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A multi-isotope study (Fe, Ge, O) of hydrothermal alteration in the Limousin ophiolite (French Massif Central)

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ABSTRACT

Geochemical studies using non-traditional stable isotopes can help tracing processes of hydrothermal alteration (or hydrothermal metamorphism) of ancient oceanic lithosphere. In this study, we have measured non-traditional Ge and Fe isotopes and traditional O isotopes in a series of ultrabasic and basic rocks from the Limousin ophiolite (French Massif Central) to decipher the different signatures of hydrothermal vs. magmatic processes. Serpentinites are strongly oxidised rocks (Fe³⁺/ΣFe: 0.58–0.71) and display δ¹⁸O values (+5.0 to +6.1‰) typical of hydrothermally altered ultrabasic rocks. They display δ⁵⁶Fe (+0.15 to +0.18‰) and δ⁷⁴Ge values (+0.48 to +0.93‰) similar to heavier than ultrabasic rocks. The negative correlation between δ⁵⁶O and δ⁷⁴Ge and between δ⁷⁴O and δ⁵⁶Fe suggests that Ge and Fe isotopes have fractionated during hydrothermal alteration. The δ⁷⁴Ge shows a slight positive correlation with the δ⁵⁶Fe, indicating concomitant Ge and Fe isotope fractionation towards heavier values during hydrothermal alteration. However, δ⁵⁶Fe values display a larger deviation from ultrabasic rocks than δ⁷⁴Ge and δ¹⁸O values, suggesting that oxidising conditions have enhanced Fe isotope fractionation to a larger extent than Ge isotopes. Amphibolites display Fe³⁺/ΣFe ratios (0.11–0.14) and δ⁵⁶Fe values (+0.03 to +0.17‰) typical of high-T hydrothermally altered MORB. δ¹⁸O values are typical of high-T hydrothermally altered MORB (+6.2 to +6.6‰). δ⁷⁴Ge values show a small range (+0.72 to +0.77‰) and are heavier than most basalts and gabbros. The δ¹⁸O slightly decreases with the increase of the δ⁵⁶Fe, indicating that Fe isotopes may have fractionated towards lighter values during hydrothermal alteration. However, the lack of correlation between δ⁷⁴Ge and δ⁵⁶Fe values indicates that Ge isotope fractionation has prevailed over Fe isotope fractionation during hydrothermal alteration of basic rocks in the absence of oxidising conditions.

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1. Introduction

Ophiolite-derived rocks composed of ultrabasic (peridotites, serpentinites) and basic rocks (gabbros, basalts) are remnants of ancient oceanic lithosphere that were accreted in convergent settings by subduction/exhumation or obduction processes. Fluid-rock interactions in subducted plates and ophiolites may be sources of significant mass transfer between the oceanic lithosphere and the fluid and volatile phases. The oceanic lithosphere undergoes various stages of hydrothermal alteration (or hydrothermal metamorphism) from its formation along mid-oceanic ridge to its accretion in convergent settings (e.g. Beinlich et al., 2010; Cartwright and Barnicoat, 1999; Muehlenbachs, 1998): 1) High-temperature (high-T; T > 350 °C up to late magmatic conditions) hydrothermally alteration close to spreading ridges and black smokers is responsible for Ca enrichment and Mg depletion in basic rocks, as well as for a decrease of the δ¹⁸O compared to mid-ocean ridge basalts (MORB; δ¹⁸O = +5.8 ± 0.3‰; Muehlenbachs, 1998, and references therein). Sulphides may precipitate on the ocean floor in black-smoker-type deposits, while gabbros are altered into epidotites under black-smokers; 2) Low-temperature (low-T; T from <100 °C to 350 °C) alteration in the upper part of the oceanic lithosphere is responsible for Mg enrichment, Ca depletion, and for a δ¹⁸O increase compared to MORB. The δ¹⁸O decreases with depth, i.e. with decreasing the amount of percolating fluids in the deeper parts of the ocean crust (gabbros); 3) Fluid–rock interactions during devolatilisation reactions related to subduction zone metamorphism if the oceanic lithosphere is subducted; 4) Fluid–rock interactions related to low- to medium-pressure metamorphism during obduction/exhumation of ophiolites related to orogenic processes; and 5) Migration of late- to post-orogenic fluids.

Studies on stable Fe and Ge isotopes showed that they can fractionate at both low-T and high-T magmatic and hydrothermal conditions and can be employed as tracers of magmatic, metamorphic and hydrothermal processes (for a review, see Sossi et al., 2016; El Korh et al., 2017a; Rouxel and Luais, 2017; Johnson et al., 2020).
Iron isotopes (masses 54, 56, 57 and 58) can fractionate among Earth reservoirs, especially if changes in redox conditions and bonding environment are involved (e.g. Polyakov and Mineev, 2000; Sossi and O’Neill, 2017). Deviation of the $^{56}$Fe/$^{54}$Fe ratio is expressed as $\delta^{56}$Fe = $\left(\frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}}} - 1\right) \times 1000$ (with $x = 56$ or 57), relative to the IRMM-014 Fe standard solution. Fe isootope fractionation in magmatic rocks mainly results from: 1) partial melting (Teng et al., 2013; Weyer and Ionov, 2007; Williams et al., 2005) and; 2) mantle metasomatism resulting from subduction of isotopically variable oceanic crust and Fe transport through fluid migration in the deep mantle (Bearc and Johnson, 2004; Poitrasson et al., 2013; Zhao et al., 2010). Magmatic and metasomatic processes are responsible for the heavier Fe isotopic signatures of oceanic basalts (MORB, ocean island basalts (OIB), and basaltic arc basin basalts (BABB)] compared to the bulk Earth mantle [+0.34 ± 0.01‰; 2σ standard error (SE)].

Mantle rocks (Cr-rich dunites, peridotites and xenoliths; $\delta^{56}$Fe from −0.540 to +0.173‰) and island arc basalts ($\delta^{56}$Fe from −0.037 to +0.143‰) (Craddock et al., 2013; Dauphas et al., 2009; Konter et al., 2016; Nebel et al., 2013, 2015; Poitrasson et al., 2013; Sossi et al., 2016; Su et al., 2015; Weyer and Ionov, 2007; Zhang et al., 2019, 2020; Zhao et al., 2010, 2017). Besides, Fe isotopic compositions of MORB and BABB (56Fe from +0.026 to +0.176‰) cover a smaller range than OIB (56Fe from −0.111 to +0.300‰) (Konter et al., 2016; Nebel et al., 2013; Schuessler et al., 2009; Sossi et al., 2016; Teng et al., 2008, 2013; Weyer and Ionov, 2007).

During hydrothermal metamorphism of the oceanic lithosphere, significant changes in redox conditions are associated with dissolution and precipitation of Fe-bearing minerals on (sub-)seafloor. Because of the higher solubility of Fe2+ compared to Fe3+ in hydrous fluids, hydrothermal processes under reducing conditions produce fluids enriched in light Fe isotopes, as well as high-T basalt-hosted vent fluids from mid-ocean ridges with a 56Fe lower of c. −0.2 to −0.7‰ than igneous rocks (Bennett et al., 2009; Rouxel et al., 2008). Fe is mainly transported as Fe-chloride complexes in fluids (Manning, 2004). Changes in the non-redox parameters [such as ligand composition (chloride, sulphide), speciation, Fe coordination] is also expected to trigger Fe isotope fractionation in Fe-bearing solutions (Hill et al., 2010).

Hydrothermal alteration produces Fe2+-bearing phases (e.g. Fe-sulphides) that are generally isotopically lighter than Fe3+-bearing secondary products (e.g. Fe-rich clays or Fe-hydroxides), which show higher 56Fe lower of c. from −0.73 to +1.39‰; mean: +0.08 ± 0.13‰; 2σ SE; Rouxel et al., 2003; Williams et al., 2009). Besides, hydrothermal alteration of abyssal peridotites produces abyssal serpentinites with high Fe2+/$^{56}$Fe ratios (Debret et al., 2014; Mével, 2003) and 56Fe ranging from −0.10‰ to +0.11‰ (Craddock et al., 2013; Debret et al., 2016).

Germanium is a trace element in most silicate rocks. Because of its oxidation state of 4+ and similar ionic and covalent radii to Si, Ge can be incorporated into SiO2 tetrahedras (Bernstein, 1985). Its five naturally occurring stable isotopes (masses 70, 72, 73, 74 and 76) can fractionate, with $\delta^{74}$Ge = $\left(\frac{(^{74}\text{Ge}/^{76}\text{Ge})_{\text{sample}}}{(^{74}\text{Ge}/^{76}\text{Ge})_{\text{NIST3120}}} - 1\right) \times 1000$ (with $x = 72, 73, 74$ or 76), relative to the NIST 3120a Ge standard solution. Ge isotope fractionation is related to the nature of fluid-rock interactions in ophiolites (French Massif Central) that were not subducted during the Variscan orogeny. This study investigates non-traditional techniques to fractionate between fluids and minerals predicts that heavier Ge isotopes are enriched in minerals with higher Ge-O bond lengths (Li et al., 2009). Thus, fluids in equilibrium with olivine are expected to be isotopically heavier than the solid phase (Rouxel and Luais, 2017), resulting in higher 54Ge measured in serpentinites compared to unaltered ultrabasic rocks (Luais, 2012).

Recent studies have shown that the subducted oceanic crust can conserve the Fe and Ge isotopic composition of their hydrothermally altered protolith during high-pressure (HP) metamorphism (Bearc and Johnson, 2004; Li et al., 2016; El Korh et al., 2017a; 2017b; Inglis et al., 2017), while Fe isotope fractionation may occur in HP blueschist-facies serpentinites (Debret et al., 2016). Deciphering the signatures of fluid-rock interactions in ophiolites can be relatively complex because these rocks often display various stages of fluid-rock interactions, fluid overprinting or polymetamorphism, especially in the case of subducted ophiolites. This study investigates non-traditional techniques to fractionate between fluids and minerals predicts that heavier Ge isotopes are enriched in minerals with higher Ge-O bond lengths (Li et al., 2009). Thus, fluids in equilibrium with olivine are expected to be isotopically heavier than the solid phase (Rouxel and Luais, 2017), resulting in higher 54Ge measured in serpentinites compared to unaltered ultrabasic rocks (Luais, 2012).

The Limousin area is located in the northwestern French Massif Central. It is part of the European Variscan belt, which was formed by the Devonian to Carboniferous collision of Laurussia (formed by the assembly of Laurentia, Baltica and Avalonia continents) and Gondwana continents (Fig. 1a) (e.g. Lardeaux et al., 2014; Matte, 2001). Two main collision stages have been characterised in the Western Variscan belt. The Variscan orogeny was initiated during the Middle Devonian by the closure of the oceanic domains (including the Rheic ocean), which were opened during the Cambro-Ordovician rifting between the continental domains, and by the dislocation of the northern margin of the Gondwana (e.g.; Kroner and Romer, 2013; von Raumer et al., 2015). The collision between Laurussia and Gondwana-derived terranes occurred during the Early Carboniferous and was followed by Late Carboniferous orogenetic collapse (Kroner and Romer, 2013; Lardeaux et al., 2014; Franke et al., 2017).

The western European Variscan belt is composed of three major domains (Fig. 1a): (1) the Rheno-Hercynian Zone (external domain), (2) the Saxothuringian Zone and, (3) the Moldanubian Zone (internal allochthonous domain) (e.g. Franke et al., 2017; Lardeaux et al., 2014). The allochthonous domain was formed by the superposition of nappes derived from peri-Gondwanan regions and includes a series of ophiolites and ophiolite-derived basic and ultrabasic rocks. (von Raumer et al., 2015, and references therein). In the Western Variscan
belt, the emplacement of the ophiolite magmatic precursors along the Gondwana margin have been interpreted as the result of a late-Cambrian active margin (intra-continental back-arc basin rifting) that has followed the closure of the Proto-Rheic ocean during the Cambrian–Ordovician (von Raumer et al., 2015). Other studies consider the ophiolites as the remnants of a narrow ocean between Gondwana and Armorica named the “Galicia-South Brittany-Moldanubian” or “Medio-European” ocean (Matte, 2001; Faure et al., 2009; Lardeaux et al., 2014).

The FMC consists of a series of nappes, which were piled during the Devonian–Early Carboniferous, and display different units (Girardeau et al., 1986; Ledru et al., 1994; Faure et al., 2009). In the Limousin area, the Upper Allochthon (or Gartempe Unit) is formed by a series of low-grade Palaeozoic metasedimentary and metavolcanic associations (Fig. 1b). The Middle Allochthon (also known as the Upper Gneiss Unit), includes rocks from the “leptyno-amphibolite groups” (LAGs) (Santallier et al., 1988): paragneisses, leptynites and amphibolites of medium to high grade metamorphism, as well as migmatic metagreywackes and relics of eclogites and granulites. The Lower Allochthon (also known as the Lower Gneiss Unit) is mainly composed of metasedimentary rocks (paragneisses, micaschists, metashales and metagreywackes), as well as Late Proterozoic–Early Cambrian and Ordovician leucocratic orthogneiss. The Parautochthon basement is composed of metasediments and metagranites.

Remnants of subducted ophiolites occur as lenses of HP–UHP eclogites (zoisite-eclogites and kyanite-eclogites; Berger et al., 2010), which crop out at the basis of the Middle Allochthon. U–Pb age data indicate that eclogites have recorded a protolith age of 475–489 Ma (zircon), indicating that their protoliths were emplaced during the Cambro-Ordovician rifting (Berger et al., 2010). The UHP event (P ~ 2.9 ± 0.5 GPa, T ~ 660 ± 70 °C) corresponds to a subduction at a depth of 100 km and is dated at 412 ± 5 Ma (Berger et al., 2010).

The Limousin ophiolite belongs to the suite of oceanic rocks recognised in the Moldanubian Zone (von Raumer et al., 2015). It corresponds to a series of 1–5 km wide non-subducted ophiolite massifs, forming a 25 km long thrust sheet of basic and ultrabasic rocks in the

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Fig. 1. Geological map of the studied area in the Limousin ophiolite (modified after Berger et al., 2005, 2010, and El Korh et al., 2019, 2020). AM, Armorican Massif; BF, Black Forest; ECM, External Crystalline Massifs of the Alps; FMC, French Massif Central; LC, Lizard Complex; Py, Pyrenees; RM, Rhenish Massif; VM, Vosges Massif; MZ, Moldanubian zone; RHZ, Rheno-Hercynian zone; STZ, Saxo-Thuringian zone.
upper part of the Middle Allochthon (Dubuisson et al., 1989); Berger et al., 2005, 2006). The Limousin ophiolite has been interpreted as the plutonic sequence of a lherzolite-harzburgite ophiolite type, emplaced in a slow-spreading mid-ocean ridge (Berger et al., 2006). The ophiolite bodies are composed of a series of serpentinised ultrabasic rocks and basic amphibolite-facies rocks, such as diopside-bearing harzburgites, harzburgites, dunites, wehrlites, harzburgites, troctolites, (meta)gabbros and amphibolites (Berger et al., 2005). Further to magma emplacement, the rocks were submitted to a pervasive sea-floor hydrothermal alteration under low-P conditions (~0.2 GPa), with temperature decreasing from high-T late-magmatic conditions to lower-T greenschist–zeolite metamorphic facies (Berger et al., 2005). The Limousin ophiolite-derived rocks have not been affected by a pervasive Variscan orogenic metamorphism, which probably

| Sample | Rock type | Locality** | Mineralogical assemblage*** |
|--------|-----------|------------|-----------------------------|
| LAU-1  | Serpentinite | Saint-Laurent | Serp-chl-spl-amph± ol± cpx |
| LAU-2  | Serpentinite | Saint-Laurent | Serp-chl-spl-Fe ox |
| CLUZ-6 | Serpentinite | Le Cluzeau   | Serp-amph-chl-spl-Fe ox± Fe sulph |
| FLOT-2a| Serpentinite | La Flotte    | Serp-chl-spl-Fe ox |
| FLOT-2b| Serpentinite | La Flotte    | Serp-chl-spl-Fe ox |
| CLUZ-1 | Amphibolite | Le Cluzeau  | Amph-chl-spl-Fe ox |
| CLUZ-1a| Amphibolite | Le Cluzeau  | Amph-chl-Fe ox± chl |
| CLUZ-4 | Amphibolite | Le Cluzeau  | Amph-plag-stn-Fe ox± Fe sulph± chl |
| CLUZ-5 | Amphibolite | Le Cluzeau  | Amph-plag-chl-Fe ox |

* Samples are from El Korh et al. (2019, 2020).
** See Fig. 1.
*** The mineral abbreviations are from Kretz (1983); Fe sulph: Fe-sulphides (pyrite).

Fig. 2. Photomicrographs of the studied serpentinites (a–d) and amphibolites (e–f) from the Limousin ophiolite. (a) Serpentinite LAU2: ultrabasic protolith totally altered into serpentinite without relics of magmatic minerals: serpentine (serp), tremolite (tr), chlorite (chl), spinel (spl). (b) Serpentinite FLOT2b: olivine (ol) replaced by serpentine. Serpentine is rimmed by coronas of amphibole (amph) (mainly tremolite) associated with chlorite and spinel. (c) Serpentinite FLOT2b: olivine partially to totally replaced by yellow serpentine. (d) Serpentinite FLOT2b: Replacement of the original magmatic minerals by serpentine, chlorite, spinel, and Fe-oxides. (e) Fine-grained amphibolite CLUZ1 slightly foliated and mainly consisting of plagioclase (plag) and hornblende (hbl). (f) Large-grained isotropic amphibolite CLUZ4: aggregates formed by large crystals of Mg-hbl replacing magmatic pyroxene. Amphibole aggregates are rimmed by plag-hbl symplectites and hbl needles.
took place before nappe emplacement and accretion of ophiolite-derived rocks (Berger et al., 2005).

### 3. Studied samples

We have investigated the Fe and Ge isotopic compositions of five serpentinites (LAU1, LAU2, CLUZ6, FLOT2a, FLOT2b) and four amphibolite-facies basic rocks (CLUZ1a, CLUZ1a, CLUZ4 and CLUZ5) from La Flotte, Le Cluzeau and Saint-Laurent ophiolite massifs (Fig. 1b; Table 1; see also El Korh et al., 2019, 2020).

The ultrabasic rocks are highly serpentined and have developed the typical mesh textures resulting from serpentinitisation at mid-ocean ridges (Bach et al., 2006; Viti and Mellini, 1998): brown Fe-spinel (XMg: 0.02–0.57), Fe-hydroxides and rare relics of olivine (LAU1). Sample LAU1 contains a higher abundance of amphibole. In the serpentinites from Le Cluzeau (CLUZ6) and La Flotte (FLOT2a, FLOT2b), serpentine (XMg: 0.55–0.93; Fe3+/ΣFe: 0.0–1.0) have partially to totally replaced olivine, and is accompanied by amphibole (tremolite to Mg-hornblende; XMg: 0.83–0.88; Fe3+/ΣFe: 0.38–0.97), chlorite, spinel (Cr-Cr-spinels in sample CLUZ6 with XMg and Fe3+/ΣFe values of 0.03 and 0.37, respectively; Al-Fe-Cr-spinels in sample FLOT2a with XMg and Fe3+/ΣFe values of 0.32–0.53 and 0.12–0.24, respectively), iron oxides (magnetite) and sulphides. In sample CLUZ6, serpentine is rimmed by coronas of amphibole (tremolite) associated with chlorite and spinel. This sample displays a texture similar to the serpentinitised troctolites described by Dubuisson et al. (1989), are composed of serpentine (XMg = 100 × mol% MgO/(mol% MgO + mol% FeOtot)), Mg-hornblende (tremolite to Mg-hornblende; XMg: 0.83–0.92; Fe3+/ΣFe: 0.38–0.97), chlorite, spinel (Cr-Cr-spinels in sample CLUZ6 with XMg and Fe3+/ΣFe values of 0.03 and 0.37, respectively; Al-Fe-Cr-spinels in sample FLOT2a with XMg and Fe3+/ΣFe values of 0.32–0.53 and 0.12–0.24, respectively), iron oxides (magnetite) and sulphides. In sample CLUZ6, serpentine is rimmed by coronas of amphibole (mainly tremolite) associated with chlorite and spinel. This sample displays a texture similar to the serpentinitised troctolites described by Dubuisson et al. (1989) and Berger et al. (2005). However, plagioclase is absent from sample CLUZ6, contrary to the samples from Berger et al. (2005), who described coronas made of amphibole, pyroxene and spinel and formed between serpentinisated olivine and plagioclase. Chlorite and amphibole abundance is variable in the samples from La Flotte. Alteration textures suggest that the samples from La Flotte correspond to serpentinisated harzburgites, while sample CLUZ6 may derive from a troctolite (Berger et al., 2005; Dubuisson et al., 1989) (Fig. 2). The serpentinites from Saint-Laurent show higher MgO contents, and lower contents of Fe2O3tot, Al2O3 and CaO than the serpentinites from La Flotte and Le Cluzeau (El Korh et al., 2019). All serpentinites have compatible and incompatible trace element compositions typical of the Primitive Mantle (Sun and McDonough, 1989), with high abundances in compatible transition metals (Sc, V, Cr, Co, Ni, Zn, Cu) and low contents of incompatible metals (Ge, Ga, Mo, Sn, Sb, W), Large-Ion Lithophile Elements (U, Li, Rare-Earth Elements (REE) and High Field Strength Elements (HFSE: Th, U, Nb, Ta, Zr, Hf) abundances (El Korh et al., 2019, 2020). Serpentinites from Le Cluzeau and La Flotte display (Ce/Yb)PM ratios of 0.40 to 0.70, while serpentinites from Saint-Laurent have light REE (LREE) abundances below detection limit (El Korh et al., 2020). The temperature of hydrothermal alteration of ultrabasic rocks is estimated between 350 and 500 °C, because of the presence of tremolitic amphibole and the absence of talc (Berger et al., 2005). In particular, despite low Li abundances, δ7Li variations in the mineral assemblage of serpentinites have allowed to determine changes in hydrothermal

### Table 2

Major and trace element composition of the studied samples.

| Sample   | SiO2 | Al2O3/SiO2 | Fe2O3tot | MgO | CaO | Na2O | XMg | Fe3+/ΣFe | Cr | Ge | Rb | Ba | Y/Ti × 10−3 | (Ce/Yb)PM*** |
|----------|------|------------|----------|-----|-----|-----|-----|---------|----|-----|----|----|-------------|---------------|
| LAU1     | 38.92| 0.05       | 7.59     | 36.33| 0.58| 0.03| 0.84| 0.63    | 2793| 0.88| bdl| bdl| 9.4        | 1.4           |
| LAU2     | 38.62| 0.04       | 7.48     | 36.06| 0.03| 0.01| 0.84| 0.71    | 3042| 0.52| 0.40| 13  | bdl         | bdl           |
| FLOT2a   | 35.53| 0.09       | 10.89    | 37.52| 0.43| bdl | 0.79| 0.58    | 3427| 0.89| 0.45| 8.7 | 1.61        | 0.47          |
| FLOT2b   | 35.39| 0.12       | 10.33    | 34.74| 0.07| bdl | 0.79| 0.67    | 2837| 0.91| 0.59| 12  | 3.00         | 0.70          |
| CLUZ5    | 39.13| 0.11       | 11.31    | 30.41| 2.86| 0.27| 0.75| 0.65    | 2436| 1.2  | 0.88| 14  | 3.56         | 0.40          |
| CLUZ1    | 46.06| 0.38       | 6.61     | 10.24| 12.43| 1.84| 0.63| 0.13    | 958 | 1.2  | 1.9  | 23  | 3.95         | 0.60          |
| CLUZ1a   | 46.82| 0.32       | 8.58     | 13.54| 11.33| 1.54| 0.64| 0.14    | 1120| 1.4  | 1.7  | 23  | 4.13         | 0.63          |
| CLUZ4    | 49.23| 0.33       | 5.28     | 11.11| 11.85| 1.42| 0.70| 0.11    | 859 | 1.4  | 1.9  | 14  | 4.33         | 0.66          |
| CLUZ5    | 48.26| 0.33       | 7.68     | 10.94| 11.74| 2.07| 0.61| 0.13    | 906 | 1.4  | 2.9  | 27  | 3.55         | 0.62          |

Major elements in wt% oxides; trace elements in ppm; XMg = 100 × mol% MgO/(mol% MgO + mol% FeOtot). bdl: below detection limit.

† Raw data from: El Korh et al. 2019 [1]; El Korh et al. 2020 [2].

⁎ (Ce/Yb)PM, normalised to the Primitive Mantle (normalisation values are from Sun and McDonough 1989).
Table 5
Germanium isotopic compositions of Ge standards and studied samples.

| Sample            | n  | δ⁶⁷Ge (‰) | Mean ± 2σ(‰) | δ⁷⁷Ge (‰) | Mean ± 2σ(‰) | δ¹⁸⁷Ge (‰) | Mean ± 2σ(‰) |
|-------------------|----|-----------|---------------|-----------|---------------|-----------|---------------|
| Aldrich Reference | 0  | 0.051     | 0.001 (se)    | 0.052     | 0.002 (se)    | 0.051     | 0.002 (se)    |
| [1]               |    | 0.051     | 0.001 (se)    | 0.052     | 0.002 (se)    | 0.051     | 0.002 (se)    |
| [2]               |    | 0.051     | 0.001 (se)    | 0.052     | 0.002 (se)    | 0.051     | 0.002 (se)    |
| JMC Reference     | 10 | 0.051     | 0.001 (se)    | 0.052     | 0.002 (se)    | 0.051     | 0.002 (se)    |

n = number of replicates; δ⁶⁷Ge values (‰) refer to NIST3120a Ge standard normalisation; 2σ uncertainties for the reference values of Aldrich and JMC standards given as 2σ standard deviations (sd); 2σ uncertainties for the measured Aldrich and JMC standards and for the studied samples are given as 2σ standard error (se) (= 2σ standard deviation / √n); ** Reference values are from: [1] Luais (2012); [2] Escoube et al. (2012).

alteration conditions, due to a temperature decrease and/or variations in the δ⁷Li composition (El Korh et al., 2019).

Two types of amphibolites were studied: fine-grained slightly foliated amphibolites (CLUZ1 and CLUZ1a) and isotropic amphibolites (CLUZ4 and CLUZ5), which derive from layered and isotropic gabbros, respectively (Berger et al., 2005). The two studied types of amphibolites are composed of green-brown amphibole (mainly hornblende with rare tremolite and pargasite), plagioclase, chlorite and iron oxides (magnesiohornblende, pargasite, tschermakite) from symplectites around clinopyroxene (mainly augite with rare orthopyroxene) in the amphibolites, plagioclase-bearing serpentinites and troctolites, mainly:

- Al-poor amphiboles, from coronas between plagioclase and olivine and
- Rare magmatic plagioclase can be also observed. Fe⁴⁺/2ΣFe and XMg values of amphibole vary between the studied samples (Fe⁴⁺/2ΣFe of 0.3–0.34, 0.28–0.35 and 0.32–0.76 in samples CLUZ1–CLUZ1a, CLUZ4 and CLUZ5, respectively; XMg of 0.62–0.77, 0.69–0.80 and 0.62–0.70 in samples CLUZ1–CLUZ1a, CLUZ4 and CLUZ5, respectively). Ranges of Al₂O₃ contents of amphibole overlap between foliated and isotropic amphibolites (3.17–14.37 and 1.58–12.64 wt.%, respectively). However, hornblende in foliated amphibolites often show higher Al₂O₃ contents than hornblende in isotropic amphibolites (6.62–14.37 and 3.66–10.21 wt.%, respectively).

Berger et al. (2005) have described different types of amphiboles in amphibolites, plagioclase-bearing serpentinites and troctolites, mainly:

1) low-Al amphibole (mainly Mg-hornblende, actinolite and tremolite) from foliated and schistose amphibolites and;
2) Al-rich amphiboles (Mg-hornblende, pargasite, tschermakite) from symplectites around Al-poor amphiboles, from coronas between plagioclase and olivine and around clinopyroxene in troctolites, and from chlorite-rich amphibolites.

Reaction textures and coronas are interpreted as the result of the reaction between olivine and plagioclase, which yielded an assemblage of orthopyroxene–clinopyroxene–spinel under low-P and high-T conditions hydrothermal metamorphism from late-magmatic conditions to greenschist facies temperatures (Berger et al., 2005).

Both studied amphibolite types display compatible and incompati

Table 2 summarises the SiO₂, Al₂O₃, Fe₂O₃tot, XMG, Na₂O, CaO, Cr, Ge, Rb and Ba concentrations, as well as the Al₂O₃/SiO₂, Y/Ti, (Ce/Yb)PM and Fe⁴⁺/ΣFe ratios (El Korh et al., 2019, 2020), that will be discussed below.

4. Analytical techniques

4.1. O isotopes

The oxygen isotope compositions of whole rocks were determined in the Stable Isotope Laboratory of the Institute of Institute of Earth Surface Dynamics (IDYST), University of Lausanne. Oxygen was extracted from 2 to 3 mg of rock powder using a 10 W New Wave CO₂ laser and F₂ gas. Isotopic composition of extracted oxygen was analysed with a Thermo-Finnigan MAT 253 gas source mass spectrometer. δ¹⁸O values are expressed in ‰ relative to VSMOW (Vienna Standard Mean Ocean Water) and are corrected to the LS₁ quartz standard (in-house standard of the University of Lausanne; 18.1‰). The LS₁ standard was analysed to monitor data accuracy and reproducibility (daily average value: +18.02 ± 0.32‰; n = 2) (Table 3).

4.2. Fe isotopes

The whole rock Fe isotope compositions were measured in liquid mode by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the CRPG-Nancy using a NeptunePlus spectrometer (ThermoFisher Scientific, Germany and USA), following the procedure
described in Liu et al. (2014) and El Korh et al. (2017a). Fe was separated according to the following chemical procedure: c.10 mg of powdered samples were dissolved in three steps using: 1) a 2:1 mixture of HF (28 N) and HNO3 (15 N) on a hot plate at 90 °C; 2) HNO3 (15 N) at 60 °C; and 3) HCl (7 N) at 60 °C. After sample centrifugation, Fe was isolated through AG-MP-1 resin-exchange chromatography columns. Fractions were eluted with HCl (2 N) and dried down. Fe recovery is 88–99%. The dry fractions were then dissolved in HNO3 (7 N) and dried down, before being re-dissolved in HNO3 (0.05 N) for MC-ICP-MS analyses.

The MC-ICP-MS instrument was equipped with a standard nebuliser and cyclonic chamber, as well as Ni skimmer and sampler cones in standard geometrical configuration. In order to solve argide polyatomic interferences on Fe masses (40Ar14No n=54Fe; 40Ar16Oo n=56Fe; 40Ar16O1H to 57Fe), analyses were performed in static mode at a high resolution (M/ΔM = 400), with 8 s integration time, after 13 min washout in HNO3 (0.6 N) and 8 + 2 min washout in HNO3 (0.05 N). Analytical sequences consisted of 60 integration cycles (9 min in total), after 200 s washout in HNO3 (0.01 N). Analytical sequences consisted of 60 integration cycles (9 min in total), after 200 s washout in HNO3 (0.01 N). The powdered samples (c. 300 mg) were dissolved in a 3:1 mixture of HF (28 N) and HNO3 (15 N) at 60–65 °C, because of the strong Ge volatility. Several steps of leaching with HF and centrifugation allowed Ge recovery in the supernatant fraction (Luais 2012). Ge was isolated using two types of resin-exchange chromatography columns: 1) a AG 50 W-X8 (hydrogen form, 200–400 mesh, 2 ml) resin-exchange column, where Ge was eluted with HNO3 (0.5 N) (Luais 2012). Ge isotope analyses were carried out on 10 ppb diluted Ge standards and samples in HNO3 (0.01 N). Standards and samples were doped with the NBS SRM 994 Ga reference international isotopic standard (δ69Ga/71Ga = 1.50676; Machlan et al., 1986), in a flow rates, torch parameters and cyclonic chamber, as well as Ni skimmer and sampler cones in standard geometrical configuration. In order to solve argide polyatomic interferences on Fe masses (40Ar14No n=54Fe; 40Ar16Oo n=56Fe; 40Ar16O1H to 57Fe), analyses were performed in static mode at a high resolution (M/ΔM = 400), with 8 s integration time, after 13 min washout in HNO3 (0.6 N) and 8 + 2 min washout in HNO3 (0.05 N). Each sample analysis was sequentially bracketed by a measurement of the IRMM-014 ultra-pure Fe standard. Prior to optimising the peak shapes and centring, the correction coefficients for the Faraday cups were determined by gain calibration. Analyses were carried out on 2–5 ppm Fe solutions, diluted in HNO3 (0.05 N). Analytical sequences consisted of 50 cycles (10 min in total), with 8 s integration time, after 13 min washout in HNO3 (0.5 N) and 8 min washout in HNO3 (0.05 N). Each sample analysis was sequentially bracketed by a measurement of the IRMM-014 standard. Fe isotope compositions are reported in ‰ standard delta values (δ56Fe and δ57Fe), relative to the IRMM-014 standard.

Data bulk external reproducibility and accuracy were estimated by replicate analyses of the FCC-1 peridotite (Austin Creek, California, USA) geostandard (USGS) which was submitted to the same chemical and analytical procedure as the samples. The mean δ56Fe and δ57Fe values are within uncertainty with the data reported in the literature (Table 4).

### 4.3. Ge isotopes

The whole rock Ge isotope ratios were measured using the Neptune Plus spectrometer MC-ICP-MS at the CRPG-Nancy (Table 5). Ge dissolution and separation followed the chemical procedure given in Luais (2012). The powdered samples (c. 300 mg) were dissolved in a 3:1 mixture of HF (28 N) and HNO3 (15 N) at 60–65 °C, because of the strong Ge volatility. Several steps of leaching with HF and centrifugation allowed Ge recovery in the supernatant fraction (Luais 2012). Ge was isolated using two types of resin-exchange chromatography columns: 1) a AG 50 W-X8 (hydrogen form, 200–400 mesh, 2 ml) resin-exchange column, where Ge was eluted with HNO3 (0.5 N) (Luais 2012). Ge isotope analyses were carried out on 10 ppb diluted Ge standards and samples in HNO3 (0.01 N). Standards and samples were doped with the NBS SRM 994 Ga reference international isotopic standard (δ69Ga/71Ga = 1.50676; Machlan et al., 1986), in a 10:1 ratio to monitor mass bias accuracy and instrumental drift during the analytical session.

The MC-ICP-MS spectrometer was equipped with a hydride generator introduction system (HGIS) to increase the sensitivity (Florin et al., 2020). Samples are mixed with a high-reducing solution of NaBH4-NaOH in excess, which allows conversion of volatile aqueous species (GeOH4) to gaseous (GeH4) hydride species (Dedina and Tsalev 1995), with a yield of 100%. Isobaric interferences that do not form hydrides (such as argides, Zn, NiO, and FeO) are thus neutralised. Analyses were performed in static mode at a low resolution (M/ΔM = 400), with Ni skimmer and sampler cones placed in standard geometrical configuration. The cup configuration consisted of: Low 3 (57Cr), Low 2 (56Fe), Axial (56Fe) and High 1 (57Fe). Cr was used for the correction of the isobaric interference between 54Cr and 54Fe intensities. Gas flow rates, torch parameters and ion lenses were optimised by measurement of the IRMM-014 ultra-pure Fe standard. Prior to optimising the peak shapes and centring, the correction coefficients for the Faraday cups were determined by gain calibration. Analyses were carried out on 2–5 ppm Fe solutions, diluted in HNO3 (0.05 N). Analytical sequences consisted of 50 cycles (10 min in total), with 8 s integration time, after 13 min washout in HNO3 (0.5 N) and 8 min washout in HNO3 (0.05 N). Each sample analysis was sequentially bracketed by a measurement of the IRMM-014 standard. Fe isotope compositions are reported in ‰ standard delta values (δ56Fe and δ57Fe), relative to the IRMM-014 standard.

Data bulk external reproducibility and accuracy were estimated by replicate analyses of the FCC-1 peridotite (Austin Creek, California, USA) geostandard (USGS) which was submitted to the same chemical and analytical procedure as the samples. The mean δ56Fe and δ57Fe values are within uncertainty with the data reported in the literature (Table 4).

### 4.3. Ge isotopes

The whole rock Ge isotope ratios were measured using the Neptune Plus spectrometer MC-ICP-MS at the CRPG-Nancy (Table 5). Ge dissolution and separation followed the chemical procedure given in Luais (2012). The powdered samples (c. 300 mg) were dissolved in a 3:1 mixture of HF (28 N) and HNO3 (15 N) at 60–65 °C, because of the strong Ge volatility. Several steps of leaching with HF and centrifugation allowed Ge recovery in the supernatant fraction (Luais 2012). Ge was isolated using two types of resin-exchange chromatography columns: 1) a AG 50 W-X8 (hydrogen form, 200–400 mesh, 2 ml) resin-exchange column, where Ge was eluted with HNO3 (0.5 N) (Luais 2012). Ge isotope analyses were carried out on 10 ppb diluted Ge standards and samples in HNO3 (0.01 N). Standards and samples were doped with the NBS SRM 994 Ga reference international isotopic standard (δ69Ga/71Ga = 1.50676; Machlan et al., 1986), in a 10:1 ratio to monitor mass bias accuracy and instrumental drift during the analytical session.

The MC-ICP-MS spectrometer was equipped with a hydride generator introduction system (HGIS) to increase the sensitivity (Florin et al., 2020). Samples are mixed with a high-reducing solution of NaBH4-NaOH in excess, which allows conversion of volatile aqueous species (GeOH4) to gaseous (GeH4) hydride species (Dedina and Tsalev 1995), with a yield of 100%. Isobaric interferences that do not form hydrides (such as argides, Zn, NiO, and FeO) are thus neutralised. Analyses were performed in static mode at a low resolution (M/ΔM = 400), with Ni skimmer and sampler cones placed in standard geometrical configuration. The cup configuration consisted of: Low 3 (69Zn), Low 2 (68Zn), Axial (70Zn), High 1 (72Zn), High 2 (73Zn), High 3 (74Zn). 68Zn was used to correct the isobaric interference between 70Ge and 70Zn mathematically. Gas flow rates, torch parameters and ion lenses were optimised by measurement of the NIST SRM 3120a ultra-pure Ge standard (Luais 2012). The correction coefficients between the Faraday cups were calculated by a gain calibration before optimising peak shapes.

Analyses were carried out on 2–4 ppm Fe solutions, diluted in HNO3 (0.05 N). Analytical sequences consisted of 60 integration cycles (9 min in total), after 200 s washout in HNO3 (0.6 N) and 8 + 2 min washout in HNO3 (0.01 N). Each sample measurement was sequentially bracketed by a measurement of the NIST SRM 3120a standard. Ge isotope compositions are expressed in ‰ standard delta values (δ72Ge, δ73Ge and δ74Ge), relative to the NIST SRM 3120a standard.
The long-term stability of the ICP mass spectrometer, the external reproducibility and accuracy of the measurements were estimated by replicate analyses of the JMC and Aldrich Ge solution standards. The average $\delta^{72}$Ge, $\delta^{73}$Ge and $\delta^{74}$Ge values (Table 5) are consistent with their respective reference values (Escoube et al., 2012; Luais 2012).

5. Results

5.1. O isotopes

O isotope compositions of the studied serpentinites, amphibolites and UHP eclogite samples are given in Table 3. Serpentinites from Saint-Laurent and La Flotte have $\delta^{18}$O values varying between +5.0 and +5.3‰. The serpentinite from Le Cluzeau (CLUZ6) shows a higher $\delta^{18}$O of 6.1‰. Amphibolites have $\delta^{18}$O values ranging from +6.2 to +6.6‰ (Fig. 3).

5.2. Fe isotopes

The Fe isotopic compositions of the studied serpentinites, amphibolites and UHP eclogite are given in Table 4. The reproducibility on $\delta^{56}$Fe for all samples is generally lower than ±0.043‰ at 2σ SE. All data plot within uncertainty on the slope of the equilibrium and kinetic theoretical mass fractionation lines in a $\delta^{57}$Fe vs. $\delta^{56}$Fe diagram (Fig. 4a). The $\delta^{56}$Fe values of serpentinites vary between +0.14 and +0.18‰ (Fig. 4a). Amphibolites have $\delta^{56}$Fe values varying from +0.03 to +0.16‰, within the same range as serpentinites. The two groups of amphibolite facies rocks can be distinguished, even if their $\delta^{56}$Fe ranges

Fig. 5. (a–f) $\text{Al}_2\text{O}_3/$SiO$_2$, SiO$_2$, Fe$_2$O$_3$, XMg, CaO and Na$_2$O vs. $\delta^{56}$Fe variations in the studied samples. In panels d and f, the correlation coefficient R$^2$ is given for the whole series of amphibolites, as well as for the three samples that correlate well with the $\delta^{56}$Fe (excluding sample CLUZ1a). Error bars are at 2σ SE external reproducibility.
overlap: the $\delta^{56}$Fe of metamorphosed dykes do not vary from one sample to the other (+0.12‰), while the metagabbros display heterogeneous $\delta^{56}$Fe values (+0.03 to +0.16‰) (Fig. 4a).

In serpentinites, the $\delta^{56}$Fe does not vary with SiO$_2$, Fe$_2$O$_3^{tot}$, CaO, Cr and Ge concentrations, nor with XMg, Al$_2$O$_3$/SiO$_2$, Y/Ti, Fe$^{3+}$/ΣFe and (Ce/Yb)$_{PM}$ ratios (Figs. 5, 6 and 7). By contrast, the $\delta^{56}$Fe displays a good negative correlation with the Ba content (Fig. 7).

In amphibolites, the $\delta^{56}$Fe values do not correlate with SiO$_2$, Ni, Cr, and Ge contents, nor with Al$_2$O$_3$/SiO$_2$, Fe$^{3+}$/ΣFe and (Ce/Yb)$_{PM}$ values (Figs. 5, 6 and 7). The $\delta^{56}$Fe shows a good negative correlation with the Fe$_2$O$_3^{tot}$ content only in 3 samples (Fig. 5c), while the Fe$^{3+}$/ΣFe only varies slightly with the Fe$_2$O$_3^{tot}$ content (Fig. 6b). The $\delta^{56}$Fe also increases with the increase of XMg and Y/Ti (Figs. 5 and 7), and with the decrease of Na$_2$O, Ba and Rb (Figs. 5f and 7e-f). While there is no clear correlation between $\delta^{56}$Fe and CaO values, the highest $\delta^{56}$Fe is measured in sample that shows the highest CaO abundance (CLUZ4; Fig. 5e).

5.3. Ge isotopes

The Ge isotopic compositions of the studied samples are presented in Table 5. All samples have a reproducibility on $\delta^{74}$Ge lower than ±0.097‰ at 2σ SE. All data plot within uncertainty on the slope of the equilibrium and kinetic theoretical mass fractionation lines in a $\delta^{76}$Ge vs. $\delta^{74}$Ge diagram (Fig. 4b). Serpentinites have $\delta^{74}$Ge values ranging from +0.48 and +0.93‰ that are similar to heavier than the values measured in ultrabasic rocks and MORB (Fig. 8). Amphibolites display a narrow range of $\delta^{74}$Ge values varying from +0.72 to +0.78‰, similar within uncertainty to the heaviest values measured in basalts (Fig. 8).

In serpentinites, the $\delta^{74}$Ge displays a poor negative correlation with SiO$_2$, as well as a good positive correlation with the (Ce/Yb)$_{PM}$ ratio (3 samples out of 5). The $\delta^{76}$Ge does not show any correlation with CaO, Fe$_2$O$_3^{tot}$, Ni, Cr, Ge, concentrations, nor with Al$_2$O$_3$/SiO$_2$, XMg and Fe$^{3+}$/ΣFe ratio (Figs. 8 and 9). Because of the narrow range of $\delta^{74}$Ge values in amphibolites, no correlation can be observed with major and trace element concentrations (Figs. 8 and 9).

6. Discussion: multi-isotope fractionation during hydrothermal alteration

6.1. O, Fe and Ge isotopic composition of serpentinites

Oxygen isotope fractionation in the oceanic lithosphere is strongly sensitive to hydrothermal alteration processes which can be distinguished by their distinct signatures (Cartwright and Barnicoat 1999; Muehlenbachs 1998). The oxygen isotopic composition of the Limousin serpentinites is typical of peridotites (+5.5 ± 0.2‰; Mattey et al., 1994) and altered ultrabasic rocks (0 to +6‰; Magaritz and Taylor, 1974) (Fig. 3). As the two ranges overlap, our data do not allow to determine whether O isotopes have fractionated during high-T hydrothermal alteration based on the $\delta^{18}$O alone. As serpentinites are strongly oxidised rocks (Fe$^{3+}$/ΣFe from 0.58 to 0.71), the comparison of redox-sensitive isotopes, (such as Fe and Ge isotopes; Polyakov and Mineev 2000; Pokrovsky et al., 2014) with oxygen isotopes are expected to decipher magmatic and hydrothermal signatures in serpentinites.

Serpentinites have Fe$_2$O$_3^{tot}$ contents (7.4–11.3‰) and Fe$^{3+}$/ΣFe typical of greenschist facies serpentinites in ophiolites (e.g. Debret et al., 2014, 2016). Iron isotopic compositions of serpentinites (+0.14 to +0.18‰) are within the range of MORB values (Sossi et al., 2016; Teng et al., 2013), but heavier than the values measured in partially to totally serpentinised abyssal peridotites (−0.10‰ to +0.11‰; Craddock et al., 2013; Debret et al., 2016) (Fig. 10). The absence of correlation between the $\delta^{56}$Fe, SiO$_2$, Al$_2$O$_3$/SiO$_2$, and the fluid-immobile trace elements Cr, Y/Ti and (Ce/Yb)$_{PM}$ ratio, as well as the correlation between the $\delta^{56}$Fe and Ba content, suggests that $\delta^{56}$Fe variations in serpentinites do not reflect the protolith signature but Fe isotope fractionation during hydrothermal alteration (Figs. 5, 6 and 7). There is no evidence of Fe leaching or addition during hydrothermal alteration and Fe oxidation, even if a weak correlation appears between Fe$_2$O$_3^{tot}$ content and Fe$^{3+}$/ΣFe values (Fig. 6b). However, Fe oxidation during hydrothermal alteration of the peridotite protoliths co-occurred with the precipitation of micrometric to nanometric Fe$^{3+}$-rich oxides (magnetite) and hydroxides (brucite) intercalated within serpentine (Bach et al., 2006; Viti and Mellini 1998). These alteration products preferentially incorporate heavy Fe isotopes (Polyakov and Mineev 2000), resulting in an increase of the $\delta^{56}$Fe of serpentinites. The good negative correlation between $\delta^{56}$Fe and $\delta^{18}$O values in serpentinites ($R^2 = 0.75$) indicates synchronous O and Fe isotope fractionation during hydrothermal alteration (Fig. 11a).

Debret et al. (2016) observed a $\delta^{56}$Fe increase with increasing Fe reducing conditions in HP Alpine serpentinites at the transition from lizardite-serpentinites [mean: −0.02 ± 0.14‰; 2σ standard deviation (SD)] to antigorite-serpentinites [$\delta^{56}$Fe from −0.011 to +0.142‰; mean: +0.08 ± 0.11‰; 2σ SD]. The authors suggested that dehydration reactions in subducted serpentinites might release oxidised sulfate-rich and/or hypersaline fluids transporting light-Fe as Fe(II)-SO$_4$ or Fe(II)-Cl$_2$ species along the mantle wedge. The $\delta^{56}$Fe composition of the Limousin serpentinites is comparable to the highest $\delta^{56}$Fe values measured in some blueschist-facies Alpine antigorite-serpentinites.

![Fig. 6. Fe$^{3+}$/ΣFe vs. $\delta^{56}$Fe (a) and Fe$^{3+}$/ΣFe vs. Fe$_2$O$_3^{tot}$ (b) variations in the studied samples. Error bars are at 2σ SE external reproducibility. Data for abyssal serpentinites, mantle and MORB are from: Christie et al. (1986); Bouxel et al. (2003); Mèvel (2003); Weyer and Ionov (2007); Dauphas et al. (2009); Cottrell and Kelley (2011); Craddock and Dauphas, 2011; Craddock et al. (2013); Teng et al. (2008, 2013); Debret et al. (2014, 2016).](image-url)
However, our results contrast with previous studies, which suggest a conservative behaviour of Fe isotopes during ocean floor hydrothermal alteration of ultrabasic rocks into serpentinites (Craddock et al., 2013; Debret et al., 2016). The heterogeneous $\delta^{56}$Fe values of abyssal serpentinites is thought to reflect variations in the protolith composition, the isotopically heavier-Fe compositions being measured in pyroxene-rich and less depleted peridotites (Williams et al., 2005; Williams and Bizimis 2014). Debret et al. (2018) have observed that the light-Fe signature of Queyras ultrabasic rocks (i.e. Alpine serpentinites) does not correlate with fluid-immobile element ratios ($\text{Al}_2\text{O}_3/\text{SiO}_2$ or $\text{Zr}/\text{Nb}$) and reflects mobilisation of Fe during prograde metamorphism. The high $\delta^{56}$Fe values measured in the Limousin serpentinites suggest that Fe isotopes may already fractionate towards heavier values during seafloor hydrothermal alteration in highly oxidised abyssal serpentinites. Thus, subsequently subducted serpentinites may carry heavy-Fe up to the fore-arc mantle wedge and may contribute to mantle Fe heterogeneities. Indeed, large Fe isotope variations from $-0.54$ to $+0.16$‰ have been recorded by bulk mantle xenoliths (e.g. Poitrasson et al., 2013; Zhao et al., 2017).

Germanium isotopic compositions of serpentinites are similar to heavier than ultrabasic rocks ($+0.46$ to $+0.76$‰) and MORB ($+0.55$ to $+0.74$‰) (Roussel et al., 2006; Escoube et al., 2012, 2015; Luais 2012; Lalonde and Rouxel, unpublished); Rouxel and Luais 2017) (Fig. 12), suggesting Ge isotope fractionation during hydrothermal alteration at $T$ between 350 and 500 °C. Besides, the increase of the $\delta^{74}$Ge values with the decrease of $\text{SiO}_2$ and with the increase of the $(\text{Ce}/\text{Yb})_{\text{PM}}$ ratio in serpentinites (Figs. 8 and 9) suggests that the Ge isotopic composition may be controlled by the protolith composition.

Fig. 7. (a–f) $(\text{Ce}/\text{Yb})_{\text{PM}}$, $\text{Y}/\text{Ti}$, $\text{Cr}$, $\text{Rb}$ and $\text{Ba}$ vs. $\delta^{56}$Fe variations in the studied samples. Error bars are at 2σ SE external reproducibility.
Fig. 8. (a–g) Al₂O₃/SiO₂, SiO₂, Fe₂O₃tot, X_Mg, CaO, Na₂O and Fe⁴⁺/ΣFe vs. δ⁷⁴Ge variations in the studied samples. Error bars are at 2σ SE external reproducibility. Data for ultrabasic rocks and MORB are from: Christie et al. (1986); Mével (2003); Luais (2012); Escoube et al. (2012, 2015); Cottrell and Kelley (2011); Debret et al. (2014); Rouxel and Luais (2017).
Previous studies have shown that Ge isotope fractionation is strongly sensitive to low-T (<350 °C) hydrothermal processes. In particular, marine hydrothermal Fe-rich deposits display δ⁷⁴Ge from −0.98 to +0.16‰, while negative δ⁷⁴Ge from −4.71 to −2.98‰ were measured in marine and terrestrial sulfide deposits (Belissont et al., 2014; Escoube et al., 2012, 2015; Rouxel et al., 2006). Hydrothermal alteration can trigger Ge isotope fractionation towards heavier δ⁷⁴Ge values in altered oceanic crust due to the interaction with heavy-Ge hydrothermal fluids and seawater (Escoube et al., 2015; Rouxel et al., 2006). Moreover, Ge has a strong affinity with Fe hydroxides that precipitate during hydrothermal alteration, which can result in Ge isotope fractionation through Ge adsorption by goethite (Escoube et al., 2015; Pokrovsky et al., 2014). Consequently, the heavier δ⁷⁴Ge values measured in serpentinites can be interpreted as the result of Ge isotope fractionation during hydrothermal alteration and oxidation of abyssal peridotites, while Ge isotopes may not have fractionated in the lighter samples.

The δ⁷⁴Ge in serpentinites displays a good negative correlation with the δ¹⁸O (R² = 0.70) and a good positive correlation with the δ⁵⁶Fe (R² = 0.70) (Figs. 13a and b), suggesting both Ge and Fe fractionation during hydrothermal alteration at T between 350 and 500 °C. However, δ⁵⁶Fe values in serpentinites show a larger deviation from the values typically measured in ultrabasic rocks than δ⁷⁴Ge and δ¹⁸O values. Hence, oxidising conditions have enhanced fractionation of Fe isotopes to a larger extent than Ge isotopes.

Fig. 9. (a–f) (Ce/Yb)PM, Y/Ti, Cr, Ge, Rb and Ba vs. δ⁷⁴Ge variations in the studied samples. Error bars are at 2σ SE external reproducibility. Data for ultrabasic and basic rocks are from: Luais (2012); Escoube et al. (2012, 2015); Rouxel and Luais (2017); El Korh et al. (2017b).
By contrast, the lowest δ\(^{56}\)Fe and δ\(^{74}\)Ge values and the highest δ\(^{18}\)O value were measured in the sample from Le Cluzeau (CLUZ6), whose major element composition differs from the other serpentinites samples (higher CaO and Fe\(_2\)O\(_3\)\(_{\text{tot}}\) contents and lower MgO abundance). Contrary to the serpentinites from La Flotte and Saint-Laurent that derive from the alteration of abyssal peridotites, sample CLUZ6 probably derives from a troctolite. Thus, its isotopic signature also reflects a difference in the initial protolith composition in addition to hydrothermal alteration.

6.2. O, Fe, and Ge isotope fractionation during high-temperature hydrothermal alteration in amphibolites

Amphibolites have δ\(^{18}\)O values (+6.2 to +6.6‰) that are slightly higher than MORB, in agreement with the δ\(^{56}\)Fe values measured in high-T hydrothermally altered basic rocks (Cartwright and Barnicoat 1999) (Fig. 3). Fe\(_2\)O\(_3\)\(_{\text{tot}}\) compositions of amphibolites (5.3–8.6%) are typical of oceanic gabbros (2.47–11.1%; Kaczmarek et al., 2008). Similarly, amphibolites Fe\(^{3+}\)/ΣFe ratios (0.11–0.14) typical of MORB (Fe\(^{3+}\)/ΣFe = 0.07–0.16; Christie et al. 1986; Cottrell and Kelley 2011). In particular, sample CLUZ4, which displays symplectites made of anorhitic plagioclase + hornblende, have conserved a MORB-like δ\(^{56}\)Fe of +0.158 ± 0.040‰. Symplectites and enrichment in Al and Mg were interpreted as the result of an interaction of preexisting amphibole or clinopyroxene with hot seawater-derived fluids, at temperature conditions of the amphibolite-to-greenschist facies transition rather than an effect of the Variscan orogenic metamorphism (see discussion in Berger et al., 2005). Thus, Fe appears to be relatively immobile during high-T hydrothermal alteration. δ\(^{56}\)Fe values of amphibolites (+0.03 to +0.16‰) are within the range of MORB, despite a lower δ\(^{56}\)Fe value measured in one of the metagabbro samples (CLUZ5) (Fig. 10). The δ\(^{56}\)Fe increase with the Fe\(_2\)O\(_3\)\(_{\text{tot}}\) decrease and XMg and Y/TiO\(_2\) increase argues that Fe isotopic composition reflects the protolith composition, despite an absence of correlation between the δ\(^{56}\)Fe and SiO\(_2\) and Al\(_2\)O\(_3\)/SiO\(_2\) contents and between the δ\(^{56}\)Fe and the fluid-immobile Cr and (Ce/Yb)\(_{\text{PM}}\) ratio (Figs. 5 and 7). Assuming that Ba concentrations in amphibolites were not significantly modified by hydrothermal alteration, the negative correlation between δ\(^{56}\)Fe and Ba values (Fig. 7f) may be caused by variations in the protolith composition as well, as Ba is compatible to mildly incompatible in plagioclase. By contrast, the δ\(^{56}\)Fe decrease with the increase of Na\(_2\)O, and Rb contents and with
the decrease of the CaO content, especially in the metagabbro CLUZ5, would suggest Fe isotope fractionation during hydrothermal alteration (Figs. 5 and 7). This hypothesis is supported by the good correlation between $\delta^{56}\text{Fe}$ and $\delta^{18}\text{O}$ values, despite the restricted range of Fe elemental and isotopic compositions and $\delta^{18}\text{O}$ values (Fig. 11a). Similarly to serpentinites, a good correlation is observed between $\delta^{56}\text{Fe}$ and $\delta^{18}\text{O}$ values ($R^2 = 0.87$); the $\delta^{18}\text{O}$ increases with the decrease of the $\delta^{56}\text{Fe}$. Sample CLUZ5 is richer in chlorite than other amphibolites, where chlorite is only present as an accessory mineral (Table 1). Chlorite formation in metagabbro CLUZ5 indicates partial re-equilibration in the greenschist facies, and thus Fe isotope fractionation under lower temperature conditions of hydrothermal alteration. This contrasts with the positive correlations observed between Fe and O isotope composition in mantle-derived rocks and high-pressure metabasites (El Korh et al., 2017a; Williams et al., 2009). In the low-T hydrothermally altered metabasalts of the Île de Groix, the $\delta^{18}\text{O}$ increases with increasing the $\delta^{56}\text{Fe}$ for each metamorphic facies (El Korh et al., 2017a). Different hypotheses were suggested to explain the coupled Fe and O isotope fractionation: 1) O and Fe fractionation did not occur concomitantly, with O isotopes reflecting the hydrothermal signature, and Fe isotopes mirroring the protolith composition; 2) the different trends observed in eclogites, blueschists and greenschists result from different diffusion rates and kinetic isotope fractionation of Fe compared to O during hydrothermal processes; 3) the temperature of hydrothermal alteration was variable (El Korh et al., 2017a). Williams et al. (2009) interpreted the positive correlation between Fe and O isotopes in bulk mantle eclogite xenoliths from kimberlite pipes as the protolith composition inherited from variable isotope fractionation during disequilibrium partial melting. However, the correlation between $\delta^{18}\text{O}$ and $\delta^{56}\text{Fe}$ may also reflect intensive mantle metasomatism (Gréau et al., 2011).

Contrary to the highly oxidised serpentinites, high-T hydrothermal alteration in amphibolites did not trigger any Fe oxidation. This may be due to the precipitation of reduced Fe$^{2+}$-rich alteration products (sulphides) (Rouxel et al., 2003) or to the low permeability of gabbroic rocks, which prevents hydrothermal fluids to migrate (Cartwright and Barnicoat 1999). Moreover, the various degrees of Fe oxidation states and Fe isotope fractionation between amphibolites and serpentinites can be explained by the different temperature of hydrothermal alteration.

![Figure 12](image1.png)
**Fig. 12.** Comparison of the $\delta^{74}\text{Ge}$ isotope compositions of the Limousin samples with published values for ultrabasic and basic rocks. Data are from: Rouxel et al. (2006); Escoube et al. (2012, 2015); Luais (2012); Lalonde and Rouxel (unpublished; cited by Rouxel and Luais 2017); Rouxel and Luais (2017); El Korh et al. (2017b).

![Figure 13](image2.png)
**Fig. 13.** $\delta^{18}\text{O}$ vs. $\delta^{74}\text{Ge}$ (a) and $\delta^{56}\text{Fe}$ vs. $\delta^{74}\text{Ge}$ (b) in the studied serpentinites, and amphibolites. Error bars are at 2$\sigma$ external reproducibility. Data for mantle and MORB are from: Weyer and Ionov (2007); Luais (2012); Teng et al. (2008, 2013); Dauphas et al. (2009); Craddock and Dauphas, 2011; Escoube et al. (2012, 2015); Craddock et al. (2013); Debret et al. (2014); Rouxel and Luais (2017).
alteration, which was lower in serpentinites (350–500 °C) than in amphibolites (570–750 °C) (Berger et al., 2005).
Amphibolites show a small range of δ74Ge values (+0.72 to +0.77‰), that are heavier than most basalts and gabbros (+0.37 to +0.74‰; for a review, see Rouxel and Luais 2017) and than high-pressure metabasites (El Korh et al., 2017b) (Fig. 11). As observed for serpentinites, hydrothermal alteration of basic rocks may have been responsible for Ge isotope fractionation towards heavier values than their protolith. However, no δ56Fe vs. δ56Fe correlation is observed, as δ56Fe values in amphibolites do not differ significantly from the δ56Fe of basic rocks, while δ56Fe values show evidence of a definite deviation from the values typically measured in basic rocks (Fig. 13b). Hence, Ge isotope fractionation has prevailed over Fe isotope fractionation during hydrothermal alteration of basic rocks. Reducing conditions have enhanced Ge isotope fractionation towards compositions heavier than MORB. A similar behaviour has also been observed during fluid-rock interactions in the retrograde greenschist facies metabasites of the Ile de Groix: in the most retrogressed samples, rehybridisation reactions in a reducing context triggered Ge isotope fractionation towards heavy compositions compared to the more oxidised greenschists and high-grade facies rocks (El Korh et al., 2017b).

7. Concluding remarks
Three isotopic systems (O, Fe and Ge) were employed to investigate processes controlling isotope fractionation in ancient non-subducted hydrothermally altered oceanic rocks from the Limousin ophiolite. The two main lithologies (serpentinites and amphibolites) display variable O, Fe and Ge compositions. The ultrabasic and basic magmatic precursors of the Limousin ophiolite-derived rocks were significantly metasomatized during the pervasive hydrothermal alteration on sea-floor that has followed magma emplacement. While Fe and Ge isotopic signatures of pre-Variscan hydrothermal processes were preserved, there is no evidence of subsequent isotope fractionation during fluid-rock interactions related to the Variscan collision in the FMC, even during nappe stacking, involving ophiolite-derived rocks, under high-temperature conditions leading regional-scale partial melting.
In particular, Fe and Ge isotopes show an opposite behaviour with contrasting redox conditions. In the highly oxidised abyssal serpentinites, Fe isotopes (δ56Fe from +0.14 to +0.18‰) may fractionate significantly towards heavier values than their magmatic ultrabasic protolith. By contrast, the δ74Ge (+0.48 to +0.93‰) only increases during intensive hydrothermal alteration of ultrabasic rocks. Amphibolite facies metabasgobs, can conserve MORB-like Fe isotopic compositions (+0.12 to +0.16‰) during hydrothermal alteration, but the δ56Fe can decrease (+0.03‰) with the increase of the δ18O during intensive hydrothermal alteration. Ge isotopes can fractionate towards heavier values than basic protoliths in metabasgobs (+0.72 to +0.78‰) that have conserved a MORB-like Fe reduced state during hydrothermal alteration. Hence, coupled O–Fe–Ge isotopes are efficient tracers of magmatic vs. hydrothermal processes.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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