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# 1 Mineralizations and transition metal mobility driven by organic carbon during 2 low-temperature serpentinization

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19

20 *Keywords:*

21 serpentinization

22 mid-ocean ridges

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

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

67

## 68 1. Introduction

69

70 It was long assumed that the net flux of most hydrothermally-derived metals to the ocean  
71 was negligible because abundant polymetallic particulate phases, predominantly in the form of Fe-  
72 sulfides and Fe-oxyhydroxides, form when vent fluids discharge at the seafloor (German et al.,  
73 1991; Mottl and McConachy, 1990). Nonetheless, the importance of hydrothermally-derived metals  
74 for ocean biogeochemistry has been revisited during the last two decades. Enrichments in dissolved

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

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

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

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

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

140

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

142

### 143 *2.1. Geological setting*

144

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

156

## 157 2.2. *Sample petrography*

158

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

177

## 178 2.3. *Sample preparation*

179

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



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

192

#### 193 *2.4. Electron microscopy*

194

195 SEM observations were performed on Au-coated, polished and unpolished, resin-free chips  
196 using a Zeiss SUPRA 55 VP field emission microscope (Service Commun de Microscopie  
197 Electronique à Balayage, UPMC, Paris, France). Beam accelerating voltage ranged between 15 kV  
198 (for backscattered electron images, microanalyses and chemical maps) and 1 kV (for high resolution  
199 secondary electron images). Images were collected using secondary electron detectors (Everhart-  
200 Thornley or InLens) and a backscattered electron detector (AsB). EDXS analyses were carried out  
201 with a PGT Sahara spectrometer. Chemical maps were acquired and processed using the Spirit<sup>®</sup>  
202 software. Spectra were fitted at each hyperspectral map point to produce elemental distributions.

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  
205 2100 microscopes operating at an accelerating voltage of 200 kV (IMPMC, Paris, France and  
206 Centro Interdipartimentale Grandi Strumenti, Modena, Italy). Both microscopes are equipped with a  
207 LaB<sub>6</sub> filament. EDXS analyses were performed using a JEOL detector at IMPMC and an Oxford  
208 INCA 100 detector at CIGS.

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 ~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

#### 244 3.1. Polyhedral and polygonal serpentine formation from hydrogarnet dissolution mediated by an 245 organic gel

246

247 Euhedral dissolution pits are often found as piercing the surface of the andraditic  
248 hydrogarnets present in the S2232-17 serpentinite as shown by SEM (Fig. 2a) also highlighting  
249 large cavities inside H-adr (Supplementary Fig. 1). This suggests that dissolution process affected  
250 the hydrogarnets, as also proposed by Ménez et al. (2012). EMPA provided for H-adr a mean  
251 formula of  $\text{Ca}_{2.71}(\text{Fe}_{1.61}^{3+}, \text{Ti}_{0.01}, \text{Al}_{0.17}, \text{Cr}_{0.03}, \text{Mg}_{0.02})(\text{Si}_{2.92}\text{O}_{10.93})(\text{OH})_{1.07}$  (Supplementary Table 1).  
252 Pits and cavities are filled by polyhedral serpentine spheroids and polygonal serpentine rods (pol-  
253 spt), both showing a wide size range (few tens to 1,000 nm - mean 350 nm; Fig. 2c). Pol-spt show  
254 an enrichment in Cr (mean  $1.18 \pm 0.89$  wt.%) and to a lesser extent in Al (mean  $4.32 \pm 2.53$  wt.%) and  
255 Fe (mean  $4.96 \pm 0.91$  wt.%) in comparison with the high temperature serpentines (i.e., the bastite,  
256 the mesh serpentine and the serpentine contouring spinels) (Fig. 3, Supplementary Fig. 2 and  
257 Supplementary Table 1). Conversely, the pol-spt display low concentrations in cobalt ( $0.07 \pm 0.12$   
258 wt.%) and manganese ( $0.06 \pm 0.08$  wt.%) while nickel reaches concentrations similar to what was  
259 found for the four other types of serpentine ( $0.22 \pm 0.25$  wt.%). When numerous, pol-spt appear to  
260 fracture the H-adr crystals (Fig. 2b). This peculiar type of serpentine is also visible around the  
261 hydrogarnets, filling various-sized voids around the H-adr spheroids (Figs. 2a, c and e), with a clear  
262 indentation of the spheroids within the surrounding fine-grained bastite (Fig. 2f). H-adr crystals and  
263 part of the bastite were progressively replaced by pol-spt that also spread inside the surrounding

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

265         The identification of pol-spt serpentines was confirmed by TEM and SAED (Figs. 4 and  
266 5d). As described in literature (Baronnet and Devouard, 1996, 2005; Baronnet et al., 2007;  
267 Andreani et al., 2008; Cressey et al., 2008, 2010), polyhedral serpentine is composed of triangular  
268 facets made of lizardite basal planes showing lateral continuity from one sector to another and  
269 forming tiny “onion like” geodesic spheroids (Fig. 4). The core of the spheroids usually hosts a  
270 small fibre contoured by the triangular facets. Given that the geodesic spheroids have the simplest  
271 formulation as icosahedra, the inner cavity is possibly defined by this geometric limit. Polygonal  
272 serpentine crystallizes as tiny fibres composed of concentric lizardite layers wrapped around the  
273 fibre axis and made of 15 or 30 sectors (Fig. 5d). The fifteen-sector fibres are the smallest (< 400  
274 nm - mean 350 nm), whereas the thirty-sector ones are larger (up to 1,000 nm - mean 610 nm).

275         SEM and TEM analyses highlight a close connection between pol-spt and H-adr (Figs. 5a-  
276 b). The globular topography of the H-adr inner cavities where pol-spt grew suggests local  
277 transformation of H-adr into spherical and coalescent pol-spt (Fig. 5a). TEM analyses of FIB foils  
278 milled on H-adr grains also show that the pol-spt enclosed in the branched and elongated  
279 dissolution cavities are embedded in a carbon-rich phase also covering the H-adr walls (Figs. 5b, d-  
280 g). This is in agreement with SEM observations collected on resin-free chips showing the presence  
281 of carbon veils within the H-adr cavities (Fig. 5c). The organic film has a gel-like appearance and  
282 does not show any structure or atomic organization using HR-TEM. It presents very low wetting  
283 angles with respect to the phyllosilicate and the hydrogarnet (Figs. 5b and d). TEM-EDXS analyses  
284 highlight the presence of Mg, Si and to a lesser extent, Ca and Fe in the gel (Fig. 5e), likely  
285 responsible for the brightness of the fluffy phase observed by HAADF-STEM (Figs. 5f-g). The  
286 organic nature of the carbon gel was further demonstrated by STXM coupled with C-XANES  
287 spectroscopy. As displayed in Fig. 6e, the C-XANES spectrum of the carbon gel shows a major  
288 peak at 288.6 eV, characteristic of carboxylic functional groups (Cody et al., 1998; Benzerara et al.,  
289 2004; Bernard et al., 2009). STXM mapping shows that this organic phase is spectroscopically  
290 homogeneous (Figs. 6d-e).

291

292 *3.2. Local enrichments in transition metals and associated carbon speciation*

293

294 Carbon-rich areas are also found as large patches in H-adr inner cracks and fractures nearby  
295 iron oxides which precipitated concomitantly with H-adr (Fig. 7a). These carbon-rich patches are  
296 associated with a complex intergrowth of late stage serpentines including pol-spt among numerous  
297 nanometric to micrometric fibrous chrysotile-like aggregates (Figs. 7 and 8a). These felt-like  
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  
300 (Figs. 9e-h, 10 and 11). These metals are strictly confined to the H-adr filling material and not  
301 dispersed in the host groundmass although some metal-rich nanophases can also be suspected in the  
302 bastite and the mesh serpentine, based on EMPA (Supplementary Fig. 2 and Supplementary Table  
303 1). With the exception of Fe, none of those elements were detected in the carbon gel embedding the  
304 pol-spt previously described in the branched and elongated dissolution cavities (Figs. 5 and 6).

305 The felt presents an organic C-rich component with variable texture and porosity, finely  
306 intermingled with various amounts of micro- to nano-crystallites. As an illustration, Fig. 9d (or  
307 Supplementary Fig. 3 for an enlarged version of Fig. 9d) shows that polyhedral serpentine geodesic  
308 spheroids and polygonal serpentines are embedded in a foamy carbon gel presenting a vesicular  
309 texture with gradients in the size of the vesicles. The foamy appearance can be a primary character  
310 or alternatively can have been induced by degassing of a light fraction or by cavitation under  
311 vacuum during measurements. The significant decompression experienced during the recovery from  
312 the seafloor can also be invoked. Variations of the texture seem however to be correlated with the  
313 presence/absence of transition metals, the gel texture being locally more massive when the carbon  
314 and metal contents are respectively lower and higher (Fig. 9). The foamy C-bearing gel is  
315 associated with the presence of Co and minor Mn, Ni, and Fe (Figs. 9d, g and 11). In contrast, Fig.  
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

318 in Co shown in Fig. 8c. In this area, Mn, Ni and Fe are also present in the C-phase but at lower  
319 concentrations (Figs. 9e-f and 11). Similarly, a compact carbon-poor and likely more crystalline  
320 matrix displaying high Mn concentrations was identified in the upper part of Fig. 9d  
321 (Supplementary Fig. 3), based on STEM-EDXS mapping (Fig. 9h). In this area, pol-spt spheroids  
322 are locally surrounded by well-crystallized Mn/Fe crusts measuring about 50 nm in thickness (Figs.  
323 10c-d and 11). The surrounding C-bearing matrix also presents high Mn, and to a lesser extent Fe,  
324 Co and Ni concentrations (Figs. 9h and 10e-h). This is confirmed by the relatively high brightness  
325 of the corresponding area by HAADF-STEM (Fig. 9h). In some locations, abundant nanometer-  
326 sized rods of Fe-(oxyhydr)oxides were also found among the tiny fibres of magnesium silicates  
327 within the carbon gel (e.g., Fig. 9g). Overall, transition metals appear to be associated with the  
328 carbon-bearing phase but selectively enriched in two domains characterized by high and low carbon  
329 concentrations for the Co-rich and Mn-Fe(-Ni) enriched areas, respectively.

330 Energy-filtered STXM images and associated C-XANES spectra collected in the same areas  
331 show that these chemically-heterogeneous organic carbon micro-domains display distinguishable  
332 signatures (Fig. 12). Similarly to what has been found for the carbon gel embedding pol-spt in the  
333 branched and elongated dissolution cavities (Fig. 6), the Mn-enriched regions display mainly  
334 absorption features of carboxylic functional groups at 288.6 eV along with the presence at a lower  
335 amount of aliphatic carbon at 287.7 eV (Cody et al., 1998; Benzerara et al., 2004; Bernard et al.,  
336 2009). A peak at 290.4 eV was also observed. According to Chan et al. (2009), it can be indicative  
337 of carboxyl groups binding iron and possibly other metals. Compared to the Mn-enriched area, the  
338 Co-rich foamy region shows increased and decreased levels in aliphatics and carboxyl functional  
339 groups, respectively, plus minor aromatic or olefinic carbon at 285.1 eV.

340

#### 341 **4. Discussion and implications**

342

343 As hypothesized by Ménez et al. (2012), textural relationships provide evidence that both H-  
344 adr 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 high-temperatures 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 grain rims (e.g., Figs. 5c and 7c and Supplementary Fig. 1). This process led to the formation of large inner cavities interpreted by Ménez et al. (2012) as the result of a cryptoendolithic microbial activity. Note that the origin of the organics found in these rocks is not discussed in the present paper and readers are referred to Ménez et al. (2012) and Pasini et al. (2013) and to the extensive discussions on organics' systematics that can be found within. Dissolution cavities provided the open space required for polyhedral serpentine to form (Andreani et al., 2008), along with the appropriate temperature conditions. Indeed, while the mesh serpentine, the bastite, and the serpentine contouring spinels are representative of the static replacement of the high temperature paragenesis during the first stages of serpentinization ( $> 200^{\circ}\text{C}$ ; Klein et al., 2014), the pol-spt are instead representative of crystallization occurring after complete hydration of the host pyroxene. Moreover, as discussed by Ménez et al. (2012), their precipitation after H-adr, which forms below  $200^{\circ}\text{C}$  (Frost and Beard, 2007; Plümper et al., 2014) attests for low-temperature conditions in agreement with Andreani et al. (2008). These authors also suggest a general enrichment in trivalent cations as a stabilizing factor for pol-spt nucleation. This requirement is met here when considering 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 concentrations, we did not succeed in determining the ferric iron content of pol-spt based on EMPA (Pasini, 2013). Nonetheless, as H-adr iron is solely in the form of Fe(III), it may suggest that at least a fraction of the pol-spt iron is present as Fe(III).

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

372 spatially-restricted areas, hence suggesting that they likely derive from the same process. Polygonal  
373 serpentine has been viewed by some authors as a more stable phase compared to chrysotile, or  
374 alternatively, as an analogous of the polyhedral serpentine (Cressey et al., 2008, 2010).  
375 Accordingly, polygonal and polyhedral serpentines may both form from a similar precursor through  
376 different growth mechanisms. Based on textural and microstructural criteria, Andreani et al. (2008)  
377 suggest that polyhedral serpentines, which are always the last serpentine type to crystallize, directly  
378 nucleate and grow radially with a layer-by-layer mechanism from a proto-serpentine colloidal phase  
379 containing a continuous solid skeleton of polymers or aggregates bathed in a liquid phase. Whether  
380 the proto-serpentine gel includes organic carbon compounds either of biogenic or abiotic origin has  
381 up to now never been documented. In the present study, the strict association of pol-spt serpentines  
382 with a Mg- and Si-bearing organic phase embedding all spheroid and tubular structures and coating  
383 the hydrogarnets walls (Figs. 5-7) suggests that organic carbon plays a role in the formation and  
384 stabilization of polyhedral serpentine and may constitute a key component of this proto-serpentine  
385 phase described by Andreani et al. (2008) as mediating the formation of polyhedral serpentines.  
386 This is supported by the presence of Mg-rich C-inclusions hosted in well-crystallized serpentine in  
387 the vicinity of the carbon gel (Figs. 9b and e) suggesting that organic carbon was involved in the  
388 last serpentinization events affecting the rock and not lately added to the system.

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



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

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

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

426 highlighted by STEM-EDXS (Figs. 9 and 11) and STXM (Fig. 12). Cobalt is systematically  
427 associated with carbon, sometimes in the form of well-crystallized Co-oxides accompanied by  
428 lower concentrations of Mn, Ni, and Fe (Figs. 9e-h, 10a-b and 11). Mn-oxides are found in carbon-  
429 poor areas also enriched in Fe and Ni, forming nanometric crusts around pol-spt spheroids (Figs. 9h,  
430 10c-h and 11).

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

453 of the organic C-bearing phases.

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

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

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

507 showing that the serpentinized oceanic lithosphere constitutes a large habitat for life and that  
508 serpentinization reactions have a high potential for abiotic organic synthesis, it is then reasonable to  
509 expect such processes to be widespread in ultramafic rocks.

510

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512

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528

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756

757 **Figure captions**

758

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

769

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

781

782 **Fig. 3.** Cr<sub>2</sub>O<sub>3</sub> (wt.%) versus X<sub>Fe</sub> diagram established from EMPA collected on the 5 groups of  
783 serpentines identified in the rock: the serpentine after olivine in the mesh texture (mesh spt), the

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

792  
793 **Fig. 4.** (a) TEM image collected on a FIB ultrathin section and showing a submicrometric spheroid  
794 grown in an elongated cavity inside a hydrogarnet (H-adr). The corresponding FIB section is shown  
795 in Fig. 6b. The spheroid was identified by SAED as geodesic polyhedral serpentine (pol-spt) whose  
796 model is drawn in the lower left inset in (b). The diffraction pattern is characteristic of a  
797 polycrystalline aggregate, with spots aligned along circles of increasing diameter due to the multiple  
798 orientations of each serpentine triangular facet. Measured inter-planar distances are compatible with  
799 lizardite lattice, in agreement with Andreani et al. (2008) who reported on the strict short-range  
800 similarity of the structure of polyhedral serpentine and lizardite, based on Raman spectroscopic  
801 characteristics.

802  
803 **Fig. 5.** The nucleation and growth of polyhedral and polygonal serpentine (pol-spt) from the  
804 hydrogarnet (H-adr) dissolution appear to be mediated by a carbon-bearing gel-like phase. (a) SEM  
805 image of a H-adr cavity milled by FIB revealing enclosed pol-spt of variable size growing on a  
806 granular H-adr surface (see Supplementary Fig. 1 for SEM views of the corresponding H-adr and  
807 FIB foil). (b) TEM image detailing the pol-spt/H-adr interface. Submicrometric chrysotile fibres are  
808 also visible. The close connection between pol-spt and H-adr, highlighted at the location shown by  
809 the white asterisk, again suggests that pol-spt grew at the expense of hydrogarnets, hence  
810 confirming the genetic link between both. Moreover, it highlights continuous coating of the



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

821

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

834

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

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

843

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

852

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

865

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

880

881 **Fig. 11.** TEM-EDXS spectra associated with (1) the polyhedral serpentine (pol-spt), (2) the Mn/Fe  
882 crust formed around the pol-spt shown in Figs. 10c-h, (3) the nanometric Co-oxides shown in Figs.  
883 10a-b, (4) the carbon matrix found in the felt. Cu X-ray peak at 8 keV arises from the TEM grid.

884

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

891 (green) and Co (blue) in the area indicated by a white square in (a), as also shown in Fig. 9h. (c) C-  
892 XANES spectra associated with the Co-bearing area and the Mn-enriched felt. It shows the  
893 presence of aromatic or olefinic carbon (285.1 eV), aliphatic carbon (287.7 eV), and carboxyl  
894 functional groups (288.6 eV). The peak at 290.4 eV can be related to carboxyl groups bounded to  
895 metals.

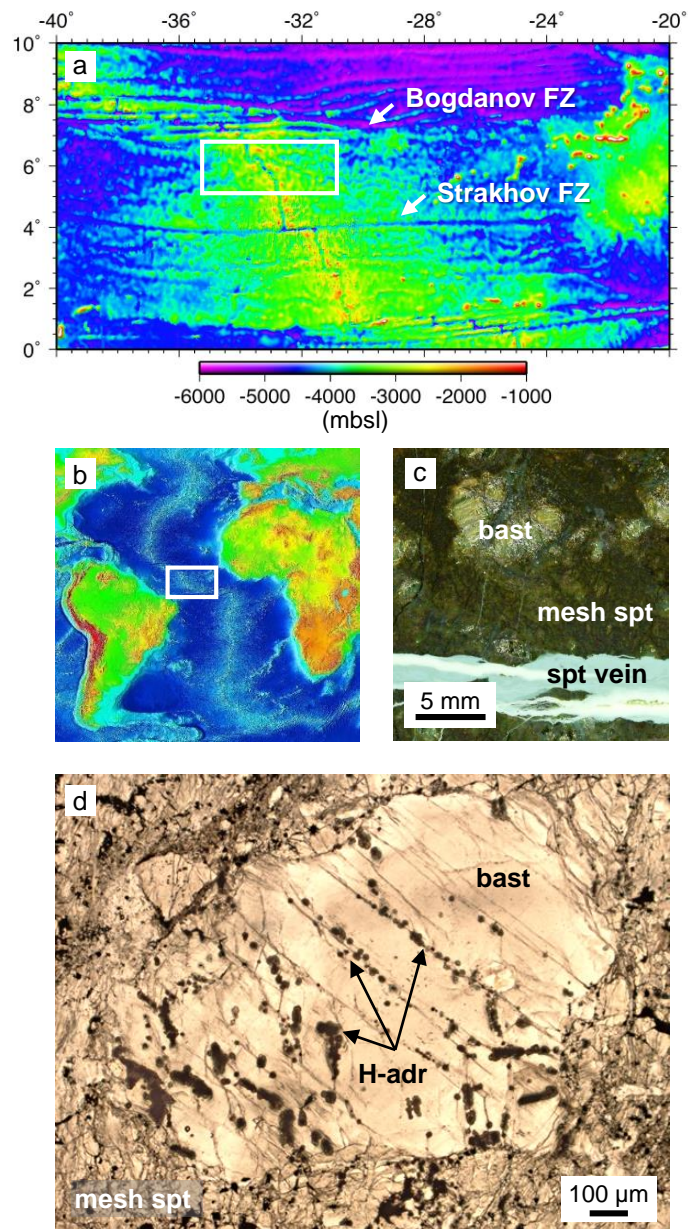
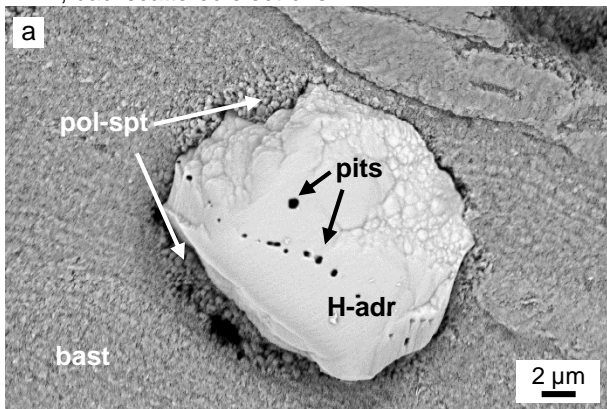


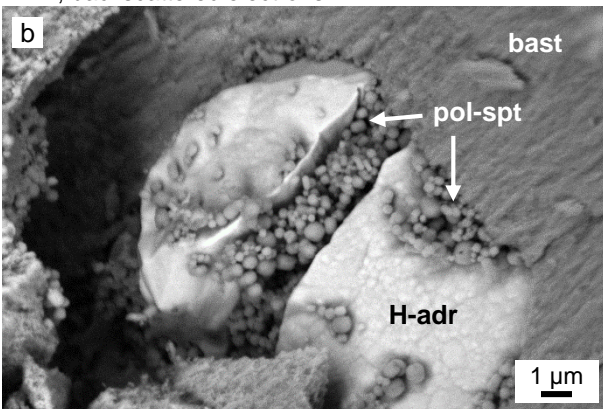
Figure 1 – Ménez et al.



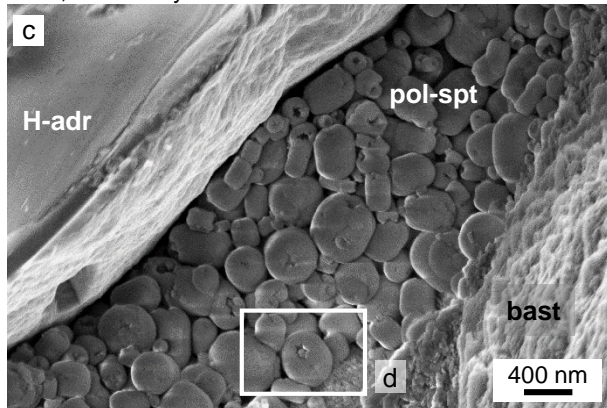
7 kV, backscattered electrons



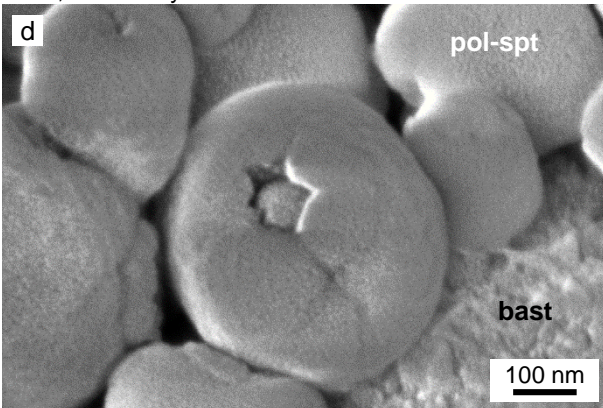
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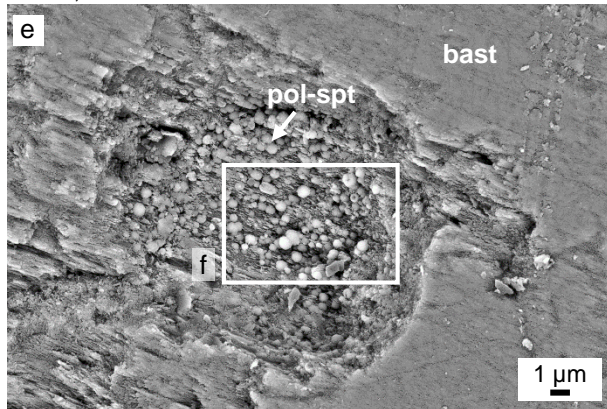
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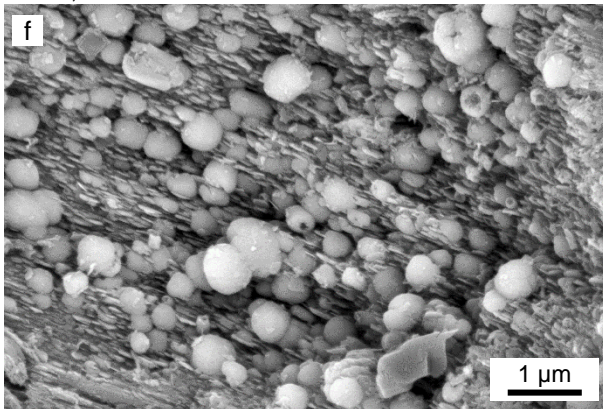
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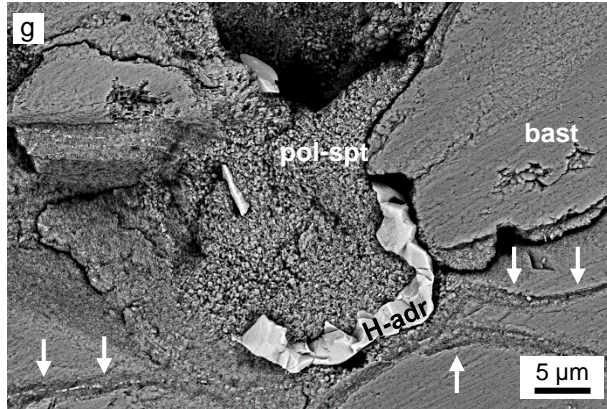
10 kV, backscattered electrons



10 kV, backscattered electrons



7 kV, backscattered electrons



10 kV, backscattered electrons

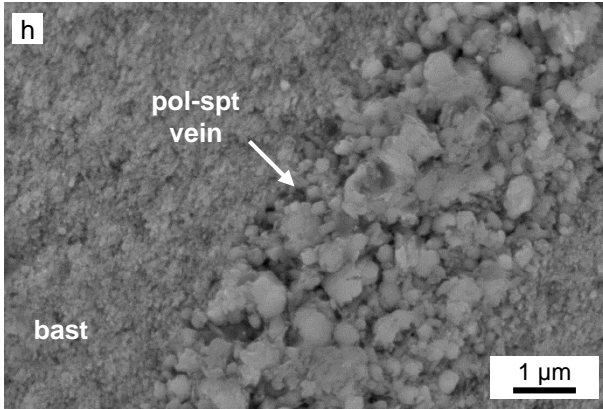


Figure 2 – Ménez et al.

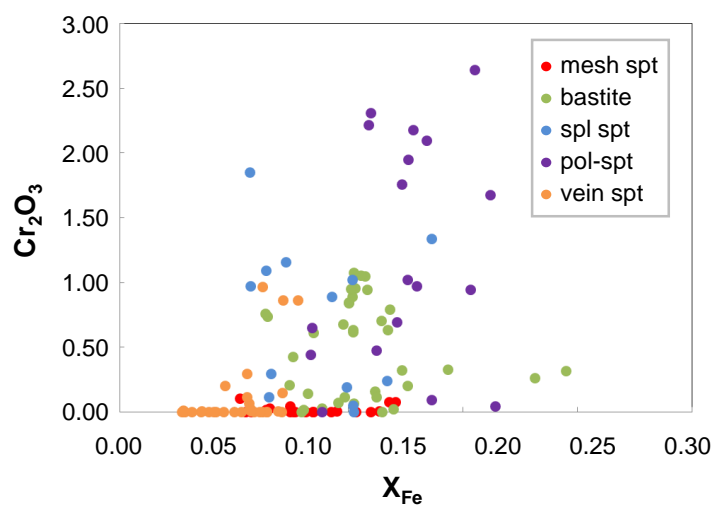


Figure 3 – Ménez et al.

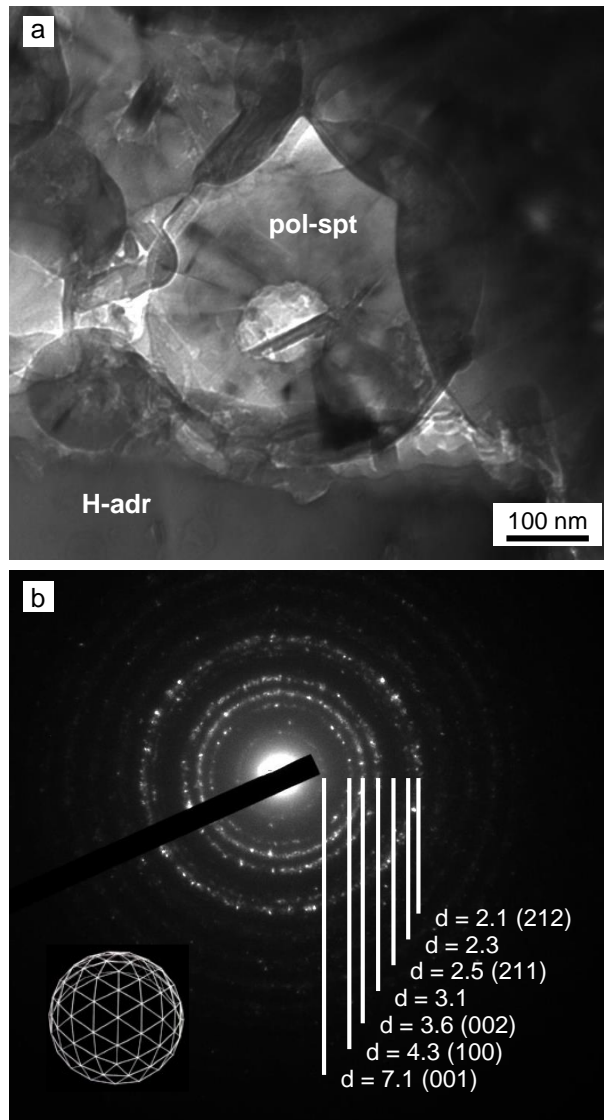
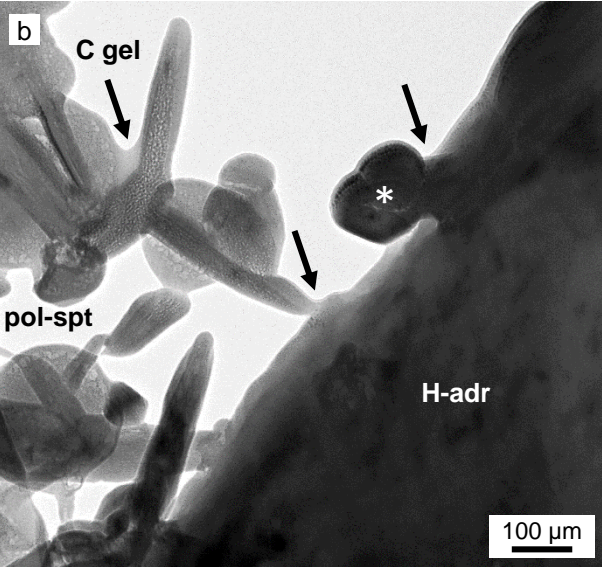
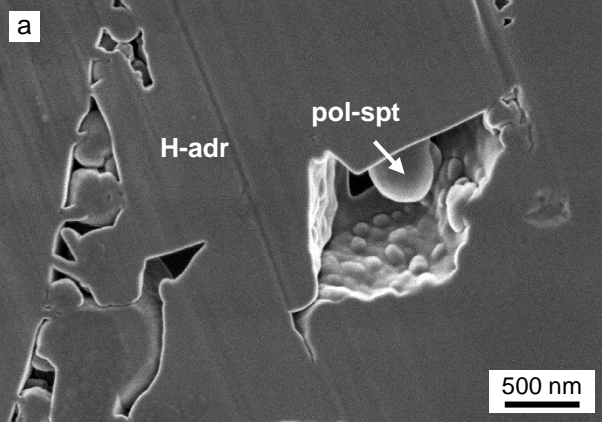


Figure 4 – Ménez et al.



1 kV, secondary electrons



15 kV, backscattered electrons

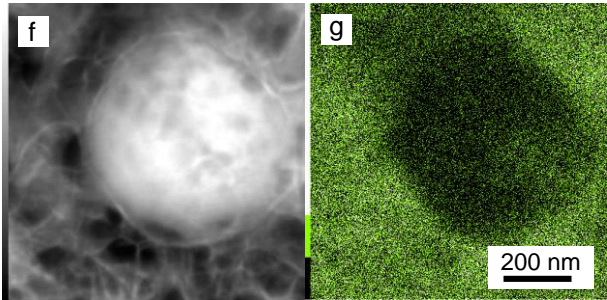
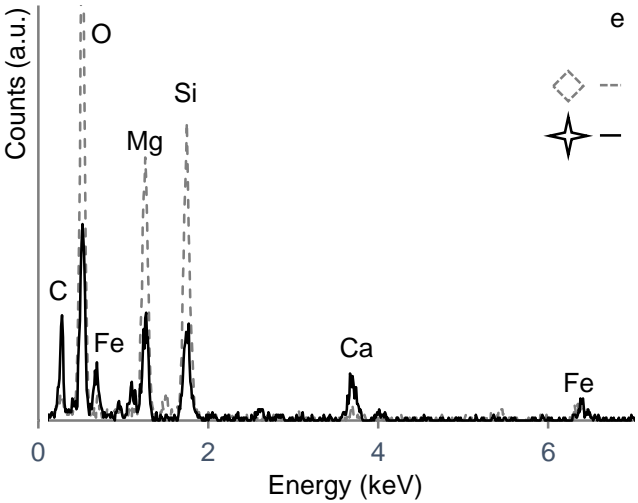
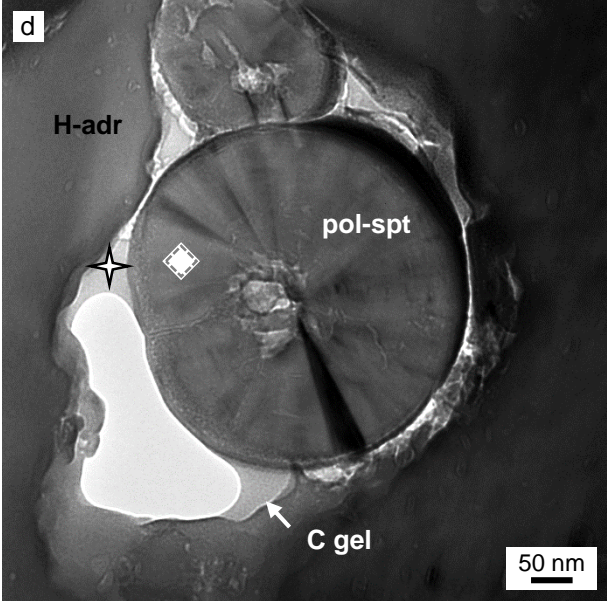
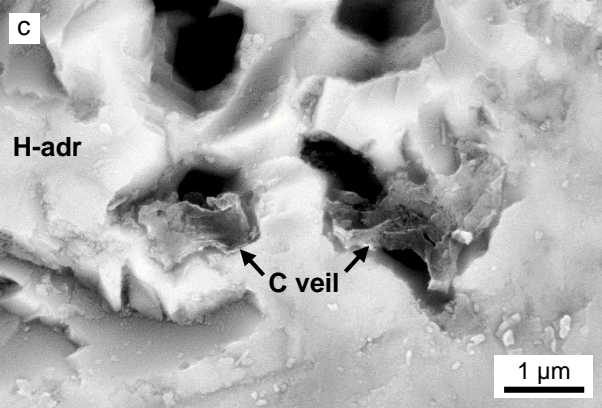
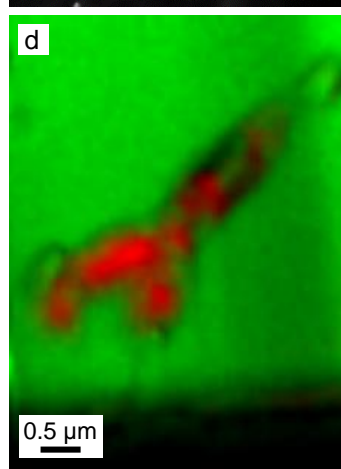
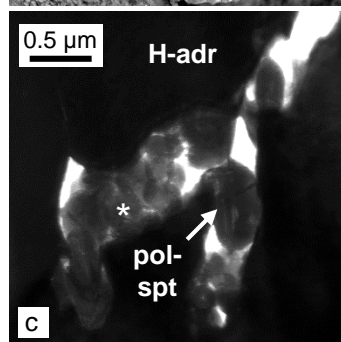
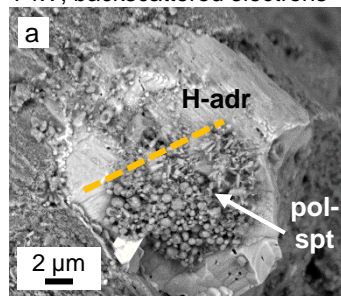


Figure 5 – Ménez et al.

7 kV, backscattered electrons



b 3 kV, secondary electrons

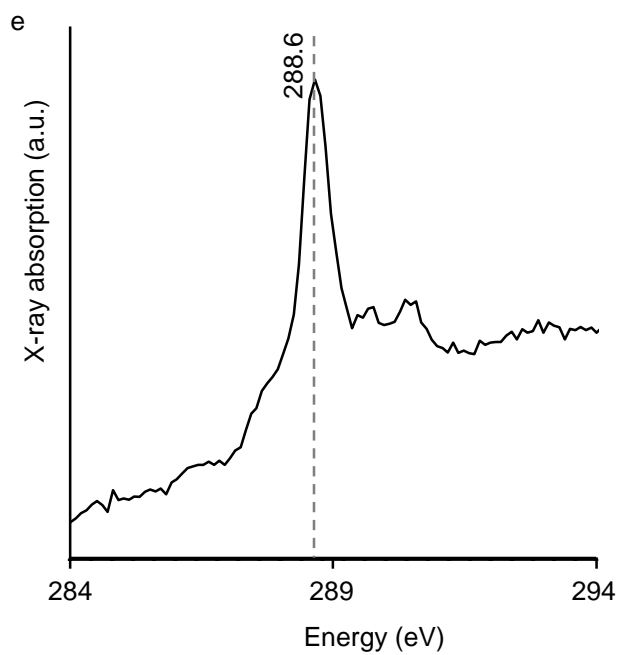
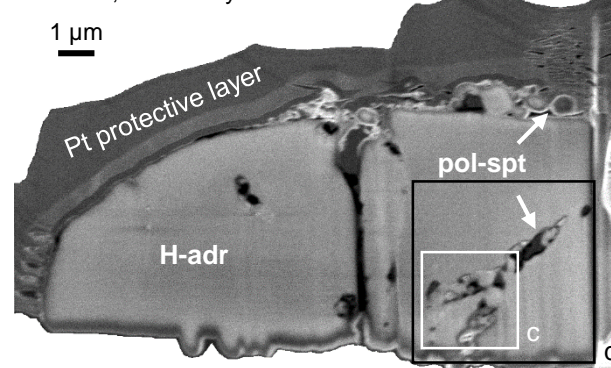
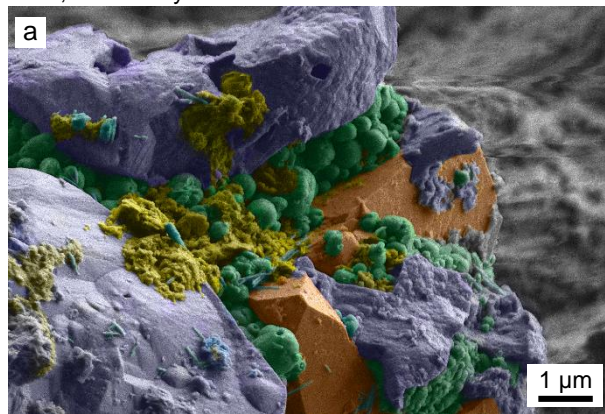


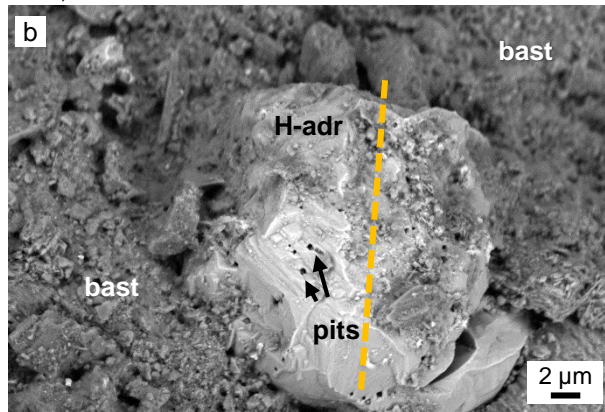
Figure 6 – Ménez et al.



2 kV, secondary electrons



7 kV, backscattered electrons



3 kV, secondary electrons

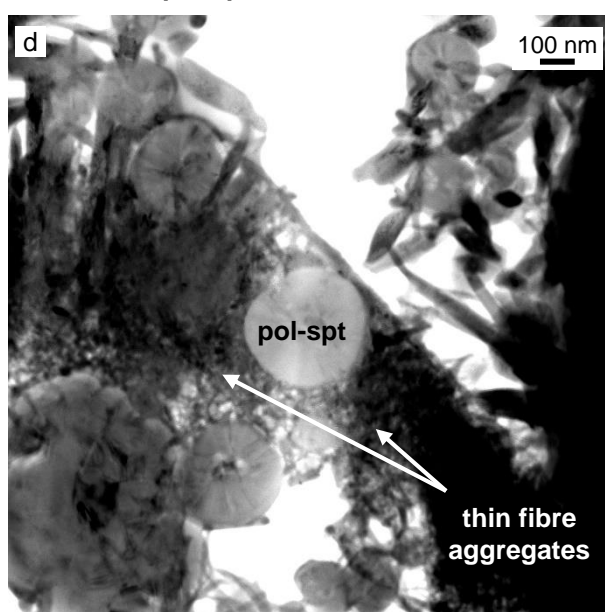
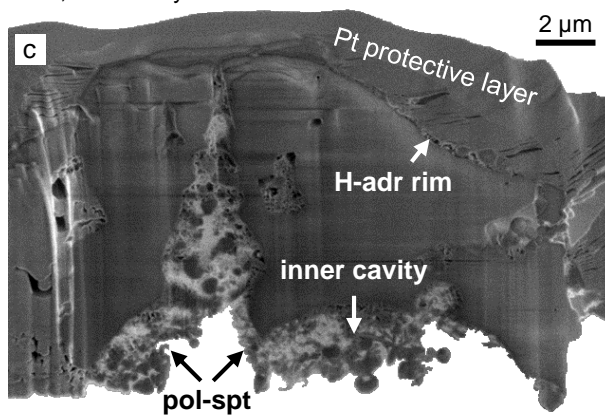


Figure 7 – Ménez et al.

10 kV, backscattered electrons

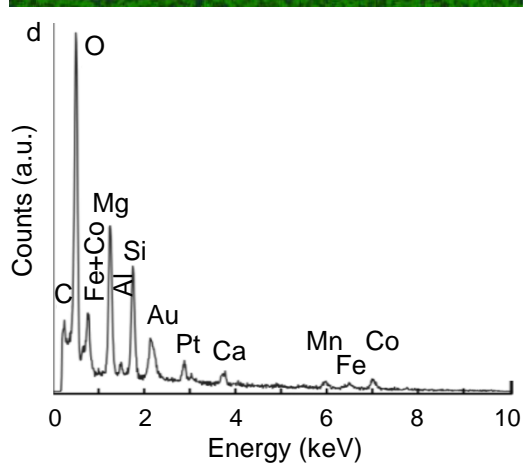
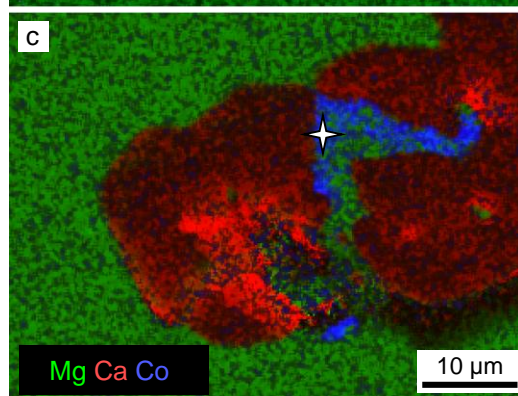
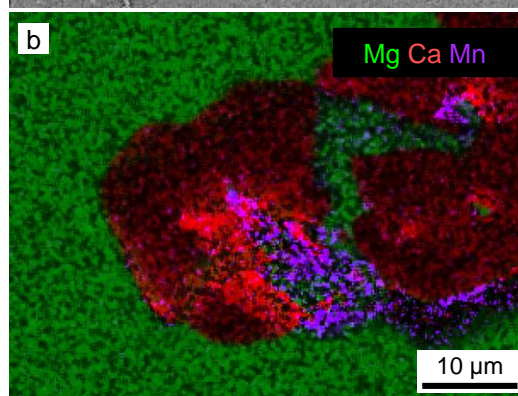
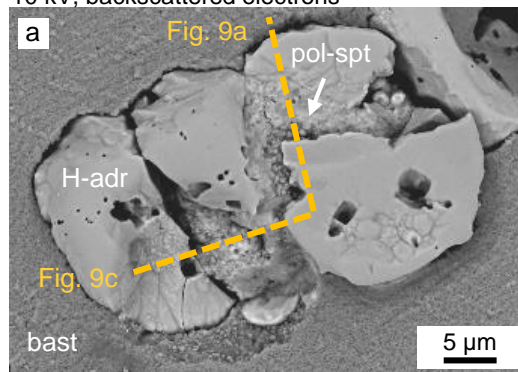


Figure 8 – Ménez et al.



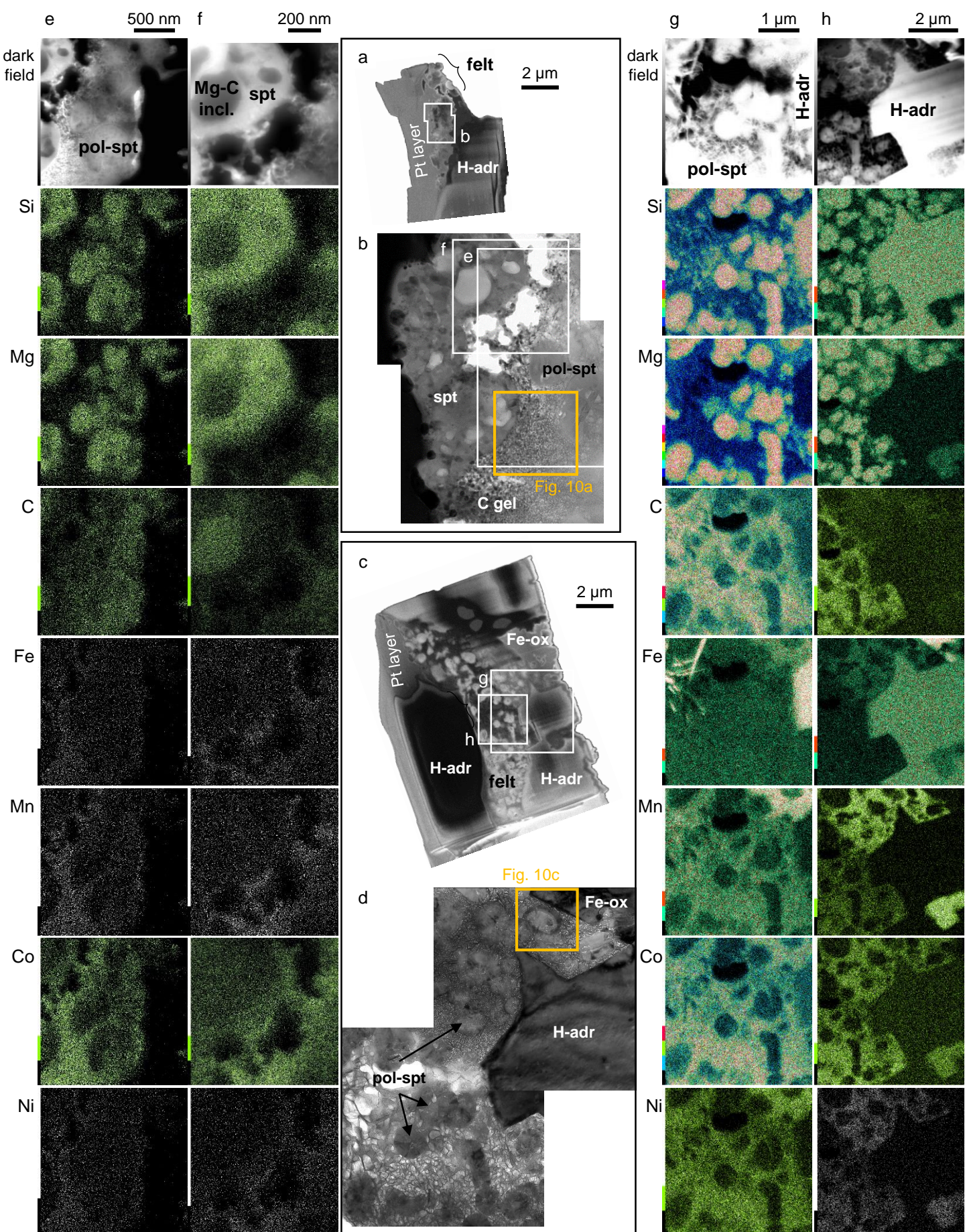


Figure 9 – Ménez et al.



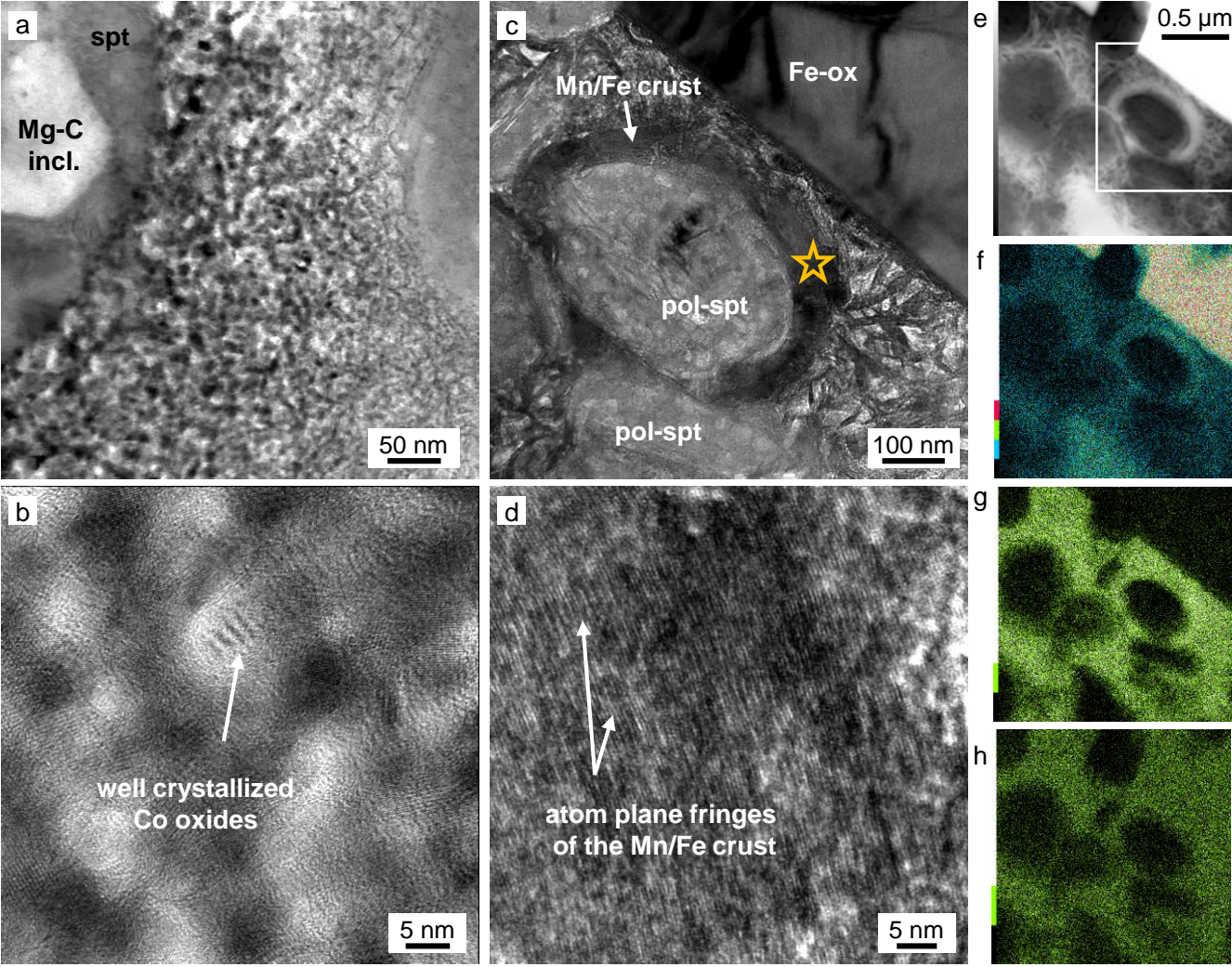


Figure 10 – Ménez et al.

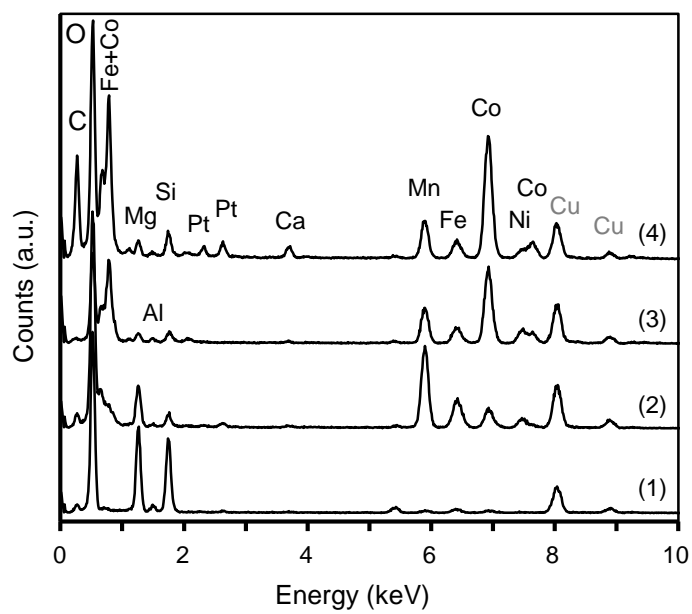


Figure 11 – Ménez et al.

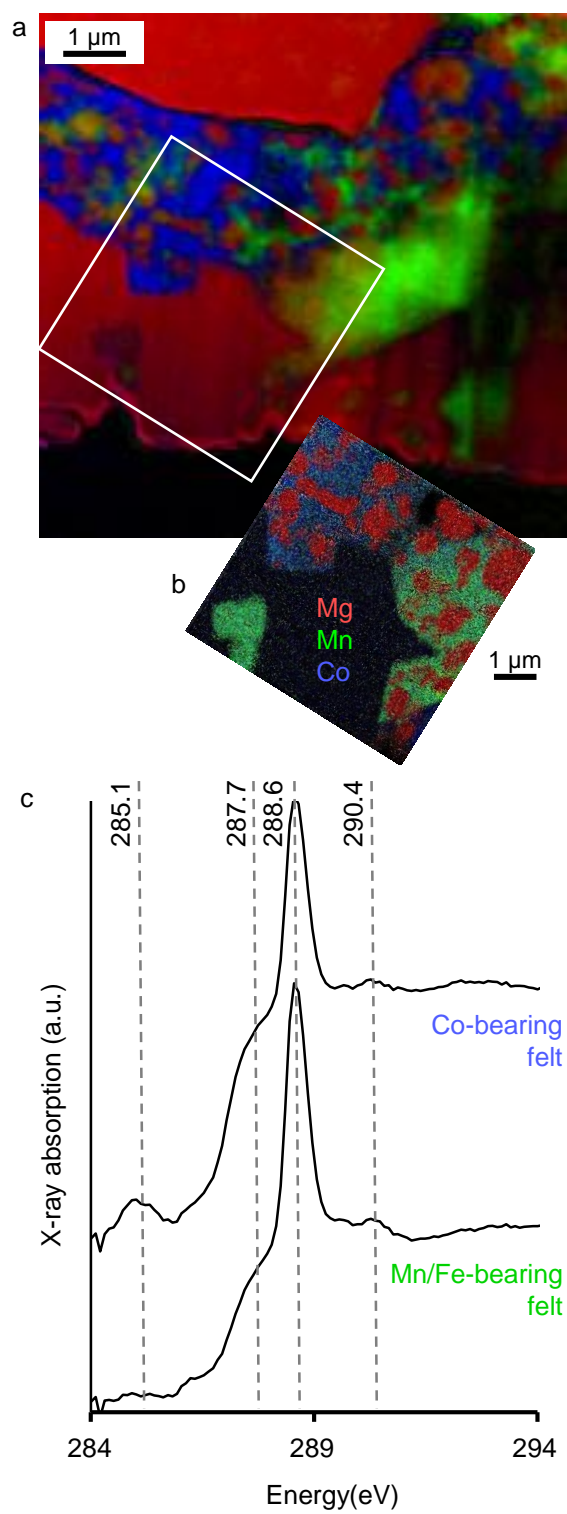


Figure 12 – Ménez et al.



