some authors as a more stable phase compared to chrysotile, or

alternatively, as an analogous of the polyhedral serpentine (Cressey et al., 2008, 2010).

Accordingly, polygonal and polyhedral serpentines may both form from a similar precursor through 375 376 different growth mechanisms. Based on textural and microstructural criteria, Andreani et al. (2008) suggest that polyhedral serpentines, which are always the last serpentine type to crystallize, directly 377 378 nucleate and grow radially with a layer-by-layer mechanism from a proto-serpentine colloidal phase containing a continuous solid skeleton of polymers or aggregates bathed in a liquid phase. Whether 379 the proto-serpentine gel includes organic carbon compounds either of biogenic or abiotic origin has 380 up to now never been documented. In the present study, the strict association of pol-spt serpentines 381 382 with a Mg- and Si-bearing organic phase embedding all spheroid and tubular structures and coating the hydrogarnets walls (Figs. 5-7) suggests that organic carbon plays a role in the formation and 383 stabilization of polyhedral serpentine and may constitute a key component of this proto-serpentine 384 phase described by Andreani et al. (2008) as mediating the formation of polyhedral serpentines. 385 This is supported by the presence of Mg-rich C-inclusions hosted in well-crystallized serpentine in 386 the vicinity of the carbon gel (Figs. 9b and e) suggesting that organic carbon was involved in the 387 last serpentinization events affecting the rock and not lately added to the system. 388

Further investigations are nonetheless needed to confirm the systematic presence of organic 389 carbon associated with the formation of polyhedral serpentine in various settings. If true, polyhedral 390 serpentines as a common mineral of the serpentinized oceanic lithosphere (e.g., Andreani et al., 391 2007; Baronnet et al., 2007: Rouméjon et al., 2015) may then be used as a proxy for the presence of 392 393 organic carbon within serpentinites. The presence of cronstedtite-derived polyhedral serpentine reported in carbonaceous chondrites (Zega et al., 2006) may also support this idea. Carbonaceous 394 chondrites are known to contain a rich mixture of complex organic compounds (e.g., Schmitt-395 Kopplin et al., 2010). As shown by Elmaleh et al. (2015), the complex oxidation mechanisms of Fe-396 rich serpentines close to the cronstedtite endmember, which are abundant alteration products in 397 chondrites, promote molecular hydrogen production and hence potential pathways for inorganic 398

carbon reduction. If organic carbon is mandatory for pol-spt to form, then it would provide
constrains on the timing of abiotic organic synthesis during the aqueous alteration of carbonaceous
chondrites, the polyhedral serpentine being already considered as the endmember of an intense
alteration sequence which may have occurred early in the chondrite or parent body history
(Browning et al., 1996; Zega et al., 2006).

From another perspective, understanding how to promote the formation of pol-spt may have 404 additional implications, notably for subsurface CO<sub>2</sub> storage. Due to the chemical potential of 405 serpentinization to favor carbonation (i.e., CO<sub>2</sub> conversion into solid carbonates), ultramafic rocks 406 have long been proposed as potential hosts for long lasting and safe storage of anthropogenic CO<sub>2</sub> 407 in the attempt to stem the currently observed consequences on climate change and ocean 408 acidification (e.g., Matter and Kelemen, 2009). One of the major criticisms raised against such a 409 technology is the high clogging potential of lizardite which subsequently forms in veins and 410 fractures following fluid-rock interactions and is commonly found as extremely fine-grained scales 411 and massive aggregates (e.g., Farough et al., 2016). If organics, by controlling the size and shape of 412 low-temperature serpentine types, promote instead the formation of pol-spt spheroids or tiny tubules 413 in veins and fractures, as observed in Figs. 2g-h, fluid flow would then be improved together with 414 the hydrodynamic properties of serpentinite. 415

Although the scattering of the data is large due to the small size of the spheroids and rods 416 compared to the electron beam size, EPMA suggest that pol-spt have incorporated a limited amount 417 of divalent metals in their structure (Fig. 3, Supplementary Fig. 2 and Supplementary Table 1). 418 Indeed, pol-spt display low concentrations in cobalt and manganese while nickel reaches higher 419 420 concentrations (Supplementary Fig. 2 and Supplementary Table 1). Then, instead of being mobilized by aqueous fluids during hydrothermal alteration, as generally acknowledged during 421 serpentinization (Pinto et al., 20017), metals unaccommodated by the pol-spt are found in the 422 surrounding carbon gel where their speciation and mobility are apparently dictated by the 423 concentration and the type of associated organic compounds (Fig. 12). The latter can be variable at 424 the microscale, as attested by the chemically-heterogeneous organic carbon micro-domains 425

highlighted by STEM-EDXS (Figs. 9 and 11) and STXM (Fig. 12). Cobalt is systematically
associated with carbon, sometimes in the form of well-crystallized Co-oxides accompanied by
lower concentrations of Mn, Ni, and Fe (Figs. 9e-h, 10a-b and 11). Mn-oxides are found in carbonpoor areas also enriched in Fe and Ni, forming nanometric crusts around pol-spt spheroids (Figs. 9h,
10c-h and 11).

Different processes can account for the local formation of these metallic oxides. Both Co 431 and Mn in their divalent form are soluble ions in hydrothermal fluids and the presence of metallic 432 oxides strongly suggests that oxidation, at least partial, occurred, turning Co(II) and Mn(II) into 433 insoluble Co(III) and Mn(III) or Mn(IV), and leading to the precipitation of Co- and Mn-oxides. 434 Whereas in the open ocean, organic-metal complexation reduces metal reactivity, increases their 435 solubility and limits their scavenging into or onto particulate phases (Bennett et al., 2008), the 436 presence of organic compounds in the present system did not play the same protective role as 437 oxidation could have been responsible for the immobilization of metals. Although oxidative 438 dissolution, as observed in the case of hydrothermal sulfides (German et al., 1991), cannot be totally 439 excluded, Co and Mn oxidation is a process primarily known to be mediated by bacteria (Murray et 440 al., 2007), in agreement with Ménez et al. (2012) who hypothesized that biological activity could 441 have been responsible for H-adr dissolution. Mn(II) oxidation can occur by direct enzymatic 442 activity (e.g., Tebo et al., 2004) or by exposure to reactive oxygen species produced by cells 443 (Learman et al., 2011). Mn(II) biological oxidation was demonstrated to represent an important 444 process in the formation of ferromanganese nodules and crusts (Nealson, 2006), sometimes also 445 enriched in Co(III) (Lee and Tebo, 1994). In aquatic environments, microbial Co and Mn oxidation 446 were also shown to be linked but the oxidation of Co can also possibly be related to the high 447 oxidative capabilities of poorly-crystalline Mn-oxides (Liao et al. 2011; Murray et al., 2007). These 448 latter are indeed known to strongly control the transfer of metals in polluted systems (Borch et al., 449 2010; Tebo et al., 2004). Due to their high sorptive capacities, Mn-oxides can also adsorb or 450 incorporate substantial amount of metals such as Co, Ni and Fe (Nealson, 2006), as observed here 451 (Figs 10 and 11). Accordingly, in our samples, they likely contributed to the enrichment in metals 452

453 of the organic C-bearing phases.

The local enrichments in transition metals and the nucleation of nanocrystallites may also 454 have been driven differentially by the organic matrix itself, depending on the affinity of metals with 455 the reactive organic functional groups locally present. Based on what was postulated by Ménez et 456 al. (2012), the organic compounds found in these rocks may have derived from the presence of 457 former cryptoendolithic microbial ecosystems solubilizing substrates by structuring themselves in 458 459 the form of biofilm. Biofilm are described as gel-like structures composed of cells and EPS showing high reactive site densities (Ha et al., 2010). Metallic divalent cations, leached from H-adr, bastite 460 and inherited Fe-ox, may then have been differentially trapped by the negatively-charged functional 461 groups present in EPS. By imposing diffusion-limited processes, low permeability EPS, well 462 acknowledged to strongly impact metal dynamics (e.g., Templeton et al., 2001; Wang et al., 2016; 463 Warren and Haack, 2001), may also have contributed to accumulate Co and Mn in spatially-464 restricted areas, hence leading to the precipitation of metallic oxides once the supersaturation with 465 respect to these oxides was locally reached. STXM imaging highlights that local enrichments in 466 transition metals are selectively associated with different types and concentrations of organic carbon 467 (Fig. 12). Cobalt was found within a carbon-rich gel-like mixture containing higher amount of 468 aliphatics and lower amount of carboxylic compounds in comparison with the Mn-enriched C-poor 469 micro-domain. However, the higher abundance of carboxyl groups in the Mn-enriched area suggests 470 that, in this micro-domain, organic compounds may have been oxidized by the Mn-oxides, hence 471 exerting locally a control on the redox state of the system. Note in addition that Co-oxides are 472 known catalysts for abiotic organic synthesis down to 30°C (e.g., Melaet et al., 2014; Varma et al., 473 474 2018). In this respect, once accumulated in the organic matrix, they also likely impacted the evolution of these organic molecules. However, the STXM spectrum of the Mn/Fe-bearing felt 475 presents similarities with the one obtained in the carbon gel embedding pol-spt in the H-adr cavities 476 (Fig. 6) and for which no enrichment in transition metals was shown. It will hence deserve further 477 investigations notably on metal speciation. 478

479

Overall, whatever the detailed mechanisms involved, our observations demonstrate that

organic compounds have the potential to immobilize metals in the form of metallic oxides or as 480 metal ions adsorbed onto organic matrices during low-temperature hydrothermal alteration of the 481 mantle-derived crust. If the impact of such processes on metal cycles is difficult to assess at the 482 scale of the oceanic lithosphere in the present state of knowledge, it may have implications for 483 ophiolites where active serpentinization also occurs. Ophiolitic massifs experiencing supergene 484 alteration are the target for ore exploration and mining. Notably, tropical alteration of ophiolites 485 yields lateritic cap rocks locally enriched in Co and Mn (Butt and Cluzel, 2013). As an illustration, 486 Dublet et al. (2017) recently described the vertical changes in Co and Mn speciation along a lateritic 487 regolith developed as a function of weathering stage upon peridotites from New Caledonia where 488 mining activities exploit nickel-bearing ore over 6 000 km<sup>2</sup>. They raised the question of the role of 489 Mn- vs. Fe-(oxyhydr)oxides on Co speciation and on the long-term stabilization of metals at the 490 whole regolith scale. Considering that the ophiolitic massif might host active microbial 491 communities over a large depth, as it was recently demonstrated in Oman (Miller et al., 2016; 492 Rempfert et al. 2017), we suggest that organic compounds along with microbial activities should 493 also be investigated in the regolith and its underlying basement to assess their respective impact on 494 Mn and Co speciation (± Ni and Fe) and hence on supergene ore formation, as already highlighted 495 for gold or platinum-group elements (Reith et al., 2010, 2016). 496

497

## 498 **5.** Conclusions

499

We show in this study that high resolution spectroscopy and microscopy are a powerful approach to image organic compounds trapped in the porosity of serpentinites and to investigate their co-occurrences with metals and minerals. We strongly suggest that organic compounds, whose origin can be diverse in serpentinites (both abiotic and biogenic), locally influence low temperature (< 200°C) fluid-rock interactions in the serpentinizing oceanic lithosphere with consequences on metal distribution, speciation and hence mobility, as well as on the nature and structure of late stage mineralizations such as polygonal and polyhedral serpentines. Given the growing body of evidences showing that the serpentinized oceanic lithosphere constitutes a large habitat for life and that
serpentinization reactions have a high potential for abiotic organic synthesis, it is then reasonable to
expect such processes to be widespread in ultramafic rocks.

510

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512

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# 529 **References**

Andreani, M., Mével, C., Boullier, A.M., Escartín, J., 2007. Dynamic control on serpentine

531 crystallization in veins: constraints on hydration processes in oceanic peridotites.

532 Geochemistry Geophysics Geosystems 8, Q02012.

Andreani, M., Grauby, O., Baronnet, A., Munoz, M., 2008. Occurrence, composition and growth of

- 534 polyhedral serpentine. European Journal of Mineralogy 20, 159-171.
- Baronnet, A., Devouard, B., 1996. Topology and crystal growth of natural chrysotile and polygonal
  serpentine. Journal of Crystal Growth 166, 952-960.
- Baronnet, A., Devouard, B., 2005. Microstructures of common polygonal serpentines from axial
  HRTEM imaging, electron diffraction, and lattice simulation data. The Canadian Mineralogist
  43, 513-542.
- Baronnet, A., Andreani, M., Grauby, O., Devouard, B., Nitsche, S., Chaudanson, D., 2007. Onion
  morphology and microstructure of polyhedral serpentine. American Mineralogist 92, 687-690.
- 542 Bassim, B.T., Kilcoyne, A.L.D., Scott, K., Chou, T., Wirick, S., Cody, G., Stroud, R.M., 2012.
- 543 Minimizing damage during FIB sample preparation of soft materials. Journal of Microscopy
  544 245, 288-301.
- 545 Bennett, S.A., Achterberg, E.P., Connelly, D.P., Statharn, P.J., Fones, G.R., Gernian, C.R., 2008.
- The distribution and stabilisation of dissolved Fe in deep-sea hydrothermal plumes. Earth and
  Planetary Science Letters 270, 157-167.
- 548 Bennett, S.A., Statham, P.J., Green, D.R.H., Le Bris, N., McDermott, J.M., Prado, F., Rouxel, O.J.,
- 549 Von Damm, K., German, C.R., 2011. Dissolved and particulate organic carbon in
- hydrothermal plumes from the East Pacific Rise, 9°50'N. Deep Sea Research Part I 58, 922931.
- Benzerara, K., Yoon, T.H., Tyliszczak, T., Constantz, B., Spormann, A.M., Brown Jr., G.E., 2004.
  Scanning transmission X-ray microscopy study of microbial calcification. Geobiology 2, 249259.
- Benzerara, K., Menguy, N., Guyot, F., Vanni, C., Gillet, P., 2005. High resolution study of silicatecarbonate-micro-organism interface prepared by focused ion beam (FIB). Geochimica et
  Cosmochimica Acta 69, 1413-1422.
- Bernard, S., Benzerara, K., Beyssac, O., Brown Jr., G.E., Stamm, L.G., Duringer, P., 2009.
- 559 Ultrastructural and chemical study of modern and fossil sporoderms by Scanning
- 560 Transmission X-ray Microscopy (STXM). Review of Palaeobotany and Palynology 156, 248-

561 261.

Borch, T., Kretzschmar, R., Kappler, A., Van Cappellen, P., Ginder-Vogel, M., Voegelin, A., 562 Campbell, K., 2010. Biogeochemical redox processes and their impact on contaminant 563 dynamics. Environmental Science & Technology 44, 15-23. 564 Boyd, P.W., Ellwood, M.J., 2010. The biogeochemical cycle of iron in the ocean. Nature 565 Geoscience 3, 675-682. 566 Browning, L.B., McSween, H.Y. Jr., Zolensky, M.E., 1996. Correlated alteration effects in CM 567 carbonaceous chondrites. Geochimica et Cosmochimica Acta 60, 2621-2633. 568 Butt, C.R., Cluzel, D., 2013. Nickel laterite ore deposits: weathered serpentinite. Elements 9, 123-569 128. 570 Chan, C.S., Fakra, S.C., Edwards, D.C., Emerson, D., Banfield, J.F., 2009. Iron oxyhydroxide 571 mineralization on microbial extracellular polysaccharides. Geochimica et Cosmochimica Acta 572 73, 3807-3818. 573 Cody, G.D., Ade, H., Wirick, S., Mitchell, G.D., Davis, A., 1998. Determination of chemical-574 structural changes in vitrinite accompanying luminescence alteration using C-NEXAFS 575 analysis. Organic Geochemistry 28, 441-455. 576 Cressey, G., Cressey, B.A., Wicks, F.J., 2008. Polyhedral serpentine: a spherical analogue of 577 polygonal serpentine? Mineralogical Magazine 72, 1229-1242. 578 Cressey, G., Cressey, B.A., Wicks, F.J., Yada, K., 2010. A disc with fivefold symmetry: the 579 proposed fundamental seed structure for the formation of chrysotile asbestos fibres, polygonal 580 serpentine fibres and polyhedral lizardite spheres. Mineralogical Magazine 74, 29-37. 581 582 Dublet, G., Juillot, F., Brest, J., Noël, V., Fritsch, E., Proux, O., Olivi, L., Ploquin, F., Morin, G., 2017. Vertical changes of the Co and Mn speciation along a lateritic regolith developed on 583 peridotites (New Caledonia). Geochimica et Cosmochimica Acta 217, 1-15. 584 Elmaleh, A., Bourdelle, F., Caste, F., Benzerara, K., Leroux, H., Devouard, B., 2015. Formation 585 and transformations of Fe-rich serpentines by aqueous alteration in asteroids: a nanoscale 586 study of the Murray chondrite. Geochimica et Cosmochimica Acta 158, 162-178. 587

- Farough, A., Moore, D.E., Lockner, D.A., Lowell, R.P., 2016. Evolution of fracture permeability of
  ultramafic rocks undergoing serpentinization at hydrothermal conditions: An experimental
  study. Geochemistry, Geophysics, Geosystems 17, 44-55.
- 591 Field, M.P., Sherrell, R.M., 2000. Dissolved and particulate Fe in a hydrothermal plume at 9°45′N,
- 592 East Pacific Rise: Slow Fe(II) oxidation kinetics in Pacific plumes. Geochimica et
- 593 Cosmochimica Acta 64, 619-628.
- 594 Fitzsimmons, J.N., John, S.G., Marsay, C.M., Hoffman, C.L., Nicholas, S.L., Toner, B.M., German,
- C.R., Sherrell, R.M., 2017. Iron persistence in a distal hydrothermal plume supported by
  dissolved–particulate exchange. Nature Geoscience 10, 195-201.
- Frost, B.R., Beard, J.S., 2007. On silica activity and serpentinization. Journal of Petrology 48,
  1351–1368.
- German, C.R., Campbell, A.C., Edmond, J.M., 1991. Hydrothermal scavenging at the Mid-Atlantic
  Ridge: modification of trace element dissolved fluxes. Earth and Planetary Science Letters
  107, 101-114.
- Ha, J., Gélabert, A., Spormann, A.M., Brown, G.E., Jr., 2010. Role of extracellular polymeric
  substances in metal ion complexation on *Shewanella oneidensis*: Batch uptake,
- thermodynamic modeling, ATR-FTIR, and EXAFS study. Geochimica et Cosmochimica Acta
  74, 1-15.
- Hawkes, J.A., Connelly, D.P., Gledhill, M., Achterberg, E.P., 2013. The stabilization and
- transportation of dissolved iron from high temperature hydrothermal vent systems. Earth and
  Planetary Science Letters 375, 280-290.
- Hawkes, J.A., Rossel, P.E., Stubbins, A., Butterfield, D., Connelly, D.P., Achterberg, E.P.,
- 610 Koschinsky, A., Chavagnac, V., Hansen, C.T., Bach, W., Dittmar, T., 2015. Efficient removal
- of recalcitrant deep-ocean dissolved organic matter during hydrothermal circulation. Nature
  Geoscience 8, 856-860.
- Kawka, O.E., Simoneit, B.R.T., 1987. Survey of hydrothermally-generated petroleums from the
- 614 Guaymas Basin spreading center. Organic Geochemistry 11, 311-328.

| 615               | Klein, F., Bach, W., Humphris, S.E., Kahl, WA., Jöns, N., Moskowitz, B., Berquó, T.S., 2014.                              |
|-------------------|---|
| 616               | Magnetite in seafloor serpentinite-Some like it hot. Geology 42, 135-138.   |
| 617               | Klevenz, V., Bach, W., Schmidt, K., Hentscher, M., Koschinsky, A., Petersen, S., 2011.                                    |
| 618               | Geochemistry of vent fluid particles formed during initial hydrothermal fluid-seawater mixing                             |
| 619               | along the Mid-Atlantic Ridge. Geochemistry, Geophysics Geosystems 12 (10), Q0AE05.  |
| 620               | Kilcoyne, A.L., Tyliszczak, T., Steele, W.F., Fakra, S., Hitchcock, P., Franck, K., Anderson, E.,                         |
| 621               | Harteneck, B., Rightor, E.G., Mitchell, G.E., Hitchcock, A.P., Yang, L., Warwick, T., Ade,                                |
| 622               | H., 2003. Interferometer-controlled scanning transmission X-ray microscopes at the  |
| 623               | Advanced Light Source. Journal of Synchrotron Radiation 10, 125–136.  |
| 624               | Konn, C., Charlou, J.L., Holm, N.G., Mousis, O., 2015. The production of methane, hydrogen, and                           |
| 625               | organic compounds in ultramafic-hosted hydrothermal vents of the Mid-Atlantic Ridge.                                      |
| 626               | Astrobiology 15, 381-399.   |
| 627               | Lang, S.Q., Butterfield, D.A., Lilley, M.D., Paul Johnson, H., Hedges, J.I., 2006. Dissolved organic                      |
| 628               | carbon in ridge-axis and ridge-flank hydrothermal systems. Geochimica et Cosmochimica                                     |
| 629               | Acta 70, 3830-3842.   |
| 630               | Lau, B.L.T., Hsu-Kim H., 2008. Precipitation and growth of zinc sulfide nanoparticles in the                              |
| 631               | presence of thiol-containing natural organic ligands. Environmental Science & Technology                                  |
| 632               | 42, 7236-7241.  |
| 633               | Learman, D.R., Wankel, S.D., Webb, S.M., Martinez, N., Madden, A.S., Hansel, C.M., 2011.                                  |
| 634               | Coupled biotic-abiotic Mn(II) oxidation pathway mediates the formation and structural                                     |
| 635               | evolution of biogenic Mn oxides. Geochimica et Cosmochimica Acta 75, 6048-6063.   |
| 636               | Lee, Y., Tebo, B.M., 1994. Cobalt(II) oxidation by the marine manganese(II)-oxidizing Bacillus sp.                        |
| 637               | strain SG-1. Applied and Environmental Microbiology 60, 2949-2957.  |
|                   | Lepot, K., Benzerara, K., Brown, G.E., Jr., Philippot P., 2009. Organic matter heterogeneity in 2.72                      |
| 638               |   |
| 638<br>639        | Ga stromatolites: alteration versus preservation by sulphur incorporation. Geochimica et                                  |
| 638<br>639<br>640 | Ga stromatolites: alteration versus preservation by sulphur incorporation. Geochimica et Cosmochimica Acta 73, 6579-6599. |

- diversity in deep-sea sediment from the cobalt-rich crust deposit region in the Pacific Ocean.
  FEMS Microbiology Ecology 78, 565-585.
- Mason, O.U., Nakagawa, T., Rosner, M., Van Nostrand, J.D., Zhou, J., Maruyama, A., Fisk, M.R.,
   Giovannoni, S.J., 2010. First investigation of the microbiology of the deepest layer of ocean
- 646 crust. PLoS One 5:e15399.
- Matter, J.M., Kelemen, P.B., 2009. Permanent storage of carbon dioxide in geological reservoirs by
  mineral carbonation. Nature Geoscience 2, 837-841.
- 649 Melaet, G., Ralston, W.T., Li, C.S., Alayoglu, S., An, K., Musselwhite, N., Kalkan, B., Somorjai,
- G.A., 2014. Evidence of highly active cobalt oxide catalyst for the Fischer-Tropsch synthesis
  and CO<sub>2</sub> hydrogenation. Journal of the American Chemical Society 136, 2260-2263.
- Ménez, B., Pasini, V., Brunelli, D., 2012. Life in the hydrated suboceanic mantle. Nature
  Geoscience 5, 133-137.
- Miller, H.M., Matter, J.M., Kelemen, P., Ellison, E.T., Conrad, M.E., Fierer, N., Ruchala, T.,
- Tominaga, M., Templeton, A.S., 2016. Modern water/rock reactions in Oman hyperalkaline
  peridotite aquifers and implications for microbial habitability. Geochimica et Cosmochimica
  Acta 179, 217-241.
- Monnin, C., Chavagnac, V., Boulart, C., Ménez, B., Gérard, M., Gérard, E., Pisapia, C.,
- 659 Quéméneur, M., Erauso, G., Postec, A., Guentas-Dombrowski, L., Payri, C., Pelletier, B.,
- 2014. Fluid chemistry of the low temperature hyperalkaline hydrothermal system of Prony
  Bay (New Caledonia). Biogeosciences 11, 5697-5706.
- Mottl, M.J., McConachy, T.F., 1990. Chemical processes in buoyant hydrothermal plumes on the
  East Pacific Rise near 21-degrees-N. Geochimica et Cosmochimica Acta 54, 1911-1927.
- Murray, K.J., Webb, S.M., Bargar, J.R., Tebo, B.M., 2007. Indirect oxidation of Co(II) in the
- presence of the marine Mn(II)-oxidizing bacterium *Bacillus* sp strain SG-1. Applied and
  Environmental Microbiology 73, 6905-6909.
- 667 Nealson, K.H., 2006. The manganese-oxidizing bacteria. In: Prokaryotes (Dworkin, M., Falkow, S.,
- 668 Rosenberg, E., Schleifer, K.H., Stackebrandt, E., eds), Springer, New York, N.Y., vol. 5, 222-

669 231.

Pasini, V., 2013. Biopetrology of the hydrating mantle along Mid-Ocean ridges. Ph.D manuscript. 670 Università di Modena e Reggio Emilia & Institut de Physique du Globe de Paris, 308 p. 671 Pasini, V., Brunelli, D., Dumas, P., Sandt, C., Frederick, J., Benzerara, K., Bernard, S., Ménez, B., 672 2013. Low temperature hydrothermal oil and associated biological precursors in serpentinites 673 from Mid-Ocean ridge. Lithos 178, 84-95. 674 Pinto, V.H.G., Manatschal, G., Karpoff, A.M., Ulrich, M., Viana, A.R., 2017. Seawater storage and 675 element transfer associated with mantle serpentinization in magma-poor rifted margins: A 676 quantitative approach. Earth and Planetary Science Letters 459, 227-237. 677 Plümper, O., Beinlich, A., Bach, W., Janots, E., Austrheim, H., 2014. Garnets within geode-like 678 serpentinite veins: Implications for element transport, hydrogen production and life-679 supporting environment formation. Geochimica et Cosmochimica Acta 141, 454-471. 680 Peive, A.A., Savel'eva, G.N., Skolotnev, S.G., Simonov, V.A., 2003. Tectonics and origin of the 681 oceanic crust in the region of 'dry' spreading in the Central Atlantic (7°10'5°N). Geotectonics 682 37, 3-25. 683 Reith, F., Fairbrother, L., Nolze, G., Wilhelmi, O., Clode, P.L., Gregg, A., Parsons, J.E., Wakelin, 684 S.A., Pring, A., Hough, R., Southam, G., Brugger, J., 2010. Nanoparticle factories: biofilms 685 hold the key to gold dispersion and nugget formation. Geology 38, 843-846. 686 Reith, F., Zammit, C.M., Saad Shar, S., Etschmann, B., Bottrill, R., Southam, G., Ta, C., Kilburn, 687 M., Oberthür, T., Ball, A.S., Brugger, J., 2016. Biological role in the transformation of 688 platinum-group mineral grains. Nature Geoscience 9, 294-298. 689 690 Rempfert, K.R., Miller, H.M., Bompard, N., Nothaft, D., Matter, J.M., Kelemen, P., Fierer, N., Templeton, A.S., 2017. Geological and geochemical controls on subsurface microbial life in 691 the Samail ophiolite, Oman. Frontiers in Microbiology 8, 56. 692 693 Resing, J.A., Sedwick, P.N., German, C.R., Jenkins, W.J., Moffett, J.W., Sohst, B.M., Tagliabue, A., 2015. Basin-scale transport of hydrothermal dissolved metals across the South Pacific 694 ocean. Nature 523, 200-203. 695

- Rossel, P.E., Stubbins, A., Rebling, T., Koschinsky, A., Hawkes, J.A., Dittmar, T., 2017. Thermally
  altered marine dissolved organic matter in hydrothermal fluids. Organic Geochemistry 110,
  73-86.
- Rouméjon, S., Cannat, M., Agrinier, P., Godard, M., Andreani, M., 2015. Serpentinization and fluid
  pathways in tectonically exhumed peridotites from the southwest Indian ridge (62-65°E).
  Journal of Petrology 56, 703-734.
- Sander, S.G., Koschinsky, A., 2011. Metal flux from hydrothermal vents increased by organic
  complexation. Nature Geoscience 4, 145-150.
- Sander, S.G., Koschinsky, A., Massoth, G., Stott, M., Hunter, K.A., 2007. Organic complexation of
   copper in deep-sea hydrothermal vent systems. Environmental Chemistry 4, 81-89.
- Sands, C.M., Connelly, D.P., Statham, P.J., German, C.R., 2012. Size fractionation of trace metals
  in the Edmond hydrothermal plume, Central Indian Ocean. Earth and Planetary Science
  Letters 319-320, 15-22.
- Santelli, C.M., Orcutt, B.N., Banning, E., Bach, W., Moyer, C.L., Sogin, M.L., Staudigel, H.,
- Edwards, K.J., 2008 Abundance and diversity of microbial life in ocean crust. Nature 453,
  653-656.
- Schmitt-Kopplin, P., Gabelica, Z., Gougeon, R.D., Fekete, A., Kanawati, B., Harir, M., Gebefuegi,
- 713 I., Eckel, G., Hertkorn, N., 2010. High molecular diversity of extraterrestrial organic matter in
- Murchison meteorite revealed 40 years after its fall. Proceedings of the National Academy of
  Sciences of the United States of America 107, 2763-2768.
- Schneider, C.A., Rasband, W.S., Eliceiri, K.W., 2012. NIH Image to ImageJ: 25 years of image
  analysis. Nature Methods 9, 671-675.
- Schrenk, M.O., Brazelton, W.J., Lang, S.Q., 2013. Serpentinization, carbon and deep life. In:
- Hazen, R.M., Jones, A.P., Baross, J.A. (Eds.), Carbon in Earth. Reviews in Mineralogy and
- Geochemistry, 75. Mineralogical Society of America, Geochemical Society, pp. 575-606.
- Seyfried, W.E., Jr., Pester, N.J., Tutolo, B.M., Ding, K., 2015. The Lost City hydrothermal system:
- 722 Constraints imposed by vent fluid chemistry and reaction path models on subseafloor heat and

- mass transfer processes. Geochimica et Cosmochimica Acta 163, 59-79.
- 724 Sharkov, E., 2012. Cyclic development of axial parts of slow-spreading ridges: Evidence from
- Sierra Leone area, the Mid-Atlantic Ridge, 5-7°N. In: Sharkov, E. (Ed.), Tectonics Recent
  Advances, pp. 3-36.
- Simoneit, B.R.T., Lein, A.Y, Peresypkin, V.I., Osipov, G.A., 2004. Composition and origin of
- hydrothermal petroleum and associated lipids in the sulfide deposits of the Rainbow Field
  (Mid-Atlantic Ridge at 36°N). Geochimica et Cosmochimica Acta 68, 2275-2294.
- Statham, P.J., German, C.R., Connelly, D.P., 2005. Iron(II) distribution and oxidation kinetics in
  hydrothermal plumes at the Kairei and Edmond vent sites, Indian Ocean. Earth and Planetary
- 732 Science Letters 236, 588-596.
- 733 Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb,
- S.M., 2004. Biogenic manganese oxides: Properties and mechanisms of formation. Annual
  Review of Earth and Planetary Sciences 32, 287-328.
- 736 Templeton, A.S., Trainor, T.P., Traina, S.J., Spormann, A.M., Brown, G.E., 2001. Pb(II)
- distributions at biofilm-metal oxide interfaces. Proceedings of the National Academy of
  Sciences of the United States of America 98, 11897-11902.
- 739 Toner, B.M., Fakra, S.C., Manganini, S.J., Santelli, C.M., Marcus, M.A., Moffett, J.W., Rouxel, O.,
- German, C.R., Edwards, K.J., 2009. Preservation of iron(II) by carbon-rich matrices in a
  hydrothermal plume. Nature Geoscience 2, 197-201.
- Varma, S.J., Muchowska, K.B., Chatelain, P., Moran, J., 2018. Native iron reduces CO<sub>2</sub> to
- intermediates and end-products of the acetyl-CoA pathway. Nature Ecology & Evolution 2,
  1019-1024.
- Warren, L.A., Haack, E.A., 2001. Biogeochemical controls on metal behaviour in freshwater
  environments. Earth-Science Reviews 54, 261-320.
- 747 Wang, Y., Gélabert, A., Michel, F.M., Choi, Y., Gescher, J., Ona-Nguema, G., Eng, P.J., Bargar,
- J.R., Farges, F., Spormann, A.M., Brown, G.E., Jr, 2016. Effect of biofilm coatings at metal-
- oxide/water interfaces I: Pb(II) and Zn(II) partitioning and speciation at *Shewanella*

- *oneidensis*/metal-oxide/water interfaces. Geochimica et Cosmochimica Acta 188, 368-392.
- 751 Wu, J., Wells, M.L., Remember, R., 2011. Dissolved iron anomaly in the deep tropical–subtropical
- 752 Pacific: Evidence for long-range transport of hydrothermal iron. Geochimica et

753 Cosmochimica Acta 75, 460-468.

- 754 Zega, T.J., Garvie, L.A.J., Dódony, I., Friedrich, H., Stroud, R.M., Buseck, P.R., 2006. Polyhedral
- serpentine grains in CM chondrites. Meteoritic & Planetary Science 41, 681-688.

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## 757 Figure captions

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Fig. 1. (a) bathymetric map of the 0-10° N region showing within a white rectangle the location of 759 the non-transform Sierra Leone Fracture Zone (FZ; 7°10'5 N) in the equatorial Mid-Atlantic Ridge 760 where the sample S2232-17 has been dredged ("mbsl" stands for meters below sea level). (b) 761 enlarged view of (a). (c) optical image of a cut section of the serpentinized S2232-17 rock; olivine 762 763 was replaced by serpentine and magnetite exhibiting a characteristic mesh texture (mesh-spt); orthopyroxene was replaced by fine grained lizardite, defined as bastite (bast). Late veins of 764 serpentine crosscut the whole (spt-vein). (d) photomicrograph in transmitted plane polarized light 765 showing and raditic hydrogarnet (H-adr) ± iron oxides distributed along exsolution lamellae in the 766 767 bastitized orthopyroxene. Clusters of hydrogarnets were also found close to the orthopyroxenes, filling veins and microfractures. 768

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770 Fig. 2. SEM images of polygonal and polyhedral serpentine (pol-spt) rods and spherules of variable sizes (10-1,000 nm) found (a) surrounding a pierced andraditic hydrogarnet (H-adr), (b) filling in 771 the interior of a fractured H-adr crystal enclosed in bastite (bast). (c) and (d) are enlarged views of a 772 hydrogarnet selvage with (d) being located in (c) with a white rectangle. (e) and (f) show that the 773 pol-spt coverage is uniform in the cavity where a hydrogarnet was formerly present. (f), which is a 774 magnified view of (e) (location indicated by a white rectangle), shows indentation of the pol-spt 775 within the fine grained orientated bastite. As hypothesized by Ménez et al. (2012), pol-spt are 776 progressively replacing hydrogarnets in this rock with (g) illustrating an advanced dissolution stage 777 778 with a hydrogarnet almost fully replaced by pol-spt. White arrows in (g) depict tiny veins ( $\leq 5 \mu m$ in width) of pol-spt branching out from the former H-adr location (detail shown in (h)). (a), (b) and 779 (g) are reproduced from Ménez et al. (2012) with permission. 780

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**Fig. 3.**  $Cr_2O_3$  (wt.%) versus  $X_{Fe}$  diagram established from EMPA collected on the 5 groups of serpentines identified in the rock: the serpentine after olivine in the mesh texture (mesh spt), the

bastite after orthopyroxene (bast), the serpentine after olivine contouring spinels (spl spt), the 784 polygonal and polyhedral serpentines associated with hydrogarnets (pol-spt) and the serpentine 785 found in the late veins crosscutting the rock (vein spt) (Fig. 1c). The uncertainties associated to 786 EMPA are within the symbol dimensions.  $X_{Fe}$  is defined as (total Fe)/(total Fe + Mg) and expresses 787 the fraction of iron incorporated into serpentine. The enrichment in Cr and to a lesser extent in Fe 788 and Al (see also Supplementary Fig. 2 and Supplementary Table 1) of the pol-spt, are in agreement 789 790 with formation from hydrogarnet dissolution, the hydroandradite displaying mean formula of  $Ca_{2.71}(Fe_{1.61}^{3+}, Ti_{0.01}, Al_{0.17}, Cr_{0.03}, Mg_{0.02})(Si_{2.92}O_{10.93})(OH)_{1.07}.$ 791

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Fig. 4. (a) TEM image collected on a FIB ultrathin section and showing a submicrometric spheroid 793 grown in an elongated cavity inside a hydrogarnet (H-adr). The corresponding FIB section is shown 794 in Fig. 6b. The spheroid was identified by SAED as geodesic polyhedral serpentine (pol-spt) whose 795 model is drawn in the lower left inset in (b). The diffraction pattern is characteristic of a 796 797 polycrystalline aggregate, with spots aligned along circles of increasing diameter due to the multiple orientations of each serpentine triangular facet. Measured inter-planar distances are compatible with 798 lizardite lattice, in agreement with Andreani et al. (2008) who reported on the strict short-range 799 similarity of the structure of polyhedral serpentine and lizardite, based on Raman spectroscopic 800 characteristics. 801

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Fig. 5. The nucleation and growth of polyhedral and polygonal serpentine (pol-spt) from the 803 hydrogarnet (H-adr) dissolution appear to be mediated by a carbon-bearing gel-like phase. (a) SEM 804 805 image of a H-adr cavity milled by FIB revealing enclosed pol-spt of variable size growing on a granular H-adr surface (see Supplementary Fig. 1 for SEM views of the corresponding H-adr and 806 FIB foil). (b) TEM image detailing the pol-spt/H-adr interface. Submicrometric chrysotile fibres are 807 also visible. The close connection between pol-spt and H-adr, highlighted at the location shown by 808 the white asterisk, again suggests that pol-spt grew at the expense of hydrogarnets, hence 809 confirming the genetic link between both. Moreover, it highlights continuous coating of the 810

assemblage by a gel-like phase (depicted by black arrows). The corresponding FIB section is shown 811 in Fig. 7c. (c) magnified SEM view of H-adr dissolution cavities in which carbon veils can be 812 found. (d) TEM image showing a 15 sector (upper fibre) and a 30 sector (bottom fibre) polygonal 813 serpentine wet by a jelly film of carbon interfacing between the serpentine and the H-adr walls. The 814 corresponding FIB section is shown in Fig. 6b. Star and diamond correspond to the locations of the 815 EDXS spectra shown in (e) and collected on the carbon gel and the pol-spt, respectively. (e) 816 associated EDXS spectra showing that the carbon gel is also bearing Si, Mg, and to a lesser extent, 817 Ca and Fe, likely inherited from the hydrogarnet and the bastite. (f) HAADF-STEM image of a 818 serpentine spheroid confirming the carbon gel to also bear heavier elements in addition to carbon. 819 (g) associated STEM-EDXS elemental image showing the distribution of carbon (green). 820

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Fig. 6. STXM characterization at the C K-edge of the carbon gel associated with polyhedral rods 822 and polygonal serpentine spheroids (pol-spt) occurring in dissolution cavities of hydrogarnet (H-823 824 adr). (a) SEM image of a subhedral andraditic hydrogarnet showing pol-spt spreading. The location where the foil was milled is indicated by the orange dashed line. (b) SEM image of the FIB foil 825 where dissolution pits and cavities filled with pol-spt spheroids are visible along with pol-spt 826 covering the H-adr rim. The platinum coating aimed at protecting milled volumes before 827 excavation. (c) TEM enlarged view of the area shown by a white square in (b) where pol-spt have 828 crystallized in the H-adr dissolution cavity. White asterisk corresponds to the location of the pol-spt 829 geodesic spheroid shown in Fig. 4. (d) composite STXM map showing the distribution of organic 830 carbon (in red) in the mineral matrix (in green). The STXM image is located using a black square in 831 (b). It confirms the organic nature of the carbon gel. (e) associated C-XANES spectrum showing 832 mainly X-ray absorption of carboxyl functional groups at 288.6 eV. 833

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Fig. 7. (a) SEM image in false colors of a mélange of polyhedral and polygonal serpentines (pol-spt
in green), along with aggregated nanometric fibres forming a felt wet by a carbon-bearing matrix
(yellow), all filling the cracks and voids of an andraditic hydrogarnet (H-adr in blue) hosting Fe-

oxides (orange). (b) SEM image of a H-adr where the FIB foil displayed in (c) was milled along the
orange dashed line. It shows dissolution pits piercing its surface. SEM image of the FIB foil in (c)
shows that these pits relate to deep inner and various-sized dissolution cavities enclosing large
quantity of felt in H-adr. (d) associated TEM image showing pol-spt enclosed in aggregated tiny
fibres likely responsible for the felt texture.

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Fig. 8. (a) SEM image of a large accumulation of carbon-bearing felt embedding numerous 844 polyhedral and polygonal serpentines (pol-spt) and trapped in a fractured hydrogarnet (H-adr) 845 (modified from Ménez et al. (2012) with permission). The orange dashed lines show the locations 846 where two FIB foils (shown in Fig. 9) were milled. (b) and (c): associated elemental distributions of 847 magnesium (green), calcium (red), manganese (purple) and cobalt (blue). Mn and Co appear 848 selectively enriched in two distinct regions of the carbon-rich felt filling H-adr cracks. (d) 849 corresponding SEM-EDXS spectrum. Collection point is located by a white star in (c). Pt and Au 850 arise from the metallic coating. 851

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Fig. 9. Electron microscopy images of the metal-bearing felt collected on the FIB foil milled in the 853 area enriched in Co [(a) and (b)] and on the FIB foil milled in the Mn-enriched region [(c) and (d)] 854 and associated STEM characterizations [from (e) to (h)] (see Fig. 8a for milling locations). (a) SEM 855 image of the FIB foil milled in the Co-enriched area. It shows a thin layer of felt interfacing an 856 andraditic hydrogarnet (H-adr) and the FIB foil protective layer of platinum. (b) associated TEM 857 images whose location is shown in (a). An enlarged view is shown is Fig. 10a. It shows black dots 858 spotting the carbon gel enclosing polyhedral serpentine (pol-spt) and well-crystallized serpentine. 859 (c) SEM image of the FIB foil milled in the Mn-enriched region showing felt enclosed within a 860 fractured H-adr. (d) associated TEM images showing numerous pol-spt enclosed in a C-rich porous 861 gel. An enlarged view is shown in Fig. 10c and in Supplementary Fig. 3. From (e) to (h): associated 862 HAADF-STEM images and corresponding STEM-EDXS elemental distributions. Locations of 863 (e)+(f) and (g)+(h) are shown using white squares in (b) and (c), respectively. 864

Fig. 10. Magnified TEM and STEM images of the metal-bearing felt collected on the FIB foil 866 867 milled in the area enriched in Co [(a) and (b)] and on the FIB foil milled in the Mn-enriched region [from (c) to (h)] (Fig. 8a). Locations of (a) and (c) are indicated in Figs. 9b and 9d, respectively. (a) 868 nanometric Co-oxides dispersed in the organic gel around a well-crystallized serpentine (spt) 869 870 presenting non crystalline Mg- and C-bearing inclusion (Mg-C incl.). (b) associated HR-TEM image showing Co-oxides. (c) polyhedral serpentine (pol-spt) spheroid contoured by a crust of Mn 871 872 and Fe close to an iron oxide (Fe-ox). (d) is a magnified view of (c) with location indicated by an 873 orange star in (c). In (b) and (d), atom plane fringes attest for the presence of well-defined crystallographic planes (white arrows). (e) larger HAADF-STEM image of the encrusted pol-spt. 874 Location of (c) is shown by a white square. From (f) to (h): STEM-EDXS elemental images 875 showing the distribution of Fe (f), Mn (g) and Co (h). They show Co homogeneously distributed 876 outside the pol-spt in both the C-bearing phase and the Fe-ox whereas Fe and, to a lesser extent, Mn 877 878 are enriched in the metallic crust contouring some of the pol-spt. Associated STEM-EDXS spectra are shown in Fig. 11. 879

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Fig. 11. TEM-EDXS spectra associated with (1) the polyhedral serpentine (pol-spt), (2) the Mn/Fe
crust formed around the pol-spt shown in Figs. 10c-h, (3) the nanometric Co-oxides shown in Figs.
10a-b, (4) the carbon matrix found in the felt. Cu X-ray peak at 8 keV arises from the TEM grid.

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Fig. 12. STXM characterization of the metal-bearing felt enclosed in a fractured hydrogarnet.
Analysis have been performed on the FIB foil displayed in Fig. 9c with associated TEM and
STEM-EDXS characterizations shown in Fig. 9d and Figs. 9g-h, respectively. (a) composite STXM
map showing the distribution of the Co- and Mn/Fe-bearing organic components contained in the
felt and appearing respectively in blue and green. The red colour figures the location of the silicate
component. (b) composite STEM-EDXS elemental image showing the distribution of Mg (red), Mn

(green) and Co (blue) in the area indicated by a white square in (a), as also shown in Fig. 9h. (c) C-

XANES spectra associated with the Co-bearing area and the Mn-enriched felt. It shows the

presence of aromatic or olefinic carbon (285.1 eV), aliphatic carbon (287.7 eV), and carboxyl

functional groups (288.6 eV). The peak at 290.4 eV can be related to carboxyl groups bounded to

895 metals.









1 kV, secondary electrons





2 kV, secondary electrons



7 kV, backscattered electrons



3 kV, secondary electrons



Figure 7 – Ménez et al.



Figure 8 – Ménez et al.



Figure 9 – Ménez et al.







