

# Major and trace elements exchanges during fluid-rock interaction at ultraslow-spreading oceanic lithosphere: Example of the South West Indian Ridge (SWIR)

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1	MAJOR AND TRACE ELEMENTS EXCHANGES DURING
2	FLUID-ROCK INTERACTION AT ULTRA-SLOW
3	SPREADING OCEANIC LITHOSPHERE: EXAMPLE OF THE
4	SOUTH WEST INDIAN RIDGE (SWIR)
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#### 15 **1. Introduction**

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17 Since the end of the 70's, numerous studies demonstrated that fluid-rock interactions 18 occurring within the oceanic lithosphere play a major role in the biogeochemical cycles. Earlier 19 studies focused on fluid-rock interaction in basaltic crust and reported chemical element fluxes 20 at the Earth surface, through high and low-temperature hydrothermal fluids venting, as well as 21 significant changes in mineralogical and chemical compositions of the MOR-type basaltic rocks 22 (e.g., Alt, 2004 for a review). More recent studies investigated the interaction of seawater-23 derived hydrothermal fluids with exhumed mantle rocks (i.e., abyssal peridotites). This process, 24 known as serpentinization, is now recognized as playing a key role in the chemical elements 25 exchanges between deep (mantle) and superficial (ocean, crust, biosphere) Earth reservoirs (Alt 26 et al., 2013; Deschamps et al., 2011; Hattori and Guillot, 2003).

27 Peridotites are strongly modified during serpentinization in terms of physical properties 28 (O'Hanley, 1996; Toft et al., 1990), oxidation degree (Andreani et al., 2013; Evans, 2008), 29 mineralogical assemblages (Mével, 2003; O'Hanley, 1996) and chemical composition. Indeed, 30 previous works on the Mid-Atlantic Ridge (MAR) and the South West Indian Ridge (SWIR) 31 showed that serpentinites can be enriched, but also depleted, in several chemical elements, such 32 as sulfur (Alt et al., 2013 and references within), carbon (Delacour et al., 2008a), Light Rare 33 Earth Elements (LREE, such as europium Eu), and Fluid Mobile Elements (FME: U, Pb, B, As, 34 Sb, Cs, Sr, Ba, Li, B; (Deschamps et al., 2011, 2012, 2013 and references within; Frisby et al., 35 2016; Lee et al., 2008; Niu, 2004; Vils et al., 2008) depending on serpentinization conditions and geological setting. Characterizing serpentinization processes and the chemical 36 37 compositions of serpentinites are thus of crucial importance to better understand the fluxes in 38 chemical elements between the ocean and the oceanic lithosphere. Understanding and quantifying the mass transfer during serpentinization would also be valuable in a more global 39

scale to i) better define the speciation and concentrations of elements that are either released to
the fluids, sustaining then deep and shallow biosphere, or stored into oceanic serpentinites, and
ii) determine the composition of the oceanic lithosphere entering subduction and therefore of
the fluids that will be released to the mantle wedge (Hattori and Guillot, 2003).

44 Studying element transfers related to serpentinization of abyssal peridotites is however 45 challenging because of the non-uniqueness of peridotite protolith, the common lack of primary 46 mineral relics due to the advanced stages of serpentinization of oceanic peridotites, the multiple 47 stages of serpentinization affecting the peridotites, and the low-temperature post-48 serpentinization processes. Indeed, low-temperature alteration processes can occur secondary 49 to serpentinization, transforming the serpentine minerals to clays and iron (oxyhydr)oxides, and 50 causing gains and losses in several chemical elements (e.g., Al, Fe, Mg; Caillaud et al., 2006, 51 2009; Destrigneville et al., 1998; Karpoff et al., 1989, 2017; Snow and Dick, 1995; Venturelli 52 et al., 1997)

53 In this study, we investigate mass transfer in major and trace elements occurring during 54 serpentinization of peridotites from the ultraslow-spreading South West Indian Ridge (SWIR), 55 and more particularly from the "smooth seafloor areas". Interest on this particular smooth 56 seafloor area is related to: 1) their near orthogonal geometry to the ridge axis, allowing to 57 evaluate the influence of serpentinization with increasing distance from the ridge and the role 58 of detachment faulting, and 2) the opportunity to determine, by comparing geochemical data 59 between smooth seafloor and MAR serpentinites, the influence of magmatic regime on fluid-60 rock interactions and chemical budget of the oceanic lithosphere. This paper will hence focus 61 on presenting and discussing major and trace elements compositions of the smooth seafloor 62 serpentinites to shed light on the consequences of fluid-rock interactions during long-lived 63 exhumation and hydration history.

66

The South West Indian Ridge is an ultraslow-spreading ridge (14 mm/yr; Patriat et al., 1997) 67 68 located in the Indian Ocean, between the Bouvet Triple Junction in the SW and the Rodrigues 69 Triple Junction (RTJ) in the NE (Fig. 1). Between the Indomed Transform Fault (TF) and the 70 RTJ, the SWIR is divided by four major transform faults (Discovery II, Gallieni, Atlantis II and 71 Melville) and shows from west to east : 1) a decrease in magmatic activity, as suggested by an 72 increase in axial valley depth (3 km in the west to 4.7 km in the east; Cannat et al., 1999) and 73 2) a decrease in oceanic crust thickness (6.7 km to the west and 2.4 km to the east; Muller et 74 al., 1997). This longitudinal evolution is due to an unusually cold mantle under the easternmost 75 part of the SWIR (Debayle and Lévêque, 1997) and the thermal influence of the Crozet hotspot 76 to the westernmost part (Sauter et al., 2009). The SWIR mantle has a heterogeneous chemical 77 and isotopic composition (Dupré and Allègre, 1983) and is believed to contain exotic 78 components, such as pieces of ancient continental crust, pyroxenites or eclogites (Gautheron et 79 al., 2015; Salters and Dick, 2002).

80 The study area is located in the easternmost part of the SWIR, eastward of the Melville TF, 81 between 62° and 65°E (Fig. 1). This zone is divided in two portions with different spreading 82 trends and rates: the eastern part of the ridge shows a nearly orthogonal spreading with an 83 Extension Spreading Rate (ESR) of 7 mm/yr, while the western part of the area spreads slightly 84 obliquely with an ESR of 6 mm/yr (Patriat et al., 1997). In the 62-65°E region, the oceanic 85 seafloor is composed of three different seafloor morphologies related to magma supply: 86 volcanic seafloor (high magma supply), corrugated seafloor (moderate magma supply) and the 87 smooth seafloor (minimal melt supply; Cannat et al., 2006). Volcanic seafloor morphology and 88 corrugated surfaces are commonly found along slow-spreading ridges, while smooth seafloor 89 was, so far, only been observed in this region of the SWIR (Cannat et al., 2006). The smooth 90 seafloor represents 37% of the SWIR seafloor surface between 62° and 65°E (Cannat et al., 91 2006). It is shaped as 15 to 30 km-long corridors, almost perpendicular to the ridge axis (Fig. 92 1; Cannat et al., 2006; Sauter et al., 2013), and is characterized by a predominance of mantle 93 peridotites (96%) with a very low proportion of mafic rocks (<3% of the dredged volume). Its 94 formation is related to nearly amagmatic conditions and mainly dominated by tectonic 95 processes (Cannat et al., 1999, 2006; Sauter et al., 2013).

96 In the 62-65°E region, mineralogical and chemical compositions of the abyssal peridotites 97 and basaltic rocks are particular. Indeed, clinopyroxenes are characterized by high Na<sub>2</sub>O and 98 low TiO<sub>2</sub> contents, compared to those of MAR peridotites, indicating metasomatic interaction 99 (Seyler et al., 2003). Low CaO and Al<sub>2</sub>O<sub>3</sub> contents together with high Na<sub>8.0</sub> and Sr contents of 100 basaltic glasses suggest that one or more early episodes of mantle partial melting occurred 101 followed by significant melt-rock interactions (Meyzen et al., 2003; Paquet et al., 2016). 102 Alteration of the smooth seafloor peridotites have been firstly investigated by Rouméjon and 103 Cannat (2014) and Rouméjon et al. (2015) with the aim to better understand the petrographic 104 textures and the fluid pathways of exhumed serpentinites in such peculiar geologic setting.

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#### 106 **3. Methods**

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The serpentinites investigated in this study were sampled during the SMOOTHSEAFLOOR (SMS) expedition in 2010 (R.V. Marion Dufresne, cruise MD183, PI: D. Sauter and M. Cannat). During this cruise, thirty-three dredges were conducted on and off axis of the SWIR along the two N-S-oriented zones of smooth seafloor, between the magnetic anomalies C5n.o at north and C3An.y at south (Fig. 1; Sauter et al., 2013). The recovered samples consisted of variously serpentinized and oxidized peridotites, with minor gabbros and basaltic rocks (Sauter et al., 2013). In this study, mineralogical and geochemical compositions of a selection of thirtyone serpentinite samples collected from the western and eastern corridors (Fig. 1) were carried out in order to assess changes in redox conditions and to better understand and evaluate exchanges in chemical elements during long-lived history of fluid-rock interactions.

118 Petrographic observations of 31 thin sections of serpentinites allows to determine the 119 primary and secondary mineral assemblages and the different serpentinization textures. 120 Protolith, primary and secondary mineral assemblages, serpentinization degree and textures are 121 presented in Table 1. Distance from the ridge was recalculated for each sample using the mean 122 position of the dredge given in Sauter et al. (2013; Fig. 1 and supplementray material). First 123 number of sample label corresponds to the dredge number; therefore, samples collected from 124 the same dredge would have similar distance from the ridge. Complementary mineral 125 identifications were performed by X-Ray Diffraction (XRD) and Raman spectroscopy to 126 determine the different serpentine types and the eventual occurrences of other phyllosilicates 127 (e.g., clays, talc). XRD patterns were recorded on a Brucker D8 diffractometer at Géosciences 128 Environnement Toulouse (GET, France) with copper anode using the CuKa radiation at 129 1.54060 nm (40 kV, 40 mA) and LinxEye detector. For each sample, XRD patterns were first 130 recorded on non-oriented bulk rock powder to investigate the presence of phyllosilicates (e.g. 131 serpentine, smectites). Non-oriented patterns were acquired over a  $2-80^{\circ} 2\theta$  range with a step 132 size of  $0.02^{\circ} 2\theta$  and 1s per step. Then the finest fraction (<2  $\mu$ m) of each sample was separated 133 and prepared as three oriented sections: air-dried, saturated with ethylene glycol (EG) and 134 heated at 500°C (Appendix A). Oriented patterns were acquired over a 2-36° 20 range with a 135 step size of  $0.02^{\circ}$  20 and 1s per step. Raman spectroscopic analyses were performed on 136 serpentine minerals of six particular samples (Table 1) at the Laboratoire de Géologie de Lyon 137 (ENS Lyon, France) with a confocal Horiba Jobin-Yvon LabRam HR800 spectrometer. The 138 used light source was an argon-ion laser at 514.5 nm wavelength and a power of 6 mW on silicate minerals. The measurements were performed between 150 and 1200 cm<sup>-1</sup> and between 139

3600 and 3800 cm<sup>-1</sup> to observe respectively the vibrational frequencies of Si-groups and OHgroups (Appendix A).

142 Chemical compositions of primary and secondary minerals were obtained using a CAMECA 143 SX100 Electron Microprobe, equipped with four WDS spectrometers and twelve diffraction 144 crystals at the Laboratoire Magmas et Volcans (LMV), Clermont-Ferrand (France). Minerals 145 were analyzed under a 15 kV tension and a 15 nA beam current, with a 5 µm spot size and a 146 counting time of 10 s. In situ mineral compositions of the studied serpentinites are presented in 147 Appendix B.

148 Bulk rock major and trace element compositions were carried out on 31 serpentinites and 149 are presented in Table 2. Major elements were measured by Inductively Coupled Plasma-150 Optical Emission Spectrometry (ICP-OES) on a Thermo Fisher iCAP 6500 at SARM 151 commercial laboratory (CRPG, Nancy, France). Additional potentiometric titration with 152 potassium dichromate after dissolution of the sample in HF/H<sub>2</sub>SO<sub>4</sub> mixture was performed on 153 all serpentinites to obtain FeO contents and to calculate Fe<sup>3+</sup>/Fetot ratios (Maxwell, 1968; 154 Carignan et al., 2001). Bulk rock trace element concentrations were measured by an Inductively 155 Coupled Plasma-Mass Spectrometer (ICP-MS) on a quadrupole Agilent 7500 at LMV, 156 Clermont Ferrand (France), after acid digestion of the sample. The reproducibility of the trace 157 analyses, given as  $2\sigma$  on 16 replicates of BCR-2 and BIR-1 USGS standards, is less than 2%158 for most of the elements, except Ni (4%) and V (20%). Additional boron concentrations were 159 also measured at SARM (CRPG, Nancy, France) by UV-visible spectrophotometry after fusion 160 with Na<sub>2</sub>CO<sub>3</sub>. Errors are given with a 99% confidence interval for all elements.

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162 4. Results
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#### 164 4.1. Petrographic description of the investigated serpentinites

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The SMS serpentinites investigated in this study are mostly serpentinized harzburgites (20 samples), lherzolites (7 samples) and dunites (2 samples; Table 1). Two other samples (SMS 5-4-17 and SMS-26-2-11) showing a higher proportion in pyroxenes (~70%,) are thus classified as serpentinized olivine websterites. The serpentinization degree of the SMS serpentinites ranges from moderate (50%) to complete (100%; Table 1).

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172 *4.1.1. Primary mineralogy* 

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174 Primary mineral assemblages of the variously serpentinized peridotites of the smooth 175 seafloor area are constituted of olivine, pyroxenes (ortho- and clino-) and Cr-spinel. Olivine is 176 present as relic mineral in the center of the serpentine mesh cells in the less serpentinized 177 samples (Fig. 2A) and represents a maximum of 35% (modal proportion) of the whole rock. 178 Relics are roundish to subhedral with a maximum size of 0.5 mm. Olivine composition ranges 179 between Fo<sub>88</sub> and Fo<sub>91</sub>, with a Fo<sub>90</sub> composition in average and a structural formula 180 Mg<sub>1.8</sub>Fe<sub>0.2</sub>SiO<sub>4</sub>, and a mean NiO content of 0.4 wt.% (Appendix B), similarly to other abyssal 181 peridotites (Komor et al., 1990; Rouméjon and Cannat, 2014; Seyler et al., 2003; Snow and 182 Dick, 1995).

Pyroxene relics are more abundant than olivine relics. No preferential orientation of the pyroxene grains was observed petrographically. However undulating extinction and kink-band deformations observed in some samples indicate high-temperature ductile deformation before serpentinization. Ortho- and clinopyroxenes were both identified in the serpentinized peridotites (Fig. 2A). Orthopyroxene is defined as enstatite, with En<sub>88</sub>Fs<sub>10</sub>Wo<sub>2</sub> as average composition (Appendix B), and frequently displays exsolution lamellae of augite (En<sub>56</sub>Fs<sub>7</sub>Wo<sub>37</sub> in average). Most of the orthopyroxenes from the SMS serpentinites have TiO<sub>2</sub> concentrations higher than 0.1 wt.% (up to 0.21 wt.%), within the range of the orthopyroxenes of the SWIR peridotites (Frisby et al., 2016; Rouméjon and Cannat, 2014; Seyler et al., 2003; Snow and Dick, 1995), but higher than those of the MAR peridotites (Cannat et al., 1992; Kodolányi et al., 2012). Clinopyroxene is present as diopside, with an average composition  $En_{46}Fs_5Wo_{49}$ , and shows frequent exsolution lamellae of augite ( $En_{56}Fs_7Wo_{37}$ ). Concentrations in Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in clinopyroxene are higher than those measured in the MAR clinopyroxenes (> 0.11 wt.%, > 4.5 wt.%, > 0.2 wt.%, respectively).

Spinel in the SMS serpentinites is present either as fresh Cr-spinel or as its alteration phase called ferritchromite. Fresh Cr-spinel is homogeneous with a brown to mahogany color in plane light and with a structural formula being  $(Fe^{2+}_{0.22}-0.36Mg^{2+}_{0.64}-0.77)(Fe^{3+}_{0.01}-0.1Cr^{3+}_{0.18}-0.54Al^{3+}_{1.38}-$ 1.75)O4. Their Cr# (= Cr/(Cr+Al) x 100 in atomic proportion) varies between 9.4 and 28.3 (Appendix B), a range that overlaps the lower end of the SWIR Cr-spinels range (14.9 – 48.8; Dick and Bullen, 1984; Seyler et al., 2003) and that is significantly lower than those of the MAR Cr-spinels (21.4 – 74.2; Komor et al., 1990; Kodolányi et al., 2012; Cannat et al., 1992).

# 205 4.1.2. Secondary mineralogy

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207 Secondary minerals being identified in the SMS serpentinites are serpentine, magnetite, 208 tremolite, chlorite, talc, hydrogarnet, goethite, hematite, carbonates and sulfides. The most 209 abundant secondary mineral present in the serpentinites and replacing both primary olivine and 210 orthopyroxene is serpentine, which gives a pale green to grey-black color in handspecimen (Fig. 211 2B and 2C). Olivine is replaced by serpentine with a classical mesh texture, where the center 212 of the mesh cells is either a relic of olivine or lizardite (for more advanced serpentinization 213 stages). Mesh cells are up to 1 mm wide and are outlined by a network of thin magnetite veins 214 (Fig. 2D). Mesh texture is predominant but ribbon texture is also observed, e.g. SMS 14-5-8, 215 17-4-2 and 30-2-2. Dark grey pseudomorphic bastite replaces orthopyroxene, either partially 216 along the rim or totally and are commonly crosscut by numerous serpentine veins (Fig. 2B). 217 RAMAN analyses on bastite pseudomorphs display a shift of the lizardite peaks (Appendix A), 218 suggesting that a very small proportion of antigorite may be present with lizardite. However, 219 antigorite remains unnoticeable on bulk rock XRD spectra. In most of the samples, serpentine 220 was identified as lizardite 1T (XRD spectra, Appendix A). Antigorite is present only in the two 221 olivine websterites (SMS 5-4-17 and 26-2-11) in replacement of pyroxenes, together with 222 tremolite and chlorite (Fig. 2E and 2F). No brucite was detected on XRD or RAMAN spectra. 223 Secondary veins of fibrous or banded serpentine, mostly chrysotile and lizardite, are abundant 224 in SMS serpentinites and crosscut the preexistent mesh texture with a preferred orientation. 225 Interlocking and interpenetrating recrystallization textures were only observed in two 226 serpentinized harzburgites, SMS 15-3-16 and 29-5-41.

227 Serpentine chemical composition (irrespectively of varieties and textures) shows a wide 228 range: SiO<sub>2</sub> ranges from 34.2 to 45.0 wt.%, MgO from 26.0 to 44.4 wt.%, FeO from 1.5 to 229 14.8 wt.% and Al<sub>2</sub>O<sub>3</sub> up to 4.5 wt.% (Appendix B). Lizardite in the mesh texture has an average 230 structural formula ( $Fe_{0.2}Mg_{2.8}$ )Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and shows higher concentrations in FeO (> 10 wt.%) 231 than bastite and serpentine veins. Antigorite is characterized by slightly higher content in Al<sub>2</sub>O<sub>3</sub> 232 as indicated by its formula  $(Fe_{0.3}Mg_{2.7})(Si_{1.9}Al_{0.1})O_5(OH)_4)$ . Bastite frequently contains 233 significant concentrations in CaO and  $Al_2O_3$  (up to ~ 2 wt.%), as indicated by its structural 234 formula (Ca<sub>0-0.1</sub>Fe<sub>0.1-0.4</sub>Mg<sub>2.5-2.9</sub>)(Si<sub>1.8-2</sub>Al<sub>0-0.2</sub>)O<sub>5</sub>(OH)<sub>4</sub>). Serpentine in recrystallized textures is 235 also slightly enriched in Al<sub>2</sub>O<sub>3</sub> compared to that in mesh textures (up to 3.5 wt.%). Chrysotile 236 veins have similar composition than lizardite in mesh textures and bastites. Na<sub>2</sub>O and NiO 237 concentrations are comparable for all serpentine textures (0-0.25 wt.% and 0-0.7 wt.%, 238 respectively).

Magnetite ( $Fe^{2+}Fe^{3+}_{2}O_{3}$ ) appears in three different habits in the SMS serpentinites. It occurs 239 240 predominantly as veins forming a network underlining the serpentine mesh cells (Fig. 2B). 241 Secondly, it is also found as alteration mineral of sulfides (pentlandite or millerite), forming a 242 grey alteration corona around the yellow sulfide core in reflected light. In both cases, its 243 composition is classical (Fe<sub>2</sub>O<sub>3</sub> 68 wt.%, FeO 31 wt.%). The magnetite is thirdly present as 244 exsolution and along the rims and cracks of Cr-spinel grains, or as ferritchromite when Cr-245 spinel replacement is complete (when all Mg, Al and Cr are replaced by Fe; Kimball, 1990). 246 Altered Cr-spinel composition is then modified, with lower concentrations in Cr<sub>2</sub>O<sub>3</sub>, MgO and Al<sub>2</sub>O<sub>3</sub> than fresh Cr-spinel and a structural formula being (Fe<sup>2+</sup>0.30-0.83Mg<sup>2+</sup>0.13-0.70)(Fe<sup>3+</sup>0.03-247 1.28Cr<sup>3+</sup>0.38-1.14Al<sup>3+</sup>0.33-1.34)O<sub>4</sub>. 248

249 Other secondary minerals include tremolite, talc, chlorite, and hydrogarnet. Tremolite, 250 whose structural formula is Ca<sub>1.9</sub>Na<sub>0.1</sub>Mg<sub>4.6</sub>Fe<sub>0.3</sub>(Al<sub>0.2</sub>Si<sub>7.8</sub>O<sub>22</sub>)(OH)<sub>2</sub>, is found as replacement 251 of clinopyroxenes forming elongated or fan-shaped crystals. Tremolite veins are scarce, being 252 only identified in two serpentinized harzburgites (SMS 5-4-14 and 27-2-19) and two olivine 253 websterites (SMS 5-4-17 and 26-2-11). In SMS 5-4-17 and 26-2-11, tremolite is found in veins 254 intertwined with antigorite and chlorite, while opaque iron oxides and hydroxides, together with 255 serpentine, replace olivine (Fig. 2E and 2F). Talc Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> is found either as 256 replacement of orthopyroxene or as veins in samples SMS 1-2-35, 4-2-1, 5-4-14, 10-5-6, 27-2-257 19 and 29-5-41 (>1% modal), indicating circulation of a Si-rich fluid. Four peridotites (SMS 1-258 2-35, 7-3-7, 22-6-13 and 34-2-17) display interstitial plagioclase that was totally replaced by 259 hydrogarnet during fluid-rock interaction (Fig. 3A) suggesting magmatic impregnation. 260 Hydrogarnet is present as clusters of very small dark crystals (10-15µm each; Fig. 3A). The 261 replacement of plagioclase by hydrogarnet releases Al that is used to precipitate clinochlore 262 (Appendix B) as alteration coronas around the hydrogarnet (Fig. 3A). Chlorite is also observed 263 associated with and related to alteration of Cr-spinel around which it forms a dark blue corona in cross-polarized light (Fig. 3A, Appendix B). Chlorite veins are only found in serpentinized
olivine websterites SMS 5-4-17 and 26-2-11. Hydrogarnet and chlorite alteration shows clearly
plagioclase impregnation in the peridotites, however, other petrographic evidences, such as
inter-pyroxenes cusps boundaries (Fig. 3B) and/or olivine-pyroxenes interstitial crystallization
textures (Table 1) suggest different degrees of melt-rock interactions (Piccardo et al., 2007;
Rampone et al., 1997).

270 Sulfide minerals are very scarce and only represent a very tiny proportion of the bulk rock 271 (<<1%). Some relics of euhedral to subhedral primary sulfides, whose size can reach up to 272 100 µm, occur predominantly as pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub>. Secondary sulfides are sub-rounded or bleb-shaped, with a maximum size of 50 µm, and are mainly pentlandite and millerite (NiS). 273 274 They frequently replace primary pentlandite in association with magnetite. The composition of 275 pentlandite (primary and secondary) ranges between 32.7-35.5 wt.% S, 27.3-42.4 wt.% Fe, 276 21.4-37.1 wt.% Ni, 0.3-4 wt.% Co and 0-2.4 wt.% Cu, while millerite is composed of 59.6-72.3 wt.% Ni, 27-35.6 wt.% S, 1.4-4.2 wt.% Fe, 0-0.7 wt.% Co and 0-1.4 wt.% Cu. Two samples 277 278 show distinct secondary sulfide mineral assemblages: SMS 2-2-11 displays an assemblage of 279 millerite + violarite (FeNi<sub>2</sub>S<sub>4</sub>) + chalcopyrite (CuFeS<sub>2</sub>), while SMS 5-4-14 contains awaruite 280 (Ni<sub>3</sub>Fe) associated to pentlandite. Awaruite generally forms during early stages of 281 serpentinization when reducing conditions predominates (Delacour et al., 2008b; Frost, 1985). 282 However, due to the high serpentinization degree of the sample (91%; Table 1), it is more likely 283 that awaruite results from the destabilization of pentlandite (Chamberlain, 1965; Kanehira et 284 al., 1975).

Nine SMS serpentinites contain significant proportions (>1% modal) of hematite (Fe<sub>2</sub>O<sub>3</sub>) and goethite (FeO(OH)) (Table 1). These Fe-minerals are precipitated as final product of complete sulfide alteration (e.g., SMS 4-2-1, 11-2-11, 14-5-8, 21-5-6), displaying then shapes, sizes and textures similar to those of their parent sulfide minerals (primary or secondary

289 pentlandite and millerite; Fig. 3C). They are also found as amorphous iron oxides and/or 290 hydroxides (named as IOH further in this manuscript, e.g., SMS 4-2-1, 5-4-14, 5-4-17, 11-2-291 11, 14-5-1, 14-5-8, 21-5-6, 26-2-11, 33-3-27), which result from the combined alteration of 292 serpentine and magnetite (Caillaud et al., 2006; Venturelli et al., 1997). These IOH are reddish 293 to orange in reflected light and replace serpentine at the center of the mesh cells (Fig. 2E-F and 294 Fig. 3C-D). Although their absence of crystallinity prevented acquisition of reliable chemical 295 analyses, their identification was suggested by peaks of weak intensity on RAMAN spectra. 296 When the IOH are present in the serpentine mesh texture, magnetite is locally absent.

297 Carbonates are present as calcite (CaCO<sub>3</sub>) in three samples. They either form dark brown 298 opaque areas with blurred limits in thin section (SMS 8-2-25) or veins of 1  $\mu$ m to 1 mm (SMS 299 10-5-6 and 29-5-41). In sample SMS 10-5-6, calcite is associated with talc in large veins. One 300 occurrence of aragonite was identified by RAMAN spectroscopy on an isolated vein in SMS 301 34-2-17. Elementary and isotope carbon analyses (Total Inorganic Carbon >600 ppm, 302  $\delta^{13}C_{TIC} \sim +3\%$ ; pers. data) suggest that two other samples (SMS 1-2-35 and 27-2-19) contains 303 little amounts of carbonates not visible in thin sections.

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# 305 <u>4.2. Bulk rock chemical composition of serpentinites</u>

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Bulk rock major and trace elements compositions of 31 serpentinites are given in Table 2. These serpentinites show a wide range of compositions: SiO<sub>2</sub> (non-anhydrous values) ranges from 36.9 to 44.6 wt.% (average 40.1 wt.%), Al<sub>2</sub>O<sub>3</sub> from 0.6 to 3.9 wt.% (av. 2.2 wt.%), Fe<sub>2</sub>O<sub>3T</sub> from 7.2 to 19.6 wt.% (av. 9.2 wt.%), MgO from 25.8 to 37.9 wt.% (av. 34.3 wt.%), CaO from 0.2 to 6.1 wt.% (av. 2.3 wt.%), Na<sub>2</sub>O from 0.1 to 0.8 wt.% (av. 0.2 wt.%) and LOI from 4.9 to

<sup>307 4.2.1.</sup> Major elements

314 14.5 wt.% (av. 11.6 wt.%). These compositions are similar to those reported in previous studies 315 on SWIR serpentinites (Niu, 2004; Rouméjon and Cannat, 2014). In a diagram MgO/SiO<sub>2</sub> vs. 316 Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (Fig. 4), the studied serpentinites follow the terrestrial array defined by Jagoutz et 317 al. (1979) and Hart and Zindler (1986) for mantle peridotites (0.65 < MgO/SiO<sub>2</sub> <1 and 318 0.015< Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> <0.09). However, one serpentinized lherzolite (SMS 11-2-4) and four IOH-319 serpentinites (containing strictly  $\geq 1\%$  modal, SMS 4-2-1, 5-4-17, 11-2-11 and 33-3-27) show 320 higher Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratios and lower MgO/SiO<sub>2</sub> ratios than SWIR and MAR peridotites (Fig. 4; 321 Niu, 2004; Paulick et al., 2006; Jöns et al., 2010; Kodolányi et al., 2012; Rouméjon, 2014; 322 Rouméjon and Cannat, 2014).

The Fe<sup>3+</sup>/Fe<sub>total</sub> ratio, used as a proxy of oxidation degree of the serpentinites, ranges from 0.39 and 0.87. This ratio increases with both LOI and estimated visual serpentinization degree of the rock (Fig. 5). Serpentinites with low serpentinization degrees (~ 50%; e.g., SMS 1-2-1) have low Fe<sup>3+</sup>/Fe<sub>total</sub> ratios and LOI (~ 4 wt.%), whereas those with high serpentinization degrees (99 %; e.g., SMS 14-5-1) have high Fe<sup>3+</sup>/Fe<sub>total</sub> ratios and LOI (14 wt.%). IOHserpentinites display high Fe<sup>3+</sup>/Fe<sub>total</sub> ratios, LOI and serpentinization degree (e.g., SMS 11-2-11, Fe<sup>3+</sup>/Fe<sub>total</sub> ratio of 0.87, 9.5 wt.% LOI).

330

#### 331 *4.2.2. Trace elements*

332

Multi-element patterns of the SMS serpentinites, volatile-free and normalized to primitive mantle (Sun and McDonough, 1989), are mostly depleted compared to primitive mantle (PM; Fig. 6A), except one serpentinite showing petrographic evidences of plagioclase impregnation, SMS 22-6-13, which is enriched 2 to 300 times to the PM. Trace element spectra of SMS serpentinites are within the range of the SWIR serpentinites (Niu, 2004) but enriched in almost all trace elements compared to MAR serpentinites (Andreani et al., 2014; Deschamps et al., 339 2013 and references within). LILE (Cs, Ba, Rb) concentrations and high positive anomalies in 340 U, Pb and Sr (between 0.1 and 100 times the PM) of SMS serpentinites are similar to those of 341 abyssal peridotites in the literature (Bodinier and Godard, 2008; Deschamps et al., 2013). 342 Positive anomalies in U, Pb and Sr are common features in serpentinites, irrespectively of their 343 context of formation (Deschamps et al., 2013). Rare Earth Elements (REE) patterns, volatile-344 free and normalized to chondrite (Fig. 6B; Sun and McDonough, 1989), show a general 345 depletion in LREE and MREE (La to Eu) compared to the chondrite value (CV; Fig. 6B), with 346 the exception of few samples, the serpentinite with plagioclase impregnation SMS 22-6-13 347 (enriched up to 38 times the CV) and five IOH- serpentinites, SMS 4-2-1, 11-2-11, 14-5-8, 5-348 4-17 and 33-3-27, which are enriched up to 10 times the CV. HREE (from Gd to Lu) 349 concentrations show a wide range, from slightly depleted (minimum  $0.12 \times CV$ ) to enriched 350 (up to  $14 \times CV$ ). Half of the SMS serpentinites show depletion in LREE compared to HREE 351 (west corridor: SMS 1-2-1, 1-2-35, 2-2-11, 2-2-17, 3-2-1, 6-3-14, 7-3-7, 8-2-17, 8-2-25, 10-5-352 6, 11-2-4, 15-3-16, 17-4-19, 17-4-32; east corridor: SMS 27-2-19, 28-4-10, 29-6-13), whereas 353 the other half (west corridor: SMS 4-2-1, 5-4-14, 5-4-17, 11-2-11, 13-4-11, 14-5-1, 14-5-8; east 354 corridor: SMS 21-5-6, 22-6-13, 29-5-41, 30-2-2, 33-3-27, 34-2-17) show enrichment in both 355 LREE and HREE (Fig. 6B). Twenty-one samples (except SMS 1-2-35, 6-3-14, 8-2-17, 8-2-25, 356 10-5-6, 17-4-19, 17-4-32, 27-2-19, 28-4-10, 29-6-13 and 30-2-2) show a Ce anomaly, which is 357 negative for most of the serpentinites  $(0.004 \text{ to } 1.56 \times \text{CV}; \text{e.g.}, \text{SMS } 11-2-11)$  and only positive 358 for two serpentinites (0.7 to  $128 \times CV$ , SMS 22-6-13 and 29-5-41; Fig. 6B). By comparison, 359 such Ce anomaly is not observed in MAR serpentinites (Fig. 6B). In addition, SMS serpentinites 360 lack Eu anomaly (Fig. 6B). The SMS serpentinites also contain higher concentrations in Fluid 361 Mobile Elements (FME) than the PM: B (33-115 ppm, average 65 ppm), Li (0.94-8.83 ppm, 362 av. 4.45 ppm), Cd (0.02-0.17 ppm, av. 0.06 ppm), As (0.22-28 ppm, av. 3.62 ppm), and Sb 363 (0.003-9.49 ppm, av. 1.03 ppm) (Table 2). These values are within the range of global abyssal
364 serpentinites (Niu, 2004; Deschamps et al., 2013 and references within).

365

### 366 **5. Discussion**

367

368 Since its formation at and along the ridge axis, via magmatic or tectonic-dominated 369 processes, the oceanic lithosphere is affected by interaction with seawater-derived, magmatic 370 or hydrothermal fluids resulting in chemical exchanges between the rocks and the fluids. 371 Quantifying these chemical transfers and understanding in which conditions they occur are 372 crucial to better constrain the biogeochemical cycles of the Earth and the compositions of the 373 different reservoirs. The smooth seafloor areas along the SWIR, sites investigated during this 374 study, have the particularity to be nearly amagmatic and to be formed by tectonically-dominated 375 processes ("flip-flop model"; Sauter et al., 2013). Consequently, fluid interaction in these zones 376 will affect predominantly the ultramafic rocks exposed on the ocean floor via detachment 377 faulting. In the following section, we will discuss the influence of long-lived interaction of 378 ultramafic rocks with fluids (magmatic, hydrothermal, seawater, ...) on chemical compositions 379 of the rocks and on chemical transfers with a focus on some specific tracers and elements. In 380 order to evaluate the effect of time and the lateral variability in such specific ultraslow-381 spreading context, chemical compositions will be regarded as a function of ridge axis distance 382 and thus of exhumation history.

383

# 384 <u>5.1. Influence of magmatic processes on protolith compositions</u>

385

386 Primary compositions of serpentinites protoliths at the smoothseafloor, i.e., harzburgites,
387 lherzolites, dunites or olivine websterites, result from magmatic processes, such as partial

388 melting and melt-rock interaction (i.e. impregnation, refertilization) and depend on underlying 389 mantle composition. Knowing precisely these primary compositions is important to evaluate 390 element mass transfer occurring during secondary fluid-rock interaction within the oceanic 391 lithosphere.

392

## 393 5.1.1. Partial melting influence on protolith composition

394

395 In order to differentiate between primary and secondary element mass transfer, it is crucial 396 to evaluate what element are mobile or immobile and how they evolve during primary and 397 secondary processes. During magmatic processes, partial melting degree and element 398 compatibility and mobility significantly impact the chemical composition of the protolith. 399 Partial melting degree in mantle-derived rocks is commonly evaluated using TiO<sub>2</sub> content of 400 the rocks, as this element is considered as immobile during hydrothermal alteration processes 401 (Finlow-Bates and Stumpfl, 1981; Deschamps et al., 2013). Therefore, any major element 402 correlating with TiO<sub>2</sub> content would then reflect the protolith composition of the SMS 403 serpentinites. During oceanic upper mantle partial melting, as partial melting degree increases, 404 SiO<sub>2</sub>, CaO, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents will progressively decrease in residual peridotites 405 whereas MgO and Fe<sub>2</sub>O<sub>3</sub> contents will increase (Bodinier and Godard, 2003; Niu et al., 1997). 406 This evolution of  $TiO_2$  with partial melting degree is shown in Figure 7 for the studied SMS 407 serpentinized peridotites: the serpentinized dunites show the lowest TiO<sub>2</sub> contents (< 408 0.02 wt.%), the serpentinized lherzolites have the highest TiO<sub>2</sub> contents (> 0.06 wt.%), and the 409 serpentinized harzburgites display intermediate values between 0.02 and 0.08 wt.%. The only 410 exception to these subgroups is the Ti-enriched serpentinized harzburgite, SMS 22-6-13, which 411 shows a high TiO<sub>2</sub> content ~0.16 wt.%. This enrichment in TiO<sub>2</sub> content for this specific sample 412 will be discussed in section 5.1.2.

413 Among major elements, Al<sub>2</sub>O<sub>3</sub> is classically considered, similarly to TiO<sub>2</sub>, as immobile 414 during fluid-rock interaction (Sinha et al., 1986), except in very alkaline conditions (Shervais 415 et al., 2005). Both MgO and CaO are commonly lost to the fluids (Coleman and Keith, 1971; 416 Kelley et al., 2001; Snow and Dick, 1995), while studies on SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O behavior 417 are limited or not fully conclusive (Malvoisin, 2015; Shervais et al., 2005; Sinha et al., 1986). 418 In the SMS serpentinites, Al<sub>2</sub>O<sub>3</sub> content exclusively results from magmatic processes, as it fully 419 correlates with TiO<sub>2</sub> content (Fig. 7). It is worthwhile to note that Al<sub>2</sub>O<sub>3</sub> contents in SMS 420 serpentinites are within the range of the SWIR peridotites but higher than that of the MAR 421 serpentinites (Fig. 4 et 7). This suggests that the depleted upper mantle of the SWIR would be 422 initially enriched in Al<sub>2</sub>O<sub>3</sub> compared to the upper mantle of the MAR. Similar to Al<sub>2</sub>O<sub>3</sub>, CaO 423 content correlates with TiO<sub>2</sub> content (Fig. 7), the highest contents being related to the 424 occurrences of clinopyroxenes in the serpentinized lherzolites. Only two samples, SMS 10-5-6 and 29-5-41, are off the trend with higher CaO contents (respectively 6.1 and 2 wt% non-425 426 anhydrous). This enrichment is related to the presence of calcite veins in the serpentinites that 427 precipitated from the combination of Ca and marine dissolved inorganic carbon (Dessimoulie, 428 pers. data), similarly to other places along mid-oceanic ridges (Kelley et al., 2001, 2005; 429 Delacour et al., 2008a; Schwarzenbach et al., 2013). The other major elements, SiO<sub>2</sub>, MgO, 430 Fe<sub>2</sub>O<sub>3T</sub> and Na<sub>2</sub>O, display rough correlation with TiO<sub>2</sub> content (Fig. 7): constant for Fe<sub>2</sub>O<sub>3T</sub> and 431 SiO<sub>2</sub>, negative for MgO and positive for Na<sub>2</sub>O, these trends resulting from mantle partial 432 melting (Bodinier and Godard, 2003). However, some discrepancies occur in those correlations, 433 in particular for IOH-serpentinites that spread out from the trend defined by the other 434 serpentinites, showing lower MgO content and higher Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O contents. These peculiar 435 compositions likely reflect mobility of these three elements during fluid-rock interactions (see 436 discussion section 5.2).

REE patterns of the serpentinites can also provide information on magmatic processes and on partial melting degree. In this study, the subparallel HREE patterns of the SMS serpentinized peridotites (Fig. 6B) indicate different partial melting degrees of a mantle source (Bodinier and Godard, 2003). HREE contents of SMS serpentinites are thus representative of the protolith composition. In contrast, overlapping occurs for LREE suggesting that concentration in these LREE were subsequently modified by later processes, i.e., melt-rock or fluid-rock interactions.

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# 444 5.1.2. Melt-rock interaction influence on protolith composition

445

446 At mid-oceanic ridges, peridotites are commonly percolated by ascending basaltic melts that 447 can modify their bulk rock composition, depending on the melt composition and the degree of 448 melt-rock interaction (Niu, 2004; Niu et al., 1997; Piccardo et al., 2007; Rampone et al., 1997). 449 Melt-rock interactions and/or impregnation processes, if not cryptic, lead to changes in major 450 and trace element compositions, as well as several petrographic evidences (e.g., plagioclase 451 impregnation, REE flat patterns, enrichment in Fe, Ti, Na, ...). Abyssal peridotites are residues 452 of partial melting and then depleted in REE compared to the primitive mantle (PM). Thus any 453 REE spectra enriched compared to the PM value could result from refertilization processes 454 (Bodinier and Godard, 2003; Deschamps et al., 2013; Niu, 2004). In addition, impregnation of 455 peridotites by basaltic melts, which are enriched in both LREE and HREE, produces flat to 456 enriched REE patterns (Bodinier and Godard, 2003; Deschamps et al., 2013; Frisby et al., 457 2016). In case of cryptic metasomatism, REE spectra show a sigmoidal shape with higher 458 enrichment in LREE than in HREE (Bodinier and Godard, 2003). Positive europium anomaly 459 in the REE spectra of the peridotites could also be related to crystallization of plagioclase from 460 percolating melts in the peridotites (Borghini and Rampone, 2007; Frisby et al., 2016; Paquet 461 et al., 2016). High TiO<sub>2</sub> content in SWIR peridotites were interpreted as related to post462 melting/refertilization processes (Niu, 2004; Paquet et al., 2016; Warren and Shimizu, 2010) 463 whereas Seyler et al. (2003) suggested that this  $TiO_2$  enrichment, together with Na<sub>2</sub>O 464 enrichment, is rather due to a very heterogeneous Ti-enriched mantle source.

465 Some SMS peridotites show peculiar mineral assemblages and textures (e.g., 466 olivine/pyroxene crystallization, interstitial plagioclase; see Table 1 and Fig. 3A et B) and/or 467 specific trace element compositions indicative of melt-rock reactions. Indeed, several 468 serpentinized abyssal peridotites are characterized by LREE-enriched and flat REE patterns 469 (e.g., SMS 22-6-13, SMS 11-2-11), while most of them show classical depletion in LREE 470 compared to HREE (Fig. 6B; Frisby et al., 2016; Niu, 2004). This enrichment is likely related 471 to melt-rock interaction as petrographic evidences of melt circulation were observed (e.g. SMS 472 11-2-4). One serpentinite, SMS 22-6-13, displays anomalously high trace element 473 concentrations, flat REE pattern (Fig. 6) and high  $TiO_2$  concentrations (Fig. 7) implying thus 474 significant refertilization during melt circulation. Enrichment in REE is also observed for some 475 serpentinites containing high proportion of IOH (e.g., SMS 4-2-1, 11-2-11 and 33-3-27; Fig. 6) 476 suggesting that such enrichment is likely due to secondary processes such as fluid-rock 477 interaction. This will be discussed in Section 5.2.

478 Serpentinized peridotites characterized by olivine or pyroxene (re)crystallization (Fig. 3B) 479 do not show specific trace element compositions. This could be explained by percolation of a 480 melt in equilibrium with the peridotite (Bodinier and Godard, 2003) or by a little amount of 481 melt that would not affect the peridotite composition at the hand-specimen scale (Paquet et al., 482 2016). The absence of Eu anomaly in samples with plagioclase impregnation (SMS 1-2-35 and 483 7-3-7) is likely related to alteration of plagioclase to hydrogarnet. Trace elements of previously 484 analyzed rodingites (i.e., plagioclase-bearing rocks altered to prehnite and grossular) display no 485 or negative Eu-anomaly, implying a leaching of Eu during the replacement of plagioclase (Tang 486 et al., 2018).

487

### 488 5.2. Influence of fluid-rock interactions on element mass transfer

489

490 Fluid-rock interaction affecting the oceanic lithosphere comprises a variety of processes 491 depending on fluid fluxes, temperature and redox conditions. Along fast-spreading ridges, 492 fluid-rock interactions are classically subdivided in high-temperature fluid-rock interaction, 493 with formation of a hydrothermal system, and low-temperature fluid-rock interaction that are 494 long-lasting processes that significantly affect the oceanic lithosphere composition (Alt, 2004; 495 Von Herzen, 2004). For slow-spreading ridge, similar evolution was reported as detachment 496 fault exhume ultramafic rocks with variable amounts of mafic rocks (i.e. gabbros; McCaig et 497 al., 2007, 2010). In the following section, we present the consequences of fluid-rock interaction, 498 with variable P-T, redox conditions and fluid compositions, on mass element transfer as a 499 function of ridge distance, so with aging and exposure of ultramafic rocks on the ocean floor in 500 an ultraslow-spreading context.

501

### 502 5.2.1. High-temperature fluid circulation

503

504 High-temperature fluid circulation in detachment-related context were reported along slow-505 spreading ridges to explain occurrences of high-temperature hydrothermal systems on 506 ultramafic rocks exposed via detachment faulting (McCaig et al., 2007, 2010; Alt et al., 2013). 507 In such settings, high-temperature fluid circulation, initiated by interaction of fluids with gabbro 508 intrusions, affects the ultramafic rocks at depth. Evidences of such high-temperature fluid 509 circulation, leading to the formation of sulfide deposits, either on the ocean floor or at depth 510 within the oceanic lithosphere, were observed in some serpentinites of the SWIR smooth 511 seafloor area. Indeed, three IOH-serpentinites, SMS 4-2-1, 5-4-17 and 11-2-11, have Fe<sub>2</sub>O<sub>3T</sub> 512 contents higher than other SMS serpentinites (>12 wt.%; Fig. 7), suggesting interaction of the 513 peridotites with high-temperature Fe-rich fluids. Interaction with such fluids (i.e., black 514 smoker-type fluids; Douville et al., 2002) also commonly lead to enrichments in S, precipitated 515 as sulfide minerals, REE and metals in the serpentinites. Enrichments in REE, FME and Cu, 516 Co and Zn characterized the three IOH-serpentinites (Fig. 6 and 11, Table 2). However, they 517 do not contain any sulfide, hematite and goethite only being present. A first possible 518 explanation of this lack of sulfide would be related to the long-lasted interaction of these 519 serpentinites with seawater or seawater-derived fluids that led to oxidation and desulfurization 520 of the sulfides (Delacour et al., 2008a; Karthe et al., 1993; Legrand et al., 2005; Richardson and 521 Vaughan, 1989). Another explanation for this lack of sulfides would be due to the circulation 522 of Cl-rich fluids, such as high-temperature hypersaline brines, which would provide an efficient 523 ligand to Fe and would favor precipitation of Fe-oxides over sulfides (Barton and Johnson, 524 2000). Further analyses of Cl and S contents and sulfur isotopes compositions of the SMS 525 serpentinites would help to better constrain the processes and formulate further interpretations. 526 Currently, the three IOH-serpentinites were collected at the most remote distance from the ridge 527 (> 40 km; Table 1), implying that interaction with high-temperature hydrothermal fluids 528 occurred, most likely at depth, during the early stages of spreading and detachment faulting.

529

# 530 5.2.2. Evolution of fluid-rock interaction with distance from the ridge

531

In order to evaluate which elements were influenced by long-lived fluid-rock interaction in the specific setting of smooth seafloor along an ultra-slow spreading ridge, profiles with distance from the ridge of serpentinization and oxidation degrees for serpentinites of both western and eastern corridors of the smooth seafloor area were considered (Fig. 8). In these profiles,  $Fe^{3+}/Fe_{total}$  ratio of the SMS serpentinites was used as proxy of serpentinization and

537 oxidation degrees, as this ratio is correlated to both visual serpentinization degree and LOI (Fig. 5; Evans, 2008; Andreani et al., 2013). In the west corridor, Fe<sup>3+</sup>/Fe<sub>total</sub> ratio of SMS 538 serpentinites clearly increases with the distance from the ridge. Serpentinites sampled at a 539 distance less than 5 km from the axis have a  $Fe^{3+}/Fe_{total}$  ratio around 0.4 (e.g., SMS 17-4-32 at 540 2.42 km with a Fe<sup>3+</sup>/Fe<sub>total</sub> ratio of 0.41; Tables 1 and Error! Reference source not found.), 541 while serpentinites collected at a distance further than 40 km have Fe<sup>3+</sup>/Fe<sub>total</sub> ratio more than 542 0.8 (e.g., SMS 4-2-1 at 55.7 km, Fe<sup>3+</sup>/Fe<sub>total</sub> ratio of 0.81; Tables 1 and Error! Reference source 543 544 not found. and Fig. 8), indicating then that distance profile from the ridge in the west corridor can be confidently used as serpentinization profiles. However, increase in Fe<sup>3+</sup>/Fe<sub>total</sub> ratio with 545 distance of the ridge axis is not observed in the east corridor, the Fe<sup>3+</sup>/Fe<sub>total</sub> ratios ranging 546 547 between 0.7 and 0.8 (Fig. 8). This difference between the two corridors is mainly related to the 548 volcanic nature of the seafloor and/or a sampling bias of this study. Indeed, dredging of the 549 southern part of the east corridor recovered mainly basaltic rocks, with few serpentinites 550 samples, apart from dredges 22 and 25 located close to the C3An.y (Fig. 1). This scarcity in 551 ultramafic rocks is linked to fewer detachment faults in the eastern corridor as identified in 552 Sauter et al. (2013). For these reasons, evaluation of chemical transfers during serpentinization 553 with time and distance of the ridge axis will only be carried out on the western smooth seafloor 554 corridor.

555

### 556 5.2.3. Long-term serpentinization

557

558 Mass transfers of chemical, major and trace, elements during serpentinization were 559 previously investigated by several authors without reaching to a consensus on the behavior of 560 some elements. Indeed, behavior of major elements are a matter of debate (e.g., Coleman and 561 Keith, 1971; Malvoisin, 2015; Mével, 2003; O'Hanley, 1996; Shervais et al., 2005; Snow and 562 Dick, 1995), due to the difficulty to access both serpentinites and their corresponding fresh 563 protolith, to the chemical heterogeneity of the peridotite protolith related to magmatic and post-564 magmatic processes and to the long-lived fluid-rock interactions that affect peridotite protolith 565 and for which P-T and redox conditions and fluid compositions can be variable. In the particular 566 smooth seafloor context, evaluation of major and trace elements concentrations versus a 567 distance profile from the ridge, and the comparison of these concentrations to those of MAR 568 and SWIR serpentinites (Fig. 9), provide new insights on mass transfer during long-term 569 serpentinization.

570

571 5.2.3.1. Influence of long-term serpentinization on major elements

572

573 Behavior of Al<sub>2</sub>O<sub>3</sub> and CaO concentrations in the SMS serpentinites was previously 574 discussed in Section 5.1.1. as these elements are inherited from the protolith (Fig. 7). The 575 absence of correlation of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents with distance from the ridge (Fig. 9) indicate 576 that partial melting degree does not vary linearly through extension of the smooth seafloor, and 577 therefore that distance profiles confidently represent serpentinization profiles. Concentrations 578 in other major elements, Fe<sub>2</sub>O<sub>3T</sub>, MgO, SiO<sub>2</sub>, Na<sub>2</sub>O do not significantly increase or decrease 579 with the distance from the ridge (Fig. 9) suggesting that behavior of these elements is not 580 affected by serpentinization progress. Nevertheless, scattering in these elements with TiO<sub>2</sub> (Fig. 581 7) may be likely related to fluid-rock interaction processes.

582 Mg is known to be mobile during fluid-rock interaction, some studies having reported a loss 583 in Mg during serpentinization related to dissolution of brucite (Snow and Dick, 1995; 584 Malvoisin, 2015). Similar loss could be evoked to explain the low MgO contents in some SMS 585 serpentinites compared to the range of the SWIR and MAR abyssal peridotites (Fig. 4) and its 586 broad correlation with TiO<sub>2</sub> (Fig. 7). Behavior of Fe is closely related to Mg mobility, as these two elements have close ionic radius and similar charge. Indeed, Fe/Mg ratio of most of the SMS serpentinites is well correlated to  $TiO_2$  (Fig. 7), with the exception of the IOHserpentinites that will be discussed in Section 5.2.4. This indicates that serpentinization does not significantly affect the mobility and thus the budget of MgO.

591 SiO<sub>2</sub> gains during serpentinization has been suggested by Malvoisin (2015), as an alternative 592 explanation to low MgO/SiO<sub>2</sub> ratios of serpentinites (Fig. 4). However, no gain is observed for 593 the SMS serpentinites as a function of distance from the ridge (Fig. 9). In addition, the presence 594 of talc veins in some serpentinites (e.g., SMS 10-5-6, Table 1), related to the circulation and 595 precipitation of Si-rich fluids, is not correlated with a gain in SiO<sub>2</sub>. This suggests that SiO<sub>2</sub> 596 concentrations variations are related to variations in MgO and FeO concentrations.

Scattering of Na<sub>2</sub>O with TiO<sub>2</sub> and as a function of ridge distance is probably due to interaction of the SMS serpentinites with NaCl-rich fluids, i.e. seawater (~1 wt.% of Na; Quinby-Hunt and Turekian, 1983) and the precipitation of halite salts in serpentinites. These salts were however not observed petrographically. Quantification of bulk rock Cl concentrations in the serpentinites are necessary to unravel the origin of this scattering in Na<sub>2</sub>O and if, similarly to previous studies (Sharp and Barnes, 2004), serpentinites of the smooth seafloor are enriched in Cl.

604

605 5.2.3.2. Influence of long-term serpentinization on Rare Earth Elements (REE)

606

Rare Earth Elements (REE) are commonly considered as immobile elements and their concentrations and distributions, shown by their spectrum shape on normalized diagrams, are commonly used to evidence magmatic and melt-rock interaction processes (Bodinier and Godard, 2003; Deschamps et al., 2013; Niu, 2004). However, recent studies reported REE mobility during fluid-rock interaction, expressed as an increase in REE concentrations with

612 advanced degrees of alteration (Andreani et al., 2014; Frisby et al., 2016, 2019; Niu, 2004; 613 Paulick et al., 2006). Serpentinites from the west corridor show REE patterns similar to 614 previously published studies on SWIR serpentinites but enriched compared to MAR 615 serpentinites (Fig. 6B). While this enrichment in REE can be related to different magmatic 616 regimes or melt-rock interaction via refertilization processes (see section 5.1.), some specific 617 REE distribution and/or anomaly more likely result from secondary fluid-rock interaction 618 processes. Indeed, the SWIR serpentinites show a Ce anomaly but no Eu anomaly in 619 comparison to the MAR serpentinites (Fig. 6; Frisby et al., 2016; Niu, 2004; Rouméjon, 2014). 620 These differences are related to fluid-rock interaction subsequently to accretion modes. Indeed, 621 along the MAR, phases of magmatic activity alternate with phases of tectonic activity that allow 622 exhumation of mafic and ultramafic rocks on the seafloor. Interaction of seawater-derived fluids 623 with these mafic rocks is known to produce hydrothermal fluids with a positive Eu anomaly due to the occurrence of plagioclase in the mafic rocks (Douville et al., 2002). Some MAR 624 625 serpentinites are thus thought to result from interaction with such evolved hydrothermal fluids 626 (Deschamps et al., 2013). In the smooth seafloor context, mafic rocks are very scarce (Fig. 1; 627 Cannat et al., 2006; Sauter et al., 2013), limiting then interaction with mafic rocks and thus 628 enhancing interaction of peridotites with seawater or seawater-derived hydrothermal fluids 629 whose chemical compositions are consequently different from those of the MAR.

Negative anomaly in Ce on REE spectra of serpentinites attests to interaction of peridotites with seawater under oxidizing conditions. However, the Ce/Ce\* ratio does not show a clear evolution with distance from the ridge (Fig. 10) and thus as serpentinization degree increases. Nevertheless, two other LREE, La and Pr, show a clear increase in concentration with distance from the ridge (Fig. 10) indicating thus a progressive enrichment in these two elements with serpentinization progress, as already suggested by Frisby et al. (2016) for SWIR serpentinites.

Fluid Mobile Elements (FME; As, B, Ba, Cd, Li, Pb, Sb, Sr, and U) are, as indicated by their 637 638 names, mobile in the fluid phase and therefore during serpentinization of peridotites. Previous 639 studies demonstrated that serpentine minerals are enriched in FME (e.g., Boschi et al., 2008; 640 Decitre et al., 2003; Vils et al., 2008; Deschamps et al., 2013 and reference therein) which are 641 then transferred into subduction zone (Deschamps et al., 2011, 2013; Vils et al., 2011). 642 However, few studies investigated the increase of these elements as a function of 643 serpentinization progress and more particularly for long-lived serpentinization context such as 644 the smoothseafloor of the SWIR.

645 In the SMS serpentinites, Li and B are the only two FME whose concentration increases 646 with the serpentinization degree and with the distance from the ridge (Fig. 11). Boron 647 enrichment is a classical feature of altered oceanic crust (Spivack and Edmond, 1987) and 648 serpentinized peridotites (Boschi et al., 2008; Seyfried and Dibble, 1979; Vils et al., 2008). In 649 serpentinites, this enrichment is related to the incorporation of B from seawater (4.5 ppm, 650 Quinby-Hunt and Turekian, 1983) into serpentine (0.2-20 ppm; Boschi et al., 2008; Deschamps 651 et al., 2011) leading to bulk B concentrations up to 239 ppm (Boschi et al., 2008; Deschamps 652 et al., 2011; Seyfried and Dibble, 1979). Lithium is also classically enriched in serpentinites 653 (up to 1.37 ppm, Decitre et al., 2002; Deschamps et al., 2011; Lee et al., 2008; Niu, 2004; Vils 654 et al., 2008), but in contrast to B, serpentine minerals show very variable Li contents (0.20-655 26.1 ppm), which are either enriched or depleted compared to primary minerals (Decitre et al., 656 2002; Deschamps et al., 2011; Lee et al., 2008; Vils et al., 2008). Enrichments in Li and B in 657 SMS serpentinites (Fig. 11) are, as suggested in earlier studies, due to their incorporation into 658 serpentine phases as serpentinization progress. Only one serpentine (SMS 5-4-17) does not 659 show such enrichment, its Li concentration being low compared to its position from the ridge 660 (Fig. 11). This low Li concentration can be likely explained by the high temperature of the serpentinizing fluid (>350°C), as indicated by its uncommon high modal proportions in chlorite 661

 + tremolite + antigorite. Indeed, precipitation of this mineral assemblage is rather favorable to Li leaching, as already observed during alteration of basalts (Seyfried et al., 1984). Similarly to Fe<sup>3+</sup>/Fe<sub>tot</sub> ratio, B and Li concentrations of serpentinites could then be used as proxies of the serpentinization degree. However, care must be taken for high temperature serpentinization and for recrystallization of lizardite and chrysotile to antigorite, these two processes leading to a release of Li and B (Deschamps et al., 2012; Kodolányi and Pettke, 2011; Ishikawa and Nakamura, 1992; Seyfried et al., 1984).

Previous studies showed that both As and Sb are stored in serpentine minerals (Deschamps et al., 2011; 2012; 2013), and that these enrichments are mainly related to circulation of a sediment-derived fluid rich in Sb and As (Deschamps et al., 2012). While SMS serpentinites are within the range of the previously published data for both elements (50 ppb to 22 ppm, (Andreani et al., 2014; Paulick et al., 2006), it is difficult to evoke similar process to explain this enrichment. Indeed, little sedimentary cover has been imaged on the outcropping mantle rocks and volcanic seafloor (Supplementary data of Sauter et al., 2013). In addition, the correlation between As and Sb with distance from the ridge axis (Fig. 11) would rather reflect an enrichment with serpentinization degree, as interaction with sediment-derived fluid would have produce scattering in the concentrations. Cadmium was not investigated in serpentinites so far, but its behavior looks similar to those of Sb and As (Fig. 11). Enrichments in these elements is favored for serpentinization processes at temperatures <300°C (Deschamps et al., 2011). As conclusion, As, Sb, and Cd concentrations could also be used, similarly to LREE, as serpentinization proxies.

684 <u>5.2.4. Late oxidative alteration</u>

Serpentinites from the smooth seafloor that experienced low-temperature serpentinization are enriched in several elements and their enrichment is proportional to the serpentinization degree and to the distance from the ridge. In contrast, IOH- serpentinites, while following the overall enrichment tendencies, show higher Fe<sup>3+/</sup>Fe<sub>tot</sub> ratios (Fig. 5), Fe<sub>2</sub>O<sub>3T</sub>, Na<sub>2</sub>O (Fig. 7), LREE and FME contents (Fig. 10 and 11), suggesting that other processes, such as late oxidative alteration, affected these IOH- serpentinites after long-term serpentinization.

692 Late oxidative alteration in these IOH-serpentinites is evidenced by the presence of both 693 hematite and goethite that leads to high Fe<sup>3+/</sup>Fe<sub>tot</sub> ratios, high Fe/Mg values (Fig. 7) and 694 enrichment in Fe<sub>2</sub>O<sub>3T.</sub> Abyssal peridotites usually contain between 8 and 9 wt.% FeO<sub>T</sub> (Bodinier 695 and Godard, 2003) that would lead to a maximum  $Fe_2O_{3T}$  content between ~9 and 10 wt.% after 696 total oxidation of FeO to Fe<sub>2</sub>O<sub>3</sub>. At the smooth seafloor areas, the IOH-free serpentinites 697 containing between 7 and 10 wt.% (Fig. 9), the high Fe<sub>2</sub>O<sub>3T</sub> content in most of the IOH-698 serpentinites can be explained by late oxidation of magnetite and serpentine. However, 699 exception occurs for samples SMS 4-2-1 and 11-2-11 (and to some extent SMS 5-4-17), as their 700 Fe<sub>2</sub>O<sub>3T</sub> content is significantly higher than the value that can be reached by total oxidation 701 suggesting that other interaction with previous Fe-rich fluids occurred and led to such 702 enrichment (see Section 5.2.1). The IOH-serpentinites are characterized by high Na<sub>2</sub>O content 703 that can be explained, similarly to other SMS serpentinites, by interaction with NaCl-rich 704 seawater. Nevertheless, their higher enrichment may be related either to longer period of 705 interaction with seawater or seawater-derived fluids as some IOH-serpentinites are located at a 706 remote distance from the ridge (e.g. SMS 11-2-11) or by highly NaCl-enriched fluids (such as 707 hydrothermal brines). Additional halite salts would then precipitate and be mixed with IOH 708 assemblage.

The precipitation of IOH during this late oxidative alteration event leads to high concentrations in La and Pr (Fig. 10 and 12), the La/Ce ratios being up to 20 and 7.9 for IOH-

711 serpentinites respectively northward and southward, and flat REE patterns (Fig. 12). Indeed, 712 iron oxides and hydroxides are known to scavenge REE from fluids (Bau, 1999; Bau and 713 Koschinsky, 2009). REE spectrum of IOH separated from SMS 11-2-11 (Fig. 12), whose 714 concentrations are between 1 and 10 x PM, reflect this scavenging process. In addition, the La 715 and Pr enrichments are responsible for the most negative Ce anomalies on the REE spectra of 716 the SMS serpentinites (Fig. 10 and 12). Similarly as REE, the high FME concentrations (As, 717 Cd, Sb; Fig. 11) of the IOH-serpentinites can be related to the occurrences of iron 718 (hydro)oxides. Indeed, several studies reported that these element can be adsorbed on metals 719 (Caillaud et al., 2009; Giménez et al., 2007). It is worthwhile to note that occurrences of IOH 720 in the serpentinites do not lead to higher concentration in Li and B (Fig. 11), strengthening that 721 their incorporation in serpentinites is not linked to the formation of oxides, but rather to the 722 precipitation of serpentine. In conclusion, post-serpentinization processes and long-time fluid-723 rock interaction under oxidizing conditions favor the incorporation of trace elements into 724 serpentinites implying thus that the oceanic lithosphere constitutes a sink for these elements.

Alteration of serpentine under low-temperature and oxidizing conditions usually leads to the formation of clays (Caillaud et al., 2006; Destrigneville et al., 1998; Karpoff et al., 2017; Venturelli et al., 1997). However, no clay could be identified in the IOH-serpentinites (see Results part and Appendix A) that could be related to the very low initial Al content of the SMS serpentinites.

730

# 731 6. Conclusions

732

Effects of serpentinization on element mass transfer between peridotites and seawater, seawater-derived and hydrothermal fluids were investigated for serpentinites collected on the smooth seafloor areas of the SWIR, and especially on the western corridor. These serpentinites clearly show an increase in LOI, visual serpentinisation degree and oxidation degree (Fe<sup>3+</sup>/Fe<sub>tot</sub>)
with distance from the ridge, allowing thus to establish distance profiles of serpentinization for
both major and trace elements and to shed light on the consequences of fluid-rock interactions
during long-lived exhumation and hydration history in an ultra-slow spreading context.

740 Significant changes in major and trace elements concentrations of the SMS serpentinites can 741 be related to magmatic or secondary fluid-rock interaction processes. Indeed, melt-rock interaction affecting the peridotites led to enrichments in TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3T</sub>, Na<sub>2</sub>O and in some trace 742 743 elements. High concentration in these elements are mainly observed in one serpentinite sample, 744 suggesting that melt-rock interaction and refertilization processes are limited due to the very 745 low magmatic activity. This low magmatic activity is also responsible for the near absence of 746 magmatic plagioclase-rich lithologies (basalts and gabbros) at the SWIR axis and along the 747 smoothseafloor areas, leading to the formation of fluids that differ significantly from those 748 associated to black smoker-type systems. It is likely that these fluids are seawater-dominated, 749 with a high Ce anomaly and the lack of Eu anomaly, a major difference with Eu-rich fluids 750 from slow and fast-spreading ridges (e.g. MAR).

751 Nevertheless, three SMS serpentinites located furthest away from the ridge (e.g., SMS 11-752 2-11) present significant enrichments in Fe<sub>2</sub>O<sub>3T</sub>, Na<sub>2</sub>O, metals, FME and LREE, suggesting 753 interaction with high-temperature fluids, most likely during the first stages of exhumation via 754 detachment faulting. These serpentinites, however, do not show sulfide mineralization 755 commonly associated with circulation of black smoker-type hydrothermal fluids. This absence 756 of sulfides may be explained either by late oxidative alteration or by circulation of a S-poor 757 brine, both processes resulting in the formation of Fe-(hydro-)oxides. These hypotheses require 758 further investigations on the S and Cl contents of the SMS serpentinites.

Long-term serpentinization at low-temperature does not influence Al<sub>2</sub>O<sub>3</sub>, its concentration
being inherited from the protolith, and CaO, while its concentration can be higher in some SMS

761 serpentinities due to the precipitation of carbonate veins. Mobility of other major elements 762 (MgO, SiO<sub>2</sub>, FeO, Na<sub>2</sub>O) is also limited, their concentrations being nearly similar to that 763 expected from mantle partial melting. Serpentinization may be responsible for slight 764 compositional variations in MgO, FeO and SiO<sub>2</sub>, but without a clear and systematic tendency. 765 Enrichments in Na<sub>2</sub>O may likely be due to incorporation of salts from seawater-derived fluids 766 or hydrothermal brines circulating into the oceanic lithosphere. Trace elements, such as Li, B, 767 La, Pr, As, Sb, Cd show enrichments with distance from the ridge. Li and B enrichments are 768 likely related to serpentinization degree, implying that their concentrations might be used as 769 serpentinization proxies (in some specific cases).

770 The presence of (Fe-(hydro-)oxides), hematite and goethite, in highly serpentinized 771 peridotites indicate long-lived fluid-rock interaction with oxidizing conditions. For most of the 772 IOH-serpentinites, the apparent enrichment in  $Fe_2O_{3T}$  is the result of the total oxidation of iron 773 content during serpentinite and magnetite alteration. The lack of clays in these IOH-774 serpentinites indicates that serpentine mineral is still stable for these conditions. Further O 775 isotope thermometry on these serpentinites is necessary to evaluate their temperature of 776 serpentinization. The late oxidative alteration that affected the IOH-serpentinites led to high 777 concentration in some trace elements, such as La, Pr, As, Sb and Cd.

We conclude that chemical exchanges during serpentinization at ultraslow-spreading ridges happened during long-term interaction of the mature exhumed mantle with low-temperature fluids. Amount of mass transfer is a function of ridge distance and hence of interaction time. In addition, despite very low magmatic activity, high-temperature hydrothermal fluids may be produced and interact with peridotites during early stages of detachment faulting. By exploring the chemical compositions of serpentinites several kilometers away from the ridge axis, we observe that fluid-rock interaction in oceanic context is only not limited to serpentinization processes and that oxidizing alteration may greatly influence the oceanic lithospherecomposition.

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#### 798 Figures, Tables and Appendices Captions

799

Figure 1: Bathymetric map of the South West Indian Ridge (SWIR) between 62° and 65°E,
showing the location of the two West and East corridors where smooth seafloor were identified.
Location of dredges of the SMOOTHSEAFLOOR (SMS) expedition in these two corridors.
Inset shows the location of the smooth seafloor area along the SWIR, between the Melville
Fracture Zone and the Rodrigues Triple Junction (RTJ). Slightly modified from Sauter et al.
(2013). SEIR: South East Indian Ridge, CIR: Central Indian Ridge, RTJ: Rodrigues Triple
Junction.

807

808 Figure 2: Photographs and microphotographs of the SWIR SMS serpentinites. A and B: 809 Moderately serpentinized lherzolite (~50%, SMS 8-2-25), showing numerous relics of olivine 810 (ol), orthopyroxene (opx) and clinopyroxene (cpx) under crossed nicols (B) and in hand 811 specimen (A). C and D: Highly serpentinized harzburgite (~99%, SMS 2-2-11), showing bastite 812 (bast) and mesh serpentine (serp) crosscut by magnetite (mt) veins, in hand specimen (C) and 813 under natural light (D). E and F: Serpentinized and oxidized olivine websterite (SMS 5-4-17), 814 displaying amorphous iron oxides and hydroxides (IOH: hematite + goethite) at the former 815 emplacements of olivine, and a mixture of antigorite (ant), tremolite (tr) and chlorite (chl) 816 replacing the pyroxenes, in hand specimen (E) and under crossed nicols (F).

817

Figure 3: Microphotographs of secondary minerals in the SMS serpentinites. (A) Former plagioclase altered to hydrogarnet (hydrogt) and chlorite (chl) in one metasomatized sample (SMS 1-2-35, parallel nicols). (B) Cusps boundaries (indicated by arrows) between ortho- and clinopyroxene in a metasomatized sample (SMS 1-2-35, crossed nicols). (C) Crystallized goethite (goeth) associated with red-orange colored iron oxides and hydroxides (IOH, SMS 14-

5-8, reflected light). (D) Amorphous IOH in a strongly oxidized sample (SMS 4-2-11, reflected
light). IOH are localized in the center of previous serpentine (serp) mesh cells, the magnetite
network having disappeared.

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827

Figure 4: Bulk rock MgO/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratios of the SMS serpentinites, compared to
MAR serpentinites (Paulick et al., 2006; Jöns et al., 2010; Kodolányi et al., 2012; Boschi et al.,
2013) and SWIR serpentinites (Niu, 2004; Rouméjon, 2014; Rouméjon and Cannat, 2014).

831 Terrestrial array and BSE value are from Jagoutz et al. (1979) and Hart and Zindler (1986).

832

Figure 5: Evolution of iron oxidation degree (Fe<sup>3+</sup>/Fe<sub>Total</sub>) with A) loss on ignition (LOI) and
B) visual serpentinization degree of the SWIR SMS serpentinites.

835

Figure 6: Trace elements spidergrams of the SMS serpentinites compared to serpentinites from
the SWIR (Niu, 2004; Rouméjon, 2014; Rouméjon and Cannat, 2014) and the MAR (Paulick
et al., 2006; Delacour et al., 2008; Jöns et al., 2010; Kodolányi et al., 2012; Boschi et al., 2013).
Values are normalized to primitive mantle and chondrites values of Sun and McDonough
(1989).

841

Figure 7: Binary diagrams showing the evolution of major elements of the SMS serpentinites
against TiO<sub>2</sub> concentrations, used as proxy of partial melting degree. Sample SMS 22-6-13
(melt-refertilized peridotite) is not considered in the description of correlation trends (see text).
CaO trend excludes the two samples, SMS 10-5-6 and 29-5-41, containing calcite veins, and
Fe/Mg trend excludes all IOH serpentinites. Error bars are comprised in the size of the marking
point. SWIR and MAR references are the same as previous figures.

848

Figure 8 : Evolution of iron oxidation degree in the SMS serpentinites (west 62°30'E and east
64°40'E) as a function of ridge distance. Ridge axis is symbolized by the red line, and location
of detachment faults is indicated by vertical dashed lines (approximated position on the seafloor
taken from Sauter et al., 2013).

853

Figure 9 : Evolution of major elements with distance from the ridge for the serpentinites of the
west smooth seafloor corridor of the SWIR. Error bars are comprised in the size of the marking
points.

857

Figure 10 : Evolution of LREE (La, Ce and Pr) for the serpentinites of the west smooth seafloor corridor of the SWIR. Ce anomaly  $(Ce/Ce^*=Ce_N/(La_N+Pr_N)^{0.5})$  is stable with the distance from the ridge serpentinization, while La and Pr contents increase.

861

Figure 11 : Evolution of FME for the serpentinites of the west smooth seafloor corridor of the SWIR. Li and B concentrations increase with distance and then with serpentinization degree, regardless of oxidation state. U is only enriched in samples that are strongly oxidized or contain high content of carbonates. Sb, As and Cd contents increase with oxidation degree of the rock.

Figure 12: REE spectra of the serpentinites of the west smooth seafloor corridor of the SWIR, compared to the MAR (Paulick et al., 2006; Delacour et al., 2008; Jöns et al., 2010; Kodolányi et al., 2012; Boschi et al., 2013) and SWIR serpentinites (Niu, 2004; Rouméjon, 2014; Rouméjon and Cannat, 2014). The SMS west corridor serpentinites are characterized by an overall depletion in REE, a negative Ce anomaly and an absence of Eu positive anomaly. The highest LREE concentrations (apart from Ce) corresponds to the IOH-bearing samples. Table

873	1: Sample names, locations from the ridge, protolith, primary and secondary mineralogical
874	assemblages, texture, serpentinization degree, and melt-rock interaction evidences of the
875	smooth seafloor serpentinites. Serpentinization degree was calculated as the sum of all
876	secondary phases modal proportions.
877	
878	Table 2: Bulk major and trace elements compositions of the smooth seafloor serpentinites.
879	
880	Appendix A: 1) X-Rays Diffraction (XRD) spectra on oriented section showing the diffraction

881 peaks of serpentine lizardite 1T, talc and clinochlore. 2) RAMAN spectrum of a lizardite +

antigorite mixture in a bastite of SMS 1-2-35.

883

Appendix B: Electron Microprobe compositions of primary and secondary minerals from theSWIR SMS serpentinites

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#### 16 cm





12 cm













#### 9 cm

Sample name (used in this study)	Ridge distance (km)	Protolith	Primary minerals (as relic)	Secondary minerals	Sulfides/oxides	Serpentine texture and veins	Serp. degree (%)	Melt-rock interaction evidences	Complementary analyses	Sample name from Smoothseafloor
SMS 1-2-1	26.7	harzburgite	ol + opx + cpx + sp	serp	$mt \pm pn$	М	69	ol cryst		SMS_DR01_2_01
SMS 1-2-35	26.7	lherzolite	ol + opx + cpx + sp	serp + tr + chl + tlc + carb	$mt \pm pn$	$M+B\ \pm Lv$	74	plagio, cpx cryst	Raman	SMS_DR01_2_35
SMS 2-2-11	28.5	harzburgite	opx + cpx + sp	serp	$mt \pm mi \pm cpy \pm vt$	M + B	90	-	Raman	SMS_DR02_2_11
SMS 2-2-17	28.5	harzburgite	sp	serp + tr + chl	± mt	M + B	98	-		SMS_DR02_2_17
SMS 3-2-1	36.4	lherzolite	opx + cpx + sp	$serp + tr + chl \pm tlc$	$\pm$ mt $\pm$ pn	M + B	93	-		SMS_DR03_2_01
SMS 4-2-1	55.2	lherzolite	opx + cpx + sp	$serp + tr + tlc \pm chl$	$hm + gt \pm mt$	M + B	94	-		SMS_DR04_2_01
SMS 5-4-14	53.9	harzburgite	opx + cpx + sp	serp $\pm$ tr $\pm$ chl $\pm$ tlc	$mt + hm + gt \pm pn \pm aw$	M + B + Cv	91	-		SMS_DR05_4_14
SMS 5-4-17	53.9	olivine websterite	cpx + sp	serp + tr + chl	$hm + gt \pm mt$	$M + Cv \ \pm Lv$	99	_		SMS_DR05_4_17
SMS 6-3-14	9.7	harzburgite	ol + opx + cpx + sp	serp	$\pm$ mt $\pm$ hm $\pm$ gt $\pm$ pn	$M\pm Lv$	60	ol cryst		SMS_DR06_3_14
SMS 7-3-7	4.2	harzburgite	ol + opx + cpx + sp	serp + tr + chl	$\pm$ mt $\pm$ pn $\pm$ mi	M + B + Cv	66	plagio	Raman	SMS_DR07_3_37
SMS 8-2-17	14.2	harzburgite	± sp	serp + chl + tlc	± mt	$M+B \ + Cv \pm Lv$	100	_		SMS_DR08_2_17
SMS 8-2-25	14.2	lherzolite	ol + opx + cpx + sp	serp + carb	$mt \pm pn$	M + B	63	cpx cryst		SMS_DR08_2_25
SMS 10-5-6	11.2	harzburgite	ol + opx + cpx + sp	serp + tr + tlc + carb	$\pm$ mt $\pm$ pn	$M+B\ \pm Lv$	52	-		SMS_DR10_5_06
SMS 11-2-4	40.6	lherzolite	opx + cpx + sp	serp + tr + chl + tlc	$\pm$ mt $\pm$ hm $\pm$ gt $\pm$ pn	$M+B\ \pm Lv$	85	cpx cryst		SMS_DR11_2_04
SMS 11-2-11	40.6	harzburgite	ol + opx + cpx + sp	serp	$hm + gt \pm mt$	М	74	ol cryst		SMS_DR11_2_11
SMS 13-4-11	25.5	harzburgite	opx + sp	serp + chl	± mt	M + B + Cv	96	-		SMS_DR13_4_11
SMS 14-5-1	12.7	dunite	sp	serp	$hm + gt \pm pn \pm mt$	$M + Ct \ \pm Lv$	98	-	Raman	SMS_DR14_5_01
SMS 14-5-8	12.7	dunite	sp	serp	$mt \pm hm \pm gt$	M + Cv	99	-	Raman	SMS_DR14_5_08
SMS 15-3-16	21.2	harzburgite	opx + sp	opx + sp serp $\pm$ mt M -		M + B + Cv	96	-		SMS_DR15_3_16
SMS 17-4-19	2.4	harzburgite	ol + opx + cpx + sp	serp	$mt \pm pn$	M + B	81	ol cryst		SMS_DR17_4_19
SMS 17-4-32	2.4	harzburgite	ol + opx + cpx + sp	serp $\pm$ carb	$mt \pm pn$	M + B	51	cpx cryst	Raman	SMS_DR17_4_32
SMS 21-5-6	16.4	lherzolite	opx + cpx + sp	serp + tr + chl	mt + hm + gt	$M + B + Ct \ \pm Lv$	90	-		SMS_DR21_5_6
SMS 22-6-13	45.5	harzburgite	opx + cpx	serp $\pm$ chl	mt	M + B + Ct	89	plagio		SMS_DR22_6_13
SMS 26-2-11	24.2	olivine websterite	ol	serp + tr + chl	$mt + hm + gt \pm pn$	V	90	-		SMS_DR26_2_11
SMS 27-2-19	11.2	harzburgite	opx + cpx + sp	serp + tr + tlc	$\pm$ mt $\pm$ pn $\pm$ mi	$M+B\ \pm Lv$	98	cpx cryst		SMS_DR27_2_19
SMS 28-4-10	3.9	harzburgite	opx + cpx + sp	serp + carb	$mt \pm pn \pm mi \pm cpt$	$M + B + Ct \ \pm Lv$	80	-		SMS_DR28_4_10
SMS 29-5-41	10.6	harzburgite	cpx + sp	$serp + tr + tlc + carb \pm chl$	mt	M + B	94	-		SMS_DR29_5_41
SMS 29-6-13	10.6	harzburgite	opx + cpx + sp	$\operatorname{serp} \pm \operatorname{chl}$	$\pm$ mt $\pm$ hm $\pm$ gt $\pm$ pn	M + B + Cv	95	-		SMS_DR29_6_13
SMS 30-2-2	39.4	harzburgite	± sp	serp	± mt	$M + B + Ct \pm Lv$	100	-		SMS_DR30_2_2
SMS 33-3-27	57.9	lherzolite	opx + cpx	serp	mt + hm + gt	M + B	76	cpx cryst		SMS_DR33_3_27
SMS 34-2-17	44.8	harzburgite	opx + cpx + sp	$serp + chl \pm tr \pm tlc \pm carb$	mt	M + B + Cv	95	plagio, cpx cryst		SMS_DR34_2_17

Table 1: Sample names, locations from the ridge, protolith, primary and secondary mineralogical assemblages, texture, serpentinization degree, and melt-rock interaction evidences of the smooth seafloor serpentinizes. Serpentinization degree was calculated as the sum of all secondary phases modal proportions.

**Abbreviations:** ± indicates that a phase modal proportion is strictly < 1%

Primary minerals: ol: olivine, opx: orthopyroxene, cpx: clinopyroxene, sp: spinel,

Serpentine texture: M: mesh, B: bastite (after pyroxene),

Secondary minerals: serp: serpentine, tr: tremolite, chl: chlorite, Tlc: talc, Carb: carbonates, mt: magnetite, pn: pentlandite, mi: millerite, cpy: chalcopyrite, vt: violarite, aw: awaruite, cpn:

chalcopentlandite, hm: hematite, gt: goethite

Veins: V: serpentine veins, Lv: lizardite veins, Cv: chrysotile veins

Melt-rock interaction evidences: plagio: plagioclase, ol cryst: olivine crystallization, cpx cryst: clinopyroxene crystallization

	SMS 1-2-1	SMS 1-2-35	SMS 2-2-11	SMS 2-2-17	SMS 3-2-1	SMS 4-2-1	SMS 5-4-14	SMS 5-4-17	SMS 6-3-14 S	SMS 7-3-7	SMS 8-2-17	SMS 8-2-25	SMS 10-5-6 S	SMS 11-2-4	SMS 11-2-11 S	SMS 13-4-11	SMS 14-5-1 S	SMS 14-5-8	SMS 15-3-16	SMS 17-4-19	SMS 17-4-32	SMS 21-5-6	SMS 22-6-13	SMS 26-2-11	SMS 27-2-19	SMS 28-4-10	SMS 29-5-41	SMS 29-6-13	SMS 30-2-2	SMS 33-3-27 SI	MS 34-2-17
Major element	concentrations (wt.%	<i>()</i>	10.52	20.25	10.07	11.10	20.74	20.22	42.11	10 7	20.00	10.77	20.15	41.01	20.51	20.4	26.01	20.04	20.24	12.1.4	10.70	20.05	20.54	41.00	20 (1	10.2	20 6	20.4	20.70		10.00
$SIO_2$	43.48	41.19	40.53	38.37	40.87	41.12	39.76	39.22	43.11	40.7	59.08 1.47	42.77	38.15 2.09	41.81	38.51 2.62	39.4 1.62	36.91 0.55	58.04 0.59	38.24 2.59	42.14	40.78	39.85	58.54 2.29	41.23	38.61 2.52	40.3	38.6	38.4	58.78 0.02	44.57	40.09
	2.90	2.02	2.55	1.81 7.81	2.83	3.8 12.97	2.38	5.25 11 2	2.40 8.46	83	1.47 8.18	2.82 8.95	2.08 7.97	3.91 8 55	2.03	7.15	0.33	0.38 9.51	2.38	2.83	2.07	9.33	2.38	2.55	2.33	2.34	0.83 7 31	8.04	0.93	3.43 10.12	0.91 7.82
FeO	4.93	3.71	2.5	2 65	2 73	2 21	2.14	2.81	4 65	33	2 32	4 92	3.11	2 44	2.28	1.76	1 51	1.57	2.22	2.03 4 78	4 58	1.73	nd	2.76	2 51	2 39	2 27	2 74	1.65	3.02	1.52
MnO	0.12	0.12	0.12	0.09	0.12	0.15	0.12	0.2	0.13	0.12	0.1	0.13	0.11	0.14	0.16	0.09	0.16	0.07	0.1	0.14	0.13	0.12	1.17	0.14	0.13	0.12	0.1	0.12	0.09	0.16	0.09
MgO	36.12	35.52	35.18	36.3	32.76	27.59	32.46	30.68	36.74	35.73	37.4	35.13	33.24	31.57	25.82	37.11	35.55	35.93	36.08	34.24	37.9	34.2	30.45	33.27	35.46	35.89	35.95	36.65	37.39	28.94	37.08
CaO	2.98	1.93	0.76	< d.1.	2.63	3.75	1.96	2.46	3.17	1.63	< d.1.	3.41	6.11	3.53	1.69	< d.l.	< d.1.	< d.1.	< d.l.	2.68	1.99	1	2	2.24	1.19	1.1	1.99	0.22	< d.1.	3.67	0.31
Na <sub>2</sub> O	0.19	0.19	0.14	0.16	0.17	0.58	0.35	0.25	0.19	0.1	0.08	0.15	0.17	0.26	0.81	0.12	0.2	0.24	0.23	0.13	0.09	0.29	0.38	0.2	0.11	0.1	0.12	0.12	0.16	0.3	0.08
K <sub>2</sub> O	< d.l.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.l.	< d.1.	< d.1.	< d.l.	< d.1.	< d.l.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	0.11	< d.1.	< d.1.	< d.l.	< d.1.				
$P_2O_5$	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.l.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.
L.O.I.	4.86	10.05	12.67	14.48	11.39	9.49	11.98	11.49	5.77	11.16	14.27	6.95	12.68	10.58	9.41	13.27	14.53	14.4	14.15	9.03	8.91	13.7	13.91	11.18	13.04	12.41	14.04	13.46	14.53	7.57	13.13
Total $\mathbf{F}^{3+}$	99.76	99.74	99.76	99.02	98.67	99.56	98.83	98.73	100.03	100.05	100.58	100.32	100.51	100.35	98.67	98.77	98.76	98.78	99.19	100.31	100.99	99.67	99.96	99.54	98.76	100.68	98.94	98.91	99.46	98.89	99.51
Fe /Fe <sub>tot</sub> Trace element	0.39	0.53	0.65	0.62	0.61	0.81	0.75	0.72	0.39	0.56	0.68	0.39	0.57	0.68	0.87	0.73	0.85	0.82	0.68	0.41	0.44	0.79		0.66	0.64	0.68	0.65	0.62	0.76	0.67	0.78
Li t	pm 3.2	2 3.5	5 7.3	3 5.2	6.9	8.3	8.8	2.7	2.6	3.2	3.5	2.7	2.7	8	6.2	6.7	2.1	3.1	6.6	1.2	0.9	4	10.8	6.3	3.8	5.7	2.1	3.6	3.5	9.2	4.5
B f	pm 40	) 60	) 76	6 80	69	82	68	50	49	38	69	33	73	58	115	50	91	69	67	25	25	83	64	67	63	71	44	50	54	48	60
Be	opb < d.1	. 0.8	3 < d.1	l. 9.2	< d.l.	70.5	4	220.4	2.2	4.3	0.6	1.1	< d.1.	5.4	305.2	20	0.2	10	258.6	5.9	4.9	59	966.8	8.2	< d.l.	0.1	9.8	5.8	8.3	255.4	8.8
Sc I	pm 3	3 14	4 12	2 10	14	21	13	17	14	14	8	16	11	17	21	6	6	5	13	15	12	5	13	15	11	12	7	12	6	20	7
	pm 393	3 430 ) 77	5 14. 7 7(	/ 2/6 0 66	337	492 214	347 114	410	441 81	332 77	39	530 81	332 56	546 124	271	137	53 68	57	343 73	478 84	411	/3 62	/92 126	2/5	329 63	347 68	39 46	323 69	148	664 159	2
Cr I	pm 2202	2 1872	2 2541	1 2646	2536	3906	2675	3309	2662	2475	2193	1903	2243	3437	3431	2180	2218	2690	2775	2515	2338	1567	1893	3170	2157	2151	2360	3093	2357	3110	2285
Mn r	pm 804	4 861	857	7 674	817	1070	821	1410	916	818	746	901	820	935	1087	632	1069	518	709	1000	922	515	8463	994	883	829	675	866	641	1168	590
Co I	pm 99	9 108	3 101	1 98	91	130	122	144	108	98	106	101	101	93	120	95	129	89	87	107	107	69	204	119	87	96	98	99	97	122	98
Ni j	pm 1972	2 2051	1 195(	U 1828	1591	1708	2037	1764	2109	1885	2110	1850	1983	1605 24	1518	1985	1934	1913	1959 • 4	1971 14	2037	1248	1719	2027	1677	1859	1927	2216	2159	1532	1945
$\mathbf{Z}\mathbf{n}$	pm 20	3 39	42	2 58	41	157	83	114	81	46	87 87	83	88	86	259	52	60	86	135	52	23 42	38 80	289	53	23 79	35	48	46	51	145	45
Ga I	pm 2	2 2	2 1.9	9 1.8	2.1	4	2.5	3.6	2	2.2	1.2	2.2	1.8	3.1	4.5	1.8	1	1.2	2.7	2.7	1.9	1.2	4	2	2	1.9	0.7	1.7	1.1	3.6	0.6
Ge I	pm 2.4	4 1.4	1 1.4	4 1.5	1.8	2	1.6	1.8	1.2	1.6	1.4	1.9	1.1	1.2	3.8	2	3.3	1.5	1.5	1.4	1.4	1.2	1.9	1.4	2.9	1.5	1.4	1.2	1.2	2	1.7
As F	pm 0.8	3  0.6	5 0.6 1 12 9	6 2.3 8 14.0	1.6	9.8	5.4	9.8 15-3	1.1	0.5	0.4	0.9	0.6	2.6	28	1	4.8	5.9	1.8	0.3	0.2	2.8	6.8 16.3	3.5	0.4	0.1	1.7	7.3	9.5 16.6	7.1	2.1
Rh r	nm = 0.2	2   0.2	$\frac{1}{2}$	2   0.2	0.2	0.4	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.2	0.1	0.2	0.2	0.1	0	< u.i. 0.2	10.5	0.3	0.1	0.1	0.1	0.1	0.1	0.5	0.1
Sr p	pm 23.6	5 49.9	) 3.6	6 3.7	8.2	14.5	8.1	10.3	12.3	4	3.2	130.2	849.2	5.4	21.7	3.9	7.1	11.3	4.1	1.9	32.2	5.7	71.4	9.7	104.9	3.0	345.8	11.9	3.2	9.0	3.3
Y	pm 2.26	5 2.10	) 1.10	0 1.30	1.91	5.44	2.35	3.36	2.74	1.99	0.65	2.71	1.68	3.10	7.49	0.57	0.90	1.15	1.12	3.81	1.60	0.64	8.30	2.20	1.70	1.95	0.30	1.15	0.52	5.47	0.34
Zr j	pm 0.9	0.96	5 0.05	5 1.45	0.59	4.39	0.54	5.73	1.4	0.95	0.3	1.43	0.87	1.57	10.33	1.03	0.14	1.33	10.04	1.98	1.54	2.10	65.08	0.48	0.86	0.67	1.31	1.12	0.74	13.55	0.2
	opb 3./1	1   1.12   5   2.82	2 - 3.40	8 3.2 2 1694	2.23 < d l	7.48 4.47	2.73	29.03 1.38	0.15	< d.l.	2.08	8.1 < d l	4.18	5.25 5.06	23.58 634	5.55 < d1	< 0.1. 10.56	12.08	48.39	4.33	0.50	17.07	0305.03	5.7 3.86	0.88 < d l	< d.1.	14.70	25.52	3.84 11.51	/50./1 4.04	18.12 < d1
Rh p	pm < d.1	. < d.1	. < d.1	l. < d.l.	< d.l.	< d.1.	< d.l.	< d.l.	< d.l.	< d.1.	< d.1.	< d.l.	< d.1.	< d.l.	< d.l.	< d.1.	< d.l.	< d.1.	< d.l.	< d.l.	< d.1.	< d.l.	< d.l.	< d.1.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.1.	< d.1.
Pd 1	opb < d.1	. < d.1	. < d.1	l. < d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.1.	< d.1.	< d.1.	< d.l.	11.96	< d.1.	< d.l.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.l.	< d.1.	< d.l.	< d.1.	< d.l.	< d.l.	< d.1.	< d.l.	< d.l.	< d.1.	< d.l.
Ag	opb 9.82	2 8.59	5.82	2 12.87	5.86	12.01	9.66	19.6	11.02	5.32	3.53	12.73	10.27	4.57	14.75	5.57	6.44	13.52	64.67	10.48	17.21	3.01	76.77	4.76	8.87	9.46	9.41	18.72	30.18	15.92	10.11
Cd j	opb 48.47	7 53.73	3 47.22 7 0.57	2 58.86	72.34	118.86	80.71	79.83	65.08	41.78	29.57	39.09	41.04	62.84	173.81	61.15	79.22	73.36	41.64	18.05	18.14	41.4	175.4	74.08	45.91	25.33	30.55	57.09 8 57	54.82	106.84	54.68
Sn t	pm 0.01	10.07 l < d.1	, 9.5 <u>-</u> . < d.1	+ 5.0 I. < d.1.	< d.l.	0.23	0.07	0.1	0.86	< d.l.	0.03	0.04	0.17	< d.l.	0.07	< d.l.	0.01	< d.l.	0.72	0.19	0.02	< d.1. < d.1.	0.64	0.02	13.90	0.02	< d.1. 0.02	0.14	0.15	1.46	2.12 < d.l.
Sb H	pm 0.22	2 0.13	3 0.09	9 0.19	0.36	3.5	1.2	3.91	0.14	0.11	0.07	0.07	0.1	0.62	9.5	0.18	0.8	1.19	0.22	< d.1.	< d.l.	0.68	3.45	1.2	0.08	0.04	0.22	0.15	0.39	1.96	0.29
Te I	pm < d.1	. < d.1	. 0.02	2 0.01	< d.l.	< d.1.	0.01	< d.1.	< d.1.	< d.1.	0.01	< d.l.	< d.1.	0.02	0.02	< d.1.	0.01	0.01	0.01	0.01	< d.1.	0.01	0.11	0.01	< d.l.	0.01	< d.1.	0.02	0.03	0.01	0.01
Cs H	pm < d.l	. < d.1	. 0.01	1 < d.l.	< d.l.	0.03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.01	< d.l.	< d.l.	< d.l.	< d.l.	0.11	0.02	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.04	< d.l.
La I	0.01	2 0.01	0.01	0 0.37	0.03	0.96	0.26	0.64	0.01	0.02	0.01	0.02	0.01	0.11	2.78	0.08	0.25	0.44	0.40	0.02	0.18	0.17	114.10	0.19	0.01	1.75 < d.l.	0.12	0.73	0.92	0.86	0.93
Ce I	pm 0.03	3 0.05	5 0.01	1 0.05	0.01	0.12	0.03	0.2	0.06	0.05	0.04	0.05	0.04	0.03	0.06	0.08	0.03	0.11	0.11	0.25	0.11	0.03	68.79	0.07	0.04	0.03	0.36	0.05	0.05	0.83	0.09
Pr p	pm 0.02	2 0.01	l < d.1	0.02	0.01	0.21	0.05	0.12	0.03	0.02	0.01	0.03	0.02	0.03	0.50	0.03	0.03	0.08	0.02	0.04	0.03	0.03	2.77	0.06	0.01	0.01	0.03	0.01	0.01	0.25	0.02
Nd I	pm 0.19	$\theta = 0.14$		1  0.13	0.09	1.00	0.26	0.56	0.26	0.14	0.05	0.23	0.15	0.26	2.09	0.14	0.16	0.37	0.12	0.38	0.19	0.16	10.97	0.34	0.13	0.13	0.11	0.09	0.07	1.18	0.07
Eu t	0.12	5 0.04	1 0.02 1 0.01	1 0.03	0.08	0.32	0.12	0.20	0.17	0.10	0.03	0.10	0.09	0.18	0.15	0.03	0.03	0.08	0.07	0.27	0.10	0.04	0.60	0.13	0.09	0.10	0.03	0.07	0.03	0.10	0.02
Tb f	pm 0.05	5 0.05	5 0.02	2 0.03	0.04	0.11	0.04	0.07	0.06	0.04	0.01	0.06	0.04	0.07	0.14	0.01	0.01	0.02	0.03	0.09	0.03	0.01	0.41	0.04	0.04	0.04	0.01	0.03	0.02	0.11	< d.1.
Gd I	pm 0.24	4 0.21	0.07	7 0.14	0.17	0.57	0.22	0.36	0.31	0.20	0.05	0.28	0.18	0.34	0.75	0.07	0.05	0.10	0.13	0.46	0.17	0.06	2.47	0.21	0.18	0.21	0.04	0.14	0.07	0.58	0.02
Dy Ho	pm 0.36	0.32	2 0.15	5 0.20	0.28	0.77	0.32	0.53	0.43	0.31	0.09	0.41	0.27	0.49	0.98	0.09	0.06	0.13	0.19	0.63	0.26	0.09	2.29	0.31	0.26	0.31	0.04	0.20	0.09	0.80	0.02
Er F	pm 0.08	5 0.00 5 0.24	4 0.12	+ 0.05 3 0.15	0.07	0.18	0.08	0.12	0.10	0.07	0.02	0.10	0.19	0.11	0.24	0.02	0.02	0.03	0.04	0.14	0.00	0.02	0.44	0.08	0.00	0.07	0.01	0.05	0.02	0.18	0.01
Tm p	pm 0.04	4 0.04	4 0.02	2 0.02	0.04	0.10	0.04	0.06	0.05	0.04	0.01	0.05	0.03	0.05	0.14	0.01	0.01	0.02	0.02	0.06	0.03	0.01	0.18	0.04	0.03	0.04	0.01	0.02	0.01	0.09	0.01
Yb p	pm 0.27	0.27	7 0.16	6 0.17	0.25	0.69	0.28	0.42	0.3	0.25	0.1	0.32	0.19	0.36	1.08	0.08	0.08	0.15	0.15	0.42	0.22	0.08	1.21	0.25	0.22	0.24	0.04	0.15	0.04	0.63	0.04
Lu p	pm 0.04		4 0.03	3 0.03	0.04	0.11	0.04	0.06	0.05	0.04	0.02	0.05	0.03	0.06	0.18	0.01	0.02	0.03	0.02	0.06	0.04	0.01	0.18	0.04	0.04	0.04	0.01	0.02	0.01	0.10	0.01
ni j Ta j	pm 0.06 00b ∠ d1	0.06 d1	d.l < d.l ، ر	ı. 0.04 I. ∠d1	0.04 2.64	/0.0 / 16 >	0.04 < d 1	\0.0 1 h >	0.08 < d 1	0.06 7 h >	10.0 / h	0.09 < d 1	0.05 < d 1	1.U 1 h >	0.04 < d 1	0.03 < d 1	0.01 < d 1	10.0 1 h >	\0.0 1 h >	0.15 < d 1	0.06 2 d 1	10.0 1 h >	1.18 79 98	0.03 2 h 1	0.05 - 11	20.0 1 h >	0.02	0.05	0.03 2 A 1	0.25 41 1	< d.l. < d 1
Re	opb < d.1	. < d.1	. < d.1	l. < d.1.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.l.	1.01	< d.1.	< d.1.
Ir	opb < d.1	. < d.1	. < d.1	l. < d.1.	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.1.	< d.1.	< d.1.	< d.1.	< d.l.	1.25	< d.1.	< d.1.	< d.1.	< d.l.	< d.1.	< d.l.	< d.1.	1.14	< d.l.	< d.l.	< d.1.	< d.l.				
Pt j	opb 3.32	2 3.45	5 2.17	7 2.68	4.82	2.69	4.91	6.74	6.84	4.92	2.84	4.50	3.60	4.88	52.13	1.30	5.09	< d.l.	3.90	5.30	5.40	2.00	14.22	3.17	3.30	3.32	6.34	4.98	1.88	7.37	4.30
AU j	ppo < d.l	. < d.l	. < d.l	1. 1.62	< d.l. 0.16	< d.l.	< d.l. 116	< d.l. 0 17	2.44	< d.l. 0 17	1.08	1.85	1.98	< d.l. 0 35	2.09	< d.l. 0.71	< d.l. 0.68	< d.l.	< d.l. 0 30	2.85	1.81 - A 1	< d.l.	3.71	< d.l. 0.05	< d.l.	< d.l.	< d.l. 0 27	< d.l. 0.27	< d.l. 0 52	3.31	< d.l.
Pb t	pm < d.1	. 0.02	5 < d.1	l. 0.08	0.05	0.24	< d.l.	0.3	0.03	0.02	0.07	0.02	0.49	0.03	0.09	0.01	0.08	0.05	5.33	0.03	0.43	0.22	48.26	0.03	0.04	< d.l.	0.27	< d.l.	< d.l.	0.02	0.03
Bi	opb < d.1	. < d.1	. < d.1	l. 1.5	< d.1.	< d.1.	< d.1.	2.35	1.98	< d.1.	2.43	1.90	2.28	1.17	< d.1.	< d.1.	2.29	2.16	92.98	2.65	1.75	< d.1.	965.29	12.87	3.20	< d.1.	1.04	4.64	< d.1.	6.73	< d.1.
U H	pm 0.36	6 0.47	7 0.15	5 0.72	0.48	0.60	0.41	0.50	0.38	0.47	0.44	0.34	0.83	0.41	1.20	0.32	0.79	0.72	0.46	0.03	0.12	0.48	0.66	0.56	0.74	0.07	0.53	0.93	0.85	0.35	0.64
Abbreviations: -	d.l.: below detection	limit, L.O.I. : Lo	oss on Ignition																												