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**Lithium behaviour and isotope fractionation during
fluid-rock interactions in Variscan oceanic suture zones:
Limousin ophiolite and Ile de Groix high-pressure
terrane (France)**

Affé El Korh, Etienne Deloule, Béatrice Luais, Marie-Christine Boiron, Luc Bastian, Nathalie Vigier

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3 **Lithium behaviour and isotope fractionation during fluid-rock interactions in Variscan**
4 **oceanic suture zones: Limousin ophiolite and Ile de Groix high-pressure terrane**
5 **(France)**
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13 **Afifé El Korh^{1,2}, Etienne Deloule², Béatrice Luais², Marie-Christine Boiron³, Luc**
14 **Bastian^{4,5}, Nathalie Vigier⁴**
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19
20 ¹Unit of Earth Sciences, Department of Geosciences, University of Fribourg, Chemin du
21 Musée 6, CH-1700 Fribourg, Switzerland
22

23
24 ²Centre de Recherches Pédrographiques et Géochimiques (CRPG), UMR 7358 CNRS-
25 Université de Lorraine, 15 rue Notre Dame des Pauvres, BP 20, F-54501 Vandœuvre-lès-
26 Nancy Cedex, France
27
28

29
30 ³GeoRessources, Université de Lorraine, CNRS, UMR 7359, boulevard des Aiguillettes, BP
31 70239, F-54506 Vandœuvre-lès-Nancy, France
32

33
34 ⁴Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), UMR 7093 Université
35 Sorbonne-CNRS, 181 chemin du Lazaret, F-06230 Villefranche-sur-Mer, France
36
37

38
39 ⁵Université de la Côte d'Azur, CNRS, Observatoire de la Côte d'Azur (OCA), Geoazur, UMR
40 7329, 250 rue Albert Einstein, Sophia-Antipolis, F-06500 Valbonne, France
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47 *Corresponding author: afife.elkorh@unifr.ch
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51 **Keywords:** lithium isotopes; hydrothermal alteration; subduction zone metamorphism;
52 ophiolite; metabasite; serpentinite; ion-microprobe; ICP-MS
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ABSTRACT

Ophiolites and high-pressure/low-temperature (HP–LT) terranes are important sites for the study of geochemical cycling in ancient oceanic lithosphere. We have analysed Li abundances and isotope composition in a series of ultrabasic and basic rocks from the Variscan Limousin ophiolite, as well as in basic and pelitic rocks from the Ile de Groix HP–LT terrane. Both bulk and in-situ analyses are employed to evaluate Li mobility and isotope fractionation in the oceanic lithosphere during fluid–rock interactions related to seafloor and sub-seafloor hydrothermal alteration, subduction and exhumation processes.

In the Limousin ophiolite, early stages of high-temperature (high-T) hydrothermal alteration of oceanic ultrabasic rocks produce serpentine with low Li abundances (0.9–4.6 ppm) and low $\delta^7\text{Li}$ (-8.9‰). The $\delta^7\text{Li}$ increase from -2.2 to +4.2‰ in the following generations of serpentine during late-stage hydrothermal alteration results from changes in the fluid composition and temperature conditions. Therefore, even if dehydrating subducted serpentinites generate high amounts of fluids during subduction, abyssal serpentinites do not constitute an important source of Li for Li-rich metabasic rocks. In the associated amphibolites, hornblende displays typical Li contents (3.1–8.2 ppm) and isotopic compositions (+3.5 to +12.5‰) similar to hydrothermally altered sheeted dykes and gabbros. By contrast, the low Li abundances and extremely high $\delta^7\text{Li}$ values recorded by omphacite and pargasitic amphibole in the ultra-high-pressure (UHP) zoisite-eclogite from the Limousin probably reflect interaction with a heavy-Li sediment-derived fluid.

The HP–LT metabasites of the Ile de Groix record different Li behaviour, with high Li abundances and low $\delta^7\text{Li}$. They contain Li abundances significantly higher than fresh mid-ocean ridge basalts (MORB) (16–124 ppm), indicating a metasomatic overprint by fluids derived from the neighbouring Li-rich micaschist (15–52 ppm) in addition to seawater during the early stages of subduction. Lithium is mainly hosted by: 1) glaucophane and omphacite in blueschists and eclogites; 2) chlorite and albite in retrograde greenschists; 3) phengite and chlorite in micaschists. The metabasites have $\delta^7\text{Li}$ values of -4.8 to +3.2‰ that are generally lower than fresh and altered MORB. The intercalated micaschists display $\delta^7\text{Li}$ values ranging

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3 from -1.7 to +0.2‰ that are typical of subducted sediments. The $\delta^7\text{Li}$ decrease from
4 blueschists to eclogites from +1.8 to -4.8‰, as well as the rimward $\delta^7\text{Li}$ decrease in
5 glaucophane from MORB-like $\delta^7\text{Li}$ values to negative values in blueschists (core: -2.4 to
6 +8.8‰; rims: -7.1 to +2.2‰), reveals that significant fluid-induced Li isotope fractionation
7 occurred at the transition from the lawsonite-blueschist facies to the epidote-blueschist
8 facies, and may be triggered by prograde lawsonite breakdown. In eclogites, the low $\delta^7\text{Li}$
9 measured in whole rocks (-4.8 to -2.5‰), omphacite (-22.4 to +3.3‰) and glaucophane (-6.9
10 to +1.4‰) indicates that Li isotope kinetic fractionation had stronger effects under eclogite
11 facies conditions. The $\delta^7\text{Li}$ increase toward positive values in the most retrogressed
12 greenschist samples suggests Li mineral/fluid isotopic exchange during rehydration reactions
13 and interaction with a Li-heavy fluid that is likely derived from the dehydrating metabasites.
14 Thus, lithium isotope fractionation in the HP–LT rocks of the Ile de Groix highlights migration
15 of heavy-Li fluids along the oceanic crust-mantle interface in the subduction zone.
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32 INTRODUCTION

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34 Lithium, the lightest alkali metal with its two isotopes ^6Li and ^7Li , is a fluid mobile element that
35 can be used as a tracer of fluid-mediated mass transfer between oceanic crust and mantle in
36 subduction zones (e.g. Brenan et al., 1998; Richter et al., 2003; Zack et al., 2003; Elliott et
37 al., 2004; Marschall et al., 2007; Tang et al., 2010; Penniston-Dorland et al., 2010, 2012,
38 2017; Wan et al., 2017). Fresh MORB and mantle have generally low Li contents (3–8 ppm;
39 Ryan & Langmuir, 1987; Niu & Batiza, 1997; Bouman et al., 2004; Tomascak et al., 2008),
40 while Li can be abundant in the altered oceanic crust (1–119 ppm; Chan et al., 2002;
41 Bouman et al., 2004; Coogan et al., 2017) and pelitic sediments (1–80 ppm; Bebout et al.,
42 1993; Bouman et al., 2004; Chan et al., 2006). Interaction with heavy Li-rich seawater
43 (+31‰; Millot et al., 2004) during hydrothermal alteration of the oceanic crust triggers Li
44 isotope fractionation, resulting in a $\delta^7\text{Li}$ increase in low-T altered rocks (-1.7 to +20.8‰; Chan
45 et al., 2002; Bouman et al., 2004; Coogan et al., 2017) compared to fresh MORB (+3.4 ±
46 1.4‰; Tomascak et al., 2008).
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3 Devolatilisation reactions during subduction zone metamorphism (or HP–LT
4 metamorphism) of Li-rich altered oceanic crust may release Li-rich fluids at shallow levels in
5 subduction zones (e.g. You et al., 1996). Studies on HP–LT rocks have also observed that Li
6 may be mobilised from metabasic (Marschall et al., 2006) and metasedimentary rocks
7 (Bebout et al., 1993, 2007) during devolatilisation reactions at intermediate depths (40–100
8 km), i.e. at the transition from blueschist to eclogite facies. However, significant amounts of Li
9 are retained in blueschists and eclogites in amphiboles (glaucofan and, to a lesser extent,
10 barrosite), pyroxenes (omphacite, aegyrine/jadeite) and high-pressure phengite (e.g.
11 Woodland et al., 2002; Spandler and Hermann, 2006; John et al., 2008; El Korh et al., 2009,
12 2011). Scambelluri et al. (2004) have shown that the Li content of the serpentinised upper
13 mantle does not vary during early hydrothermal processes and is preserved in high-pressure
14 (HP) antigorite serpentinites. The serpentinised oceanic mantle can carry Li until depths
15 >100 km, below which Li-rich fluids are released during antigorite breakdown, which is
16 considered as a major source of fluids for arc lava magmatism (Scambelluri et al., 2004;
17 Bouvier et al., 2008; Halama et al., 2011).

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Lithium isotopes can fractionate during fluid-rock interactions related to subduction
zone metamorphism (e.g. Zack et al., 2003; Marschall et al., 2007; Penniston-Dorland et al.,
2010, 2012; Wan et al., 2017). Because of the large relative mass difference between the
two isotopes (16%; Tomascak, 2004) and the higher diffusivity of ^6Li compared to ^7Li , the two
Li stable isotopes can fractionate significantly by kinetic fractionation during chemical
diffusion (Richter et al., 2003). With increasing metamorphic degree and temperature, kinetic
isotope fractionation becomes predominant over equilibrium fractionation (Richter et al.,
2003; Marschall et al., 2007). Kinetic isotope fractionation during fluid-rock interactions is
enhanced by dissolution–precipitation reactions between mineral assemblages stable under
varying P–T conditions (John et al., 2012). Variations in Li concentration and isotope
composition in subduction-related rocks have been employed as tracers of metasomatic
processes during subduction zone metamorphism (Marschall et al., 2007; Halama et al.,

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3 2011; John et al., 2012; Penniston-Dorland et al., 2010, 2012, 2017; Taetz et al., 2016,
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5 2018).

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7 Recent studies have documented a wide range in Li isotopic composition resulting
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9 from metasomatic processes (-6 to +14.5‰) in metabasic and metasedimentary rocks (Chan
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11 et al., 2006; Penniston-Dorland et al., 2010, 2012; Simons et al., 2010; Halama et al., 2011;
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13 Qiu et al., 2011; Romer & Meixner, 2014; Coogan et al., 2017). Penniston-Dorland et al.
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15 (2012) have shown that the bulk $\delta^7\text{Li}$ value of the metabasic rocks from the Catalina Schists
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17 (California, USA), a mélange HP terrane, reflects overprinting by fluids derived from the
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19 neighbouring metasediments rather than from low-T seafloor processes. Only small-scale re-
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21 equilibration of the bulk $\delta^7\text{Li}$ values and Li mobilisation were observed, despite of intense
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23 dehydration during subduction. However, Li mobilisation during sediment dehydration is not
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25 sufficient to reset the bulk $\delta^7\text{Li}$ value of the metasediments (Penniston-Dorland et al., 2012).
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28 Eclogites display a large range of Li compositions (1–94 ppm), and $\delta^7\text{Li}$ values
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30 decreasing from MORB-like to extremely light values (+6 to -21.9‰ with an average value of
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32 $-2.2 \pm 11.6\%$; Zack et al., 2003; Marschall et al., 2007; Halama et al., 2011). At the
33
34 blueschist to eclogite facies transition, significant amounts of Li (up to 60% of the whole rock
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36 content) can be mobilised by fluids from blueschists during devolatilisation reactions
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38 involving glaucophane and phengite in eclogitic selvages along a prograde dehydration fluid
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40 channel (Beinlich et al., 2010). At the same time, the $\delta^7\text{Li}$ decreases during fluid-induced
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42 eclogitisation reactions towards fluid channels (John et al., 2012; Taetz et al., 2018). Li
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44 diffusion modelling and chronometry indicate that the time scale of fluid–rock interactions
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46 along vein channels during an individual fluid flow event is short-lived, with a duration on the
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48 order of 80–500 years (John et al., 2012).
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51 Different models were proposed to explain Li fractionation during subduction zone
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53 metamorphism. Based on whole rock and bulk omphacite analyses, Zack et al. (2003) show
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55 that the $\delta^7\text{Li}$ value of the slab decreases progressively during subduction, according to the
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57 initial $\delta^7\text{Li}$, the temperature and the amount of fluid released. Similarly, Agostini et al. (2008)
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59 interpret the correlation between the $\delta^7\text{Li}$ and other tracers of slab-derived fluids as the result
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3 of significant Li fractionation towards low $\delta^7\text{Li}$ at shallow depth during subduction. By
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5 contrast, the model of Marschall et al. (2007) suggests that the $\delta^7\text{Li}$ of the subducting crust
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7 should only weakly decreases during subduction. They conclude that the light-Li signature
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9 recorded by orogenic eclogites is not only due to subduction-related metamorphism, but also
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11 results from the mobilisation of Li during eclogitisation or subsequent exhumation. This
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13 model predicts that the deeply subducted eclogites should have a higher $\delta^7\text{Li}$ than the
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15 mantle.
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18 Thus, the model defined by Marschall et al. (2007) shows that the heavy-Li fluids
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20 released into the fore-arc mantle wedge are consequently responsible for heavy-Li arc
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22 magmas or enriched MORB (E-MORB), distinct from lighter-Li normal-MORB (N-MORB)
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24 (Tomascak et al., 2000, 2002; Elliott et al., 2004, 2006). This expectation is supported by Li
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26 isotopic data from pore fluids and sediments in active subduction zone, which allowed
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28 estimation of $\delta^7\text{Li}$ values of deep slab-derived fluids to vary between +22 and +38‰ (Chan &
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30 Kastner, 2000). In addition, oceanic crust recycling in subduction zones is thought to be the
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32 source of abnormal Li isotopic composition of mantle xenoliths (-35 to +8‰; Tang et al.,
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34 2007, 2010, 2012, 2014; Agostini et al., 2008; Wan et al., 2017) compared to the "normal"
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36 MORB mantle (+4 ± 2‰; Chan et al., 1992, 2002; Jeffcoate et al, 2007; Tomascak et al.,
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38 2008; Gao et al., 2011).
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41 Lithium partitioning and isotope fractionation during fluid-rock interactions through
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43 hydrothermal alteration, subduction zone metamorphism and post-collision exhumation
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45 processes is still a matter of debate within the geoscience community. This study focuses on
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47 Li behaviour and isotope fractionation in a series of rocks from two units from the
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49 Moldanubian zone of the Variscan belt: 1) hydrothermally altered basic and ultrabasic rocks
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51 from the Limousin low-pressure ophiolite and 2) metabasic and metasedimentary rocks for
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53 the Ile de Groix HP–LT terrane. It aims to examine Li mobility and isotopic fractionation in
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55 whole rocks and metamorphic minerals with regards to the variations of pressure and
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57 temperature and fluid-rock interactions during seafloor hydrothermal alteration and
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59 subduction zone metamorphism. We employ a novel approach combining bulk and in-situ
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3 elemental and isotopic analyses to investigate Li mobility during fluid-rock interactions related
4 to low-T and high-T hydrothermal alteration, subduction-related devolatilisation and
5 rehydration reactions in ancient oceanic rocks. The results will allow deciphering the modes
6 of Li isotopic fractionation in remnants of ancient Variscan oceanic lithosphere under various
7 pressure and temperature conditions related to seafloor and sub-seafloor hydrothermal
8 alteration, subduction and exhumation processes.
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18 **GEOLOGICAL CONTEXT AND INVESTIGATED SAMPLES**

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20 The Limousin and Ile de Groix areas are part of the European Variscan belt, which results
21 from the Devonian to Carboniferous collision of two major continental domains, Laurussia
22 (formed of Laurentia, Baltica and Avalonia) and Gondwana (Fig. 1a). The continental
23 domains were separated by the Rheic and Palaeotethys Oceans, two major pre-Variscan
24 oceanic domains opened during the Cambrian–Ordovician (e.g. Stampfli et al., 2011; Nance
25 et al., 2010; von Raumer et al., 2013 Kroner and Romer, 2013). Three main collision events
26 were involved during the Variscan orogeny: 1) Middle Devonian subduction of the oceanic
27 crust under Gondwana and Laurussia, followed by the dislocation of the northern margin of
28 the Gondwana; 2) Early Carboniferous continental collision between Avalonia-Laurussia and
29 Gondwana-derived continental terranes; and 3) Late Carboniferous final collision (von
30 Raumer et al., 2013; Kroner and Romer, 2013). The allochthonous domain (Moldanubian
31 Zone; Fig. 1a) consists of superposed peri-Gondwanan nappes, and includes a series of
32 Devonian ophiolites, which can be follow from the Sudetes to the Iberian Peninsula (see von
33 Raumer et al., 2013, 2015 and references therein). The ophiolites are emplaced along the
34 northern Gondwana margin, and derive from magmatic rocks that are contemporaneous with
35 the Cambro-Ordovician rifting associated to the opening of the Rheic Ocean (von Raumer et
36 al., 2013). In western France, the Limousin ophiolite and the Ile de Groix blueschist terrane
37 are recognised as remnants of rocks with oceanic affinity within the same Allochthon domain
38 (Figs. 1b and c).
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Limousin ophiolite

The Limousin ophiolite belongs to the French Massif Central (FMC), which is part of the western European Variscan belt (e.g. Dubuisson et al., 1989; Berger et al., 2005; 2010a). Formation of the FMC results from the piling of a series of nappes during the Devonian–Early Carboniferous (Girardeau et al., 1986; Ledru et al., 1989, 1994; Demange, 1994; Faure et al., 2009): 1) the Upper Allochthon, called Gartempe Unit in the North Limousin, corresponds to a group of low-grade Palaeozoic rocks; 2) the Middle Allochthon (Upper Gneiss Unit), is a composite unit that contains rocks from the "leptyno-amphibolite groups" (LAGs) (Santallier et al., 1988), formed by paragneisses, leptynites and amphibolites of medium to high grade metamorphism, as well as migmatitic metagreywackes and relicts of eclogites and granulites; 3) the Lower Allochthon (Lower Gneiss Unit) consists of metasediments (paragneisses, micaschists, metashales and metagreywackes) and Late Proterozoic–Early Cambrian and Ordovician leucocratic orthogneisses; 4) the Parautochthon basement, deriving from metasediments and metagranites; and 5) the Southern Palaeozoic Nappes, corresponding to continental margin/platform series.

The Limousin ophiolite occurs as a 25 km long belt of basic and ultrabasic rocks, located in the upper part of the Middle Allochthon unit (Fig. 1b). It consists of a series of 1–5 km wide ophiolite massifs segmented by Variscan and late Carboniferous faults (Berger et al., 2005, 2006). Based on petrological and geochemical data, the Limousin ophiolite has been interpreted as the remnants of an ancient oceanic lithosphere (Dubuisson et al., 1989; Berger et al., 2005, 2006). It corresponds to a Iherzolite-harzburgite ophiolite type, emplaced in a slow-spreading mid-ocean ridge (Berger et al., 2006). Main lithologies include diopside-bearing harzburgites, harzburgites, dunites, wehrlites, troctolites, (meta)gabbros and amphibolites (Berger et al., 2005). The ultrabasic rocks are highly serpentinised, with only rare relicts of olivine, spinel or pyroxene. Alteration of abyssal peridotites and amphibolite-facies metamorphism of the gabbros and mafic dykes result from intensive seafloor hydrothermal alteration under low-P conditions (~0.2 GPa) and temperature decreasing from

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3 high-T late-magmatic conditions to greenschist–zeolite metamorphic facies, following magma
4 emplacement (Berger et al., 2005).
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7 The base of the Middle Allochthon unit also includes lenses of high-pressure (HP) to
8 ultra-high-pressure (UHP) zoisite-eclogites, zoisite-kyanite-eclogites and kyanite-eclogites
9 (Berger et al., 2010a). Eclogites were formed by deep subduction at a depth of 100 km ($P \sim$
10 2.9 ± 0.5 GPa, $T \sim 660 \pm 70^\circ\text{C}$). Ultra-high-pressure eclogites show variable degrees of fluid-
11 rock interactions. Kyanite-eclogites have a composition similar to supra-subduction zone
12 basalts and were relatively preserved from metasomatism (Berger et al., 2010a). Zoisite-
13 eclogites were interpreted as former iron-rich plagioclase cumulates and display geochemical
14 evidences of interaction with fluids derived from subducted terrigenous sediments during the
15 UHP metamorphic stage (Berger et al., 2010a). Geochronological data show that the zoisite-
16 eclogite has recorded a protolith age of 475–489 Ma (U–Pb; zircon) (Berger et al., 2010a).
17 Crystallisation of the magmatic protolith of the UHP eclogites is contemporaneous to the
18 emplacement of the orthogneisses from the Lower Allochthon unit (446 ± 6 to 521 ± 7 Ma;
19 Melleton et al., 2010) and occurred during the Cambro-Ordovician rifting. The UHP event
20 was dated at 412 ± 5 Ma (Berger et al., 2010a).
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37 In this study, we have investigated the Li trace element and isotope composition in six
38 serpentinites, four amphibolites and one zoisite-eclogite from La Flotte, Le Cluzeau and
39 Saint-Laurent ophiolite massifs (Fig. 1c; Table 1). The whole rock compositions are given in
40 the Supplementary Table A1. Serpentinites display the typical mesh textures resulting from
41 hydrothermal alteration of ultrabasic rocks at mid-ocean ridges (Bach et al., 2006), with
42 brown serpentine cores rimmed by a second yellow generation (Figs. 2a and b). The
43 serpentinites from Saint-Laurent (LAU1, LAU2) are rich in MgO, and show low abundances
44 of Fe_2O_3 , FeO, Al_2O_3 and CaO. They consist of an assemblage of Mg-rich serpentine,
45 chlorite forming veins, spinel, amphibole (composition from tremolite to Mg-hornblende) and
46 rare relicts of olivine (Fig. 2a). These samples may correspond to the highly serpentinised
47 dunitites described by Dubuisson et al. (1989). Core parts of serpentine are slightly richer in
48 FeO. Serpentine along contact zones with chlorite veins are also richer in FeO and contain
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3 Fe-hydroxides. The serpentinites from La Flotte (FLOT1, FLOT2a, FLOT2b) and Le Cluzeau
4 (CLUZ6) are slightly richer in Al_2O_3 , Fe_2O_3 and FeO, and have a lower XMg than samples
5 from Saint-Laurent. They are composed of serpentine that have partially to totally replaced
6 olivine and pyroxene, and also contain large lenses of chlorite + amphibole (tremolite to Mg-
7 hornblende), spinel, iron oxides and sulphides (Fig. 2b). Serpentine is often zoned in FeO
8 and MgO, displaying a rimward increase of the Mg# (Supplementary Table A2). These
9 samples may be related to the serpentinitised harzburgites or troctolites described by
10 Dubuisson et al. (1989) and Berger et al. (2005). The studied amphibolites consist of two fine
11 grained slightly foliated amphibolites (CLUZ 1 and CLUZ 1a) and two isotropic amphibolites
12 (CLUZ 4 and CLUZ 5), which derive from isotropic or layered gabbros (Berger et al., 2005).
13 They display an assemblage of green-brown amphibole (mainly Mg-hornblende),
14 plagioclase, chlorite and iron oxides (Figs. 2c and d). Magmatic plagioclase relicts are
15 sometimes present. Amphibole often shows evidences of alteration in iron hydroxydes along
16 grain rims and fractures. The studied zoisite-eclogite L04-143 (from Berger et al. 2010a) is
17 composed of garnet, zoisite, omphacite, pargasitic amphibole, and rutile rimmed by ilmenite.
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36 **Ile de Groix**

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38 The Ile de Groix (Armorican Massif, France) corresponds to the outcropping part of a HP-LT
39 unit, also located in the Middle Allochthon unit of the Variscan belt. The metamorphic rocks
40 of the Ile de Groix are composed of 20% metabasic rocks of hydrothermally altered E-MORB
41 affinity interlayered with 80% pelitic micaschists (Audren et al., 1993; Bernard-Griffiths et al.,
42 1986; Bosse et al., 2002; El Korh et al., 2009, 2013, 2017a) (Fig. 1c). The rocks recorded
43 two metamorphic phases: 1) a prograde blueschist to eclogite facies metamorphism M1
44 related to subduction, and 2) a greenschist facies overprint M2 related to exhumation (e.g.
45 Carpenter, 1976; Quinquis, 1980; Quinquis & Choukroune, 1981; Barrientos & Selverstone,
46 1993; Bosse et al., 2002; Ballèvre et al., 2003; El Korh et al., 2009, 2013). The eastern part
47 of the Ile de Groix is dominated by eclogites, and epidote-blueschist facies rocks, whereas
48 greenschist facies rocks are dominant on the western part. The difference in mineral
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3 assemblages between eclogites and epidote-blueschist facies metabasites may result from
4 small variations in the protolith composition and by small differences in temperature (50–
5 75°C) for the peak metamorphic conditions (El Korh et al., 2009). The peak P–T conditions,
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7 estimated at 1.6–2.5 GPa and 500–600°C in eclogites correspond to the blueschist to
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9 eclogite facies transition, which is expected to have taken place at c. 60–70 km depth in a
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11 subduction zone with an intermediate thermal regime (El Korh et al., 2009). Based on P–T
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13 calculations using the NFMASH system for metapelites, Bosse et al. (2002) have defined two
14
15 metamorphic units divided by a ductile thrust: the Upper Unit (1.6–1.8 GPa, 450–500°C) in
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17 the eastern part of the island, and the Lower Unit (1.4–1.6 GPa, 400–450°C) in the West.
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21 The HP–LT event was dated at 358–365 Ma with the $^{40}\text{Ar}/^{39}\text{Ar}$ (phengite) and Rb–Sr
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23 (whole rock, phengite and epidote) methods, while a younger age of 345–353 Ma was
24
25 determined for the greenschist metamorphic event (Bosse et al., 2005). Rare albite gneisses
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27 interlayered within micaschists and chloritoschists on the Ile de Groix provided protolith ages
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29 of 480.8 ± 4.8 Ma and 492.7 ± 3.2 Ma, respectively (U–Pb dates on zircon; El Korh et al.,
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31 2012; Paquette et al., 2017), contemporaneous with the Cambro-Ordovician rifting, widely
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33 recognised in the internal parts of the Variscan belt (e.g. von Raumer et al., 2013). Fe
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35 isotope measurements have shown that the metabasites of the Ile de Groix derive from an
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37 unusual heavy-Fe mantle source, and were probably emplaced during the intracontinental
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39 back-arc basin rifting that occurred along the northern Gondwana margin after the closure of
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41 the Proto-Rheic ocean (von Raumer et al., 2015; El Korh et al., 2017a). During the Variscan
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43 subduction, the metabasalts and their sedimentary cover were sheared off and imbricated in
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45 an accretionary prism (El Korh et al. 2012).
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50 Based on trace element and $\delta^{18}\text{O}$ analyses, El Korh et al. (2013) have shown that
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52 large-scale fluid-rock interactions occurred as open system only during seafloor hydrothermal
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54 alteration and early subduction prograde metasomatism. The retrograde metamorphism was
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56 interpreted as an overprint of fluids likely derived from the basic rocks without involving
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58 infiltration of externally derived fluids at P–T conditions lower than 1 GPa and 400°C (El Korh
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60 et al., 2011). Metabasites that underwent pervasive alteration by pre-HP metasomatism

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3 processes, show greater effects of retrogression (El Korh et al., 2013). Consequently, the
4 large-scale zonation of the Ile de Groix was interpreted as the result of superimposed effects
5 of the low-temperature hydrothermal alteration and variable dehydration states due to distinct
6 peak P–T conditions in the two tectonic units (Bosse et al., 2002; El Korh et al., 2013).
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11 Peak metamorphic assemblages in metabasites (blueschists and eclogites) are
12 composed of garnet, glaucophane, epidote, phengite, apatite, quartz, titanite and/or rutile.
13 Omphacite porphyroblasts are only present in eclogites (Figs. 2e and f). Blueschist facies
14 rocks often contain pseudomorphs after lawsonite, composed of epidote, white mica
15 (phengite, paragonite), actinolite, and albite (Ballèvre et al., 2003). Partial retrogression of
16 eclogites and blueschists is evidenced by: 1) barroisite + albite symplectites replacing
17 omphacite, 2) barroisite and actinolite overgrowths along glaucophane rims, and 3) partial
18 replacement of garnet by chlorite and rutile by titanite (Figs. 2e and f). Retrograde
19 assemblages in greenschists correspond to epidote, chlorite, actinolite, barroisite, albite,
20 magnetite, and titanite. High-pressure garnet is partially to totally replaced by chlorite,
21 actinolite and by a retrograde generation of epidote. "Albitic greenschists" contain large albite
22 porphyroblasts ± calcite, and have experienced intensive fluid-rock interactions during
23 retrogression (El Korh et al., 2013).
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39 Eighteen samples were studied, typical of each metamorphic facies and lithology (Fig.
40 1b; Table 1). They include thirteen metabasites (blueschists GR02, 04, 11b, 12b, 25a and
41 GROA56; eclogites GR21, 24a and 29; greenschists GR06a, 23 and 25b, and albitic
42 greenschists GROA43 and 52), two blueschist-facies metapelites (GROA110 and 111a) and
43 two greenschist-facies metapelites (GR26b and GROA104). For the detailed description of
44 the samples, see El Korh et al. (2009, 2011, 2013).
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53 **ANALYTICAL TECHNIQUES**

54 **Whole rock Li elemental and isotopic composition**

55 The whole rock Li abundances in the samples from the Ile de Groix and Limousin were
56 measured using a Varian 220FS Atomic Absorption Spectrometer at the SARM (Service
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3 d'Analyse des Roches et Minéraux; CRPG, Nancy). 1σ uncertainties are 2%, 5%, 10 % and
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5 20% for abundances of >100 ppm, 50–100 ppm, 10–50 ppm and 0.5–10 ppm, respectively.
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8 The Li isotope analyses of the whole rock samples from the Ile de Groix and
9 separated glaucophane and omphacite from sample GR29 were analysed at the CRPG-
10 Nancy. Lithium was separated following the procedure detailed in Vigier et al. (2008;
11 modified after James & Palmer, 2000). In summary, 10 mg of powdered samples were
12 dissolved in three steps using: 1) a 2:1 mixture of HF (28 N) and HNO₃ (15 N) on a hot plate
13 at 120°C; 2) HNO₃ (15 N) at 60°C; and 3) HCl (1 N) at 60°C. The total dissolution of the
14 samples took approximately 1 week. After total dissolution of the samples and centrifugation,
15 Li was eluted and purified through cationic AG50X12 resin-exchange chromatography
16 columns. The same chemical procedure has been applied to blank solutions. Chemistry
17 blanks were systematically less than 15 pg Li.
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29 Lithium isotopes were measured by multi-collector inductively coupled plasma mass
30 spectrometry (MC-ICPMS) using a NeptunePlus instrument (ThermoFisher Scientific,
31 Germany and USA) at the CRPG-Nancy. Samples were introduced in the MC-ICPMS via a
32 cyclonic spray chamber. The instrument was operating in static mode at a low resolution
33 ($M/\Delta M = 400$). The cup configuration consisted of: Low 4 (⁶Li) and High 4 (⁷Li). The gas flow
34 rates, torch parameters and ion lenses were optimised using a solution of the NIST L-SVEC
35 RM 8545 Li standard. The correction coefficients between the Faraday cups were obtained
36 by a gain calibration before optimising the peak shapes and centring the peaks. Analyses
37 were performed on 25 ppb Li solutions, diluted in HNO₃ (0.05 N). Thirty-five integration
38 cycles were measured during 294 s (+ 300 s take up time), after a washout time of 440 s in
39 HNO₃ (0.05 N) and a background measurement of 67 s.
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52 Typical acquisition series consisted of alternate measurements of the L-SVEC
53 standard and a sample. Each measurement is corrected for the background value (measured
54 in 0.05 N HNO₃). Background intensities for the ⁷Li isotope were 0.06–0.1 V. Background-
55 corrected intensities for the ⁷Li isotope were ≤ 0.01 V for blank solutions, and generally 2–3 V
56 for standards and samples solutions. The Li isotope ratios normalised to the L-SVEC
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3 standard, expressed as $\delta^7\text{Li}_{\text{L-SVEC}}$, were calculated using the sample standard bracketing
4 method (SSB), as follows:
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$$\% \delta^7\text{Li}_{\text{L-SVEC}} (\text{sample}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}} / ({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000$$

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11 The Li^7N standard (nominal $\delta^7\text{Li}$ value: +30.1‰; +30.1 ± 1.1‰ to +30.2 ± 0.3‰; Carignan et
12 al., 2007) served as external secondary standard to monitor the accuracy and the precision
13 of the isotopic measurements. An average $\delta^7\text{Li}$ value of +30.1 ± 0.2‰ was obtained (2σ SE
14 as external reproducibility; n = 12), consistent with the reference and published values. The
15 $\delta^7\text{Li}_{\text{L-SVEC}}$ of the samples is calculated by averaging replicate analyses of the same sample
16 solution. For this reason, uncertainties are given as 2σ standard errors (2σ SE).
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26 **XRD measurements**

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28 The serpentine species in sample FLOT2b were characterised on a 50 µm polished thin
29 section using a Rigaku Ultima IV X-ray diffractometer (XRD) at the University of Fribourg
30 (Switzerland). Analyses were carried out in continuous scan mode using Bragg-Brentano
31 geometry. Operating conditions included a 2θ step size of 0.02°/step, a counting time/step of
32 0.5°/min between 5 and 70°, and X-ray tube conditions of 40 kV and 40 mA (Cu $K\alpha$). The
33 detection limit for mineral determination is c. 5 wt%. The mineral assemblage was identified
34 using the software PDXL2 (Rigaku).
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45 **Determination of mineral Li abundances**

46 *Limousin ophiolite*

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48 Because of the low Li content of serpentinites and amphibolites, the mineral Li abundances
49 in the rocks of the Limousin area were measured by secondary ion mass spectrometry
50 (SIMS) using a Cameca ims1280 instrument at the CRPG. Analyses were performed on
51 gold-coated thin sections, using a 8–14 nA primary projected O^- beam with 15–20 µm spot
52 size. Secondary ions were measured by peak hopping in monocollection mode using SEM
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3 detector for ${}^7\text{Li}$, and Faraday cup FC2 for ${}^{28}\text{Si}$, at a resolution of 1500 (M/ Δ M). The primary
4 and secondary beam accelerating voltages were -13 kV and +10kV, respectively. Analyses
5 were performed using a 28 eV energy window, with an energy offset of -50 eV. 20 integration
6 cycles were measured during c. 15 min, after 120s of pre-sputtering. Si was employed as
7 internal standard, using the mineral SiO_2 content (see Electronic Appendix). Reference
8 basaltic glasses KL2-G (5.1 ppm Li; 50.5% SiO_2) and StHs60/80-G (20.7 ppm Li; 63.7%
9 SiO_2) of the Max-Planck-Institut-Dingwell (MPI-DING) served as external standards to
10 determine the Li ionisation yield relative to Si, as a function of the sample Si content. The
11 daily 2σ external reproducibility of the standards, given as 2σ standard error (2σ SE), was
12 0.69–1.8%.
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27 *Ile de Groix*

28 A part of the Li abundances in minerals from the samples of the Ile de Groix were analysed
29 by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) during previous
30 studies (El Korh et al., 2009; El Korh, 2010). Supplementary Li abundances in minerals from
31 the samples of the Ile de Groix were performed by LA-ICPMS at the GeoRessources
32 laboratory, University of Lorraine (Vandœuvre-lès-Nancy, France). The instrument consists
33 of an Agilent 7500c quadrupole ICPMS interfaced to a GeoLas Pro 193 nm ArF excimer
34 laser ablation system (Lambda Physik, Germany). The laser was operating at a 5 Hz
35 repetition rate, a fluence of ~ 10 J/cm 2 , and a 44 μm spot size. Helium was used as the cell
36 gas (0.8 L/min) and was mixed with Ar prior to its introduction in the plasma (1.5 L/min). Peak
37 hopping mode was employed, as well as dual (counting and analogue) secondary electron
38 multiplier (SEM) detector mode. Dwell times were 20 ms for ${}^7\text{Li}$ and 10 ms for ${}^{42}\text{Ca}$ and ${}^{29}\text{Si}$.
39 The ${}^{248}\text{ThO}^+ / {}^{232}\text{Th}^+$ and $\text{Ca}^{2+} / \text{Ca}^+$ ratios were optimised to about 0.3–0.7 and 0.3–0.5%
40 respectively, by ablation of the National Institute of Standards and Technology reference
41 material SRM 610, a synthetic glass doped with trace elements. Acquisition times for
42 background and ablation intervals amounted to 60 and 40 s, respectively. The NIST SRM
43 610 reference material was employed as external standard, using the preferred values of
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3 average element abundances from the GeoRem database (Max Planck Institut für Chemie,
4 Mainz, Germany; <http://georem.mpch-mainz.gwdg.de>).

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7 Analytical series consisted of 10–16 measurements of samples, bracketed by a run of
8
9 2 measurements of the standard before and after the samples. Intensity vs. time data were
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11 reduced using an Excel spreadsheet, following the procedure defined in Longerich et al.
12
13 (1996). Internal standards were ^{42}Ca (epidote, garnet, omphacite, titanite, calcite) and ^{29}Si
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15 (glaucofane, albite, chlorite, phengite), based on the mineral major element compositions
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17 (El Korh et al., 2009). Intervals of 45 and 25 s were selected for the background and the
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19 ablation signal, respectively, with an offset of 3 s from the beginning of the ablation. No
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21 correction for down-hole fractionation was applied. The instrumental mass bias was
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23 corrected using a linear regression function, considering an equal time interval between each
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25 analysis. The minimum detection limit, corresponding to three times the standard deviation of
26
27 the net background measurement, is based on the 99% confidence level over the Gaussian
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29 counting statistics. Limits of detection were 1.5–20 ppm. Uncertainties on individual
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31 measurements at 1σ are generally 2.0–12%. The NIST SRM 612 glass was employed as
32
33 secondary standard and yielded a Li concentration of 39.4 ± 2.2 ppm (95% confidence level
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35 (CL); $n = 11$), similar within uncertainty to the GeoRem preferred value (40.2 ± 1.3 ppm; 95%
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37 CL).
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43 **In-situ Li isotope analysis in minerals**

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45 In-situ Li isotopes in minerals were measured on gold-coated thin sections by SIMS using a
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47 Cameca ims1280 instrument at the CRPG. Analyses in the Li-rich minerals (omphacite and
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49 glaucophane from the metabasites of the Ile de Groix) were performed using a 5.3–6.3 nA
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51 projected primary O^- beam with c. 20 μm spot size. The Li-poor minerals (serpentine, olivine
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53 and hornblende in the samples from the Limousin) were analysed using a 15–20 nA focused
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55 primary O^- beam with c. 35 μm spot size. Secondary ^6Li and ^7Li ions were measured by peak
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57 hopping in monocollection mode using SEM detector for intensities $< 5 \cdot 10^5$ cps, and FC2
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59 detector for intensities $> 5 \cdot 10^5$ cps, at a resolution of 1500 ($M/\Delta M$). The primary and
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3 secondary beam accelerating voltages were of -13 kV and +10 kV, respectively. Analyses
4 were performed using a 50 eV energy window, without energy offset. 20 integration cycles
5 were measured during c. 20 min, after 120 s of pre-sputtering.
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9 Studies of matrix effects during Li isotope analyses by SIMS (Decitre et al., 2002;
10 Kasemann et al., 2005) have shown that there is no significant matrix dependence on the
11 $\delta^7\text{Li}$ values between different mineral phases with close Mg#. Besides, matrix effects occur if
12 the Mg# value of standards and samples varies. External calibration to the L-SVEC and
13 correction of the daily instrumental fractionation was performed using a series of
14 clinopyroxenes, olivine and orthopyroxenes of various Mg# and $\delta^7\text{Li}_{\text{L-SVEC}}$ values, which were
15 measured at the beginning and at the end of each analytical series (Decitre et al., 2002; Su
16 et al., 2015; see the Supplementary Table A3 for the detailed list of the standards). 1σ
17 internal errors on individual measurements were 0.3–2.7‰. 1-day 2σ external reproducibility
18 of the standards was 0.4–2.7‰ (2σ SE).
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30 During this study, no significant variation of the instrumental mass bias between
31 different phases of similar Mg# (e.g. olivine, clinopyroxene and glass) occurred. Therefore,
32 we observed a variation of the instrumental mass bias with the Mg#. As the Mg# of the
33 studied samples of the Ile de Groix is significantly lower than that of standards (0.52–0.66
34 and 0.86–0.92, respectively), we have calculated the mass bias, or instrumental mass
35 fractionation (IMF), for the sample from the Ile de Groix as follow: $\text{IMF} = \alpha * \text{Mg\#} + \beta$.
36 Coefficients α and β were obtained by a linear regression using the mean IMF value plotted
37 against the mean Mg# of the various standards. We have also employed MC-ICPMS data of
38 mean glaucophane and omphacite from eclogite GR 29 to constrain the linear regression.
39 The final $\delta^7\text{Li}$ values, relative to the NIST L-SVEC RM 8545, are calculated as follow:
40 $\delta^7\text{Li}_{\text{L-SVEC}}(\text{sample}) = \delta^7\text{Li}_{\text{L-SVEC}}(\text{SIMS}) - \text{IMF}$. Minerals from the Limousin ophiolite with a lower
41 Mg# (0.71–0.77) than standards were corrected as well.
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56 During the different sessions, no significant variation of the measured $\delta^7\text{Li}$ could be
57 observed in association with the orientation of the serpentine, chlorite or amphibole minerals,
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3 when compared to the 1-day 2σ external reproducibility. This agrees with the observation of
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5 Siron et al (2017, 2018) for $\delta^{18}\text{O}$, H_2O , F and Cl in-situ measurement by SIMS on biotite.
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8 In this study, the range of mineral $\delta^7\text{Li}$ values in each sample is discussed using
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10 mean $\delta^7\text{Li}$ values. Despite large 2σ SD uncertainties due to mineral heterogeneities, the
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12 mean $\delta^7\text{Li}$ values are employed to calculate the fractionation factors between mineral pairs
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14 and whole rocks. This makes it possible to minimise extreme values, which can be
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16 unrepresentative, especially since no outlier rejection is undertaken. Fractionation factors
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18 between minerals and whole rocks provide information on Li isotopic equilibrium or
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20 disequilibrium, as well as on the extent of Li isotope fractionation, during the various stages
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22 of hydrothermal alteration and subduction zone metamorphism.
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26 **RESULTS**

27 **Li elemental and isotopic composition in the rocks from the Limousin ophiolite**

28 *Whole rocks*

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30 The studied serpentinites from the Limousin ophiolite have Li abundances of 2.4–4.6 and
31
32 0.9–3.0 ppm, respectively. The UHP eclogite has a Li content of 2.3 ppm, while the
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34 amphibolites display significant higher Li contents (3.1–8.2 ppm). These values are
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36 comparable with the range of values of fresh MORB (3–8 ppm) (Ryan & Langmuir, 1987; Niu
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38 & Batiza, 1997) and altered MORB (1–119 ppm; Chan et al., 2002; Bouman et al., 2004;
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40 Coogan et al., 2017) (Fig. 3; Table 2).
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47 *Minerals*

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49 Minerals from the Limousin ophiolite generally display low Li abundances (Fig. 3 and Table
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51 3). In serpentinites, serpentine is the main host for Li (0.33–8.2 ppm). Lithium abundances in
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53 Fe-richer serpentine (1.2–8.2 ppm) are generally higher than in Mg-rich serpentine (0.33–3.6
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55 ppm). The less abundant olivine and amphibole (tremolite to Mg-hornblende) display similar
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57 Li contents as Mg-rich serpentine (1.5–3.0 and 1.1–3.5 ppm, respectively), while chlorite has
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59 low Li abundances (0.24–1.0 ppm). In amphibolites, Li abundances are higher in hornblende
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3 (1.3–11 ppm) than in plagioclase (0.09–1.0 ppm). In the UHP zoisite-eclogite, Li is mainly
4 hosted by pargasitic amphibole (1.5–31 ppm) and omphacite (1.5–10 ppm), while low Li
5 concentrations are measured in garnet (0.15–0.90 ppm) and zoisite (0.03–0.38 ppm).
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9 The detailed study of serpentinite LAU2 shows that serpentine has a mean $\delta^7\text{Li}$ value
10 of $-8.9 \pm 5.2\text{‰}$ (2σ SD). Altered serpentine, richer in FeO, has a similar $\delta^7\text{Li}$ value of $-8.7 \pm$
11 3.1‰ (2σ SD), leading to a fractionation factor $\Delta^7\text{Li}_{\text{Fe-serp-Mg-serp}}$ value of $+0.2 \pm 6.1\text{‰}$ (2σ)
12 (Table 3). Even if the two generations of serpentine are identical within uncertainty, the large
13 2σ SD values result from mineral heterogeneities, which are probably related to local isotopic
14 disequilibria during hydrothermal alteration processes. Serpentine from the sample FLOT-2a
15 has a $\delta^7\text{Li}$ value of $-2.5 \pm 5.5\text{‰}$ (2σ SD), while relicts of olivine have a $\delta^7\text{Li}$ value of $+6.3 \pm$
16 2.9‰ (2σ SD) (Fig. 4; Table 3). During olivine alteration in serpentine, the $\Delta^7\text{Li}_{\text{serp-ol}}$ value
17 amounts to $-8.8 \pm 6.3\text{‰}$ (2σ) (Table 3; Fig. 4a). Serpentine from sample CLUZ6 is strongly
18 zoned in $\delta^7\text{Li}$: Fe-rich cores, replacing olivine, have a $\delta^7\text{Li}$ of $-2.2 \pm 3.0\text{‰}$ and Mg-rich rims
19 have a $\delta^7\text{Li}$ of $+4.2 \pm 3.5\text{‰}$ (2σ SD). Co-existing amphibole (tremolite to Mg-hornblende) has
20 a $\delta^7\text{Li}$ of $+6.6 \pm 4.6\text{‰}$ (2σ SD) (Fig. 4; Table 3). $\Delta^7\text{Li}_{\text{Fe-serp-Mg-serp}}$, $\Delta^7\text{Li}_{\text{Fe-serp-amph}}$, and $\Delta^7\text{Li}_{\text{Mg-}}$
21 serp-amph values correspond to -6.4 ± 4.6 , -8.8 ± 5.5 and $-2.5 \pm 5.8\text{‰}$, respectively (Table 3).
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37 Hornblende in amphibolite CLUZ1 has a MORB-like $\delta^7\text{Li}$ of value of $+3.5 \pm 4.4\text{‰}$ (2σ
38 SD). A higher value of $+9.8 \pm 0.9\text{‰}$ (2σ SD) was recorded in altered parts. Hornblende in
39 amphibolite CLUZ4 (metagabbro) has a higher value of $+12.5 \pm 9.6\text{‰}$ (2σ SD) (Table 3).
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43 In the UHP zoisite-eclogite L04-143, omphacite is the main host for Li during the UHP
44 metamorphic stage. It has a positive $\delta^7\text{Li}$ value of $+21.9 \pm 5.0\text{‰}$ (2σ SD) (Fig. 4; Table 3).
45 Secondary pargasitic amphibole has a $\delta^7\text{Li}$ value of $+18.7 \pm 7.2\text{‰}$ (2σ SD). The resulting
46 $\Delta^7\text{Li}_{\text{amph-omph}}$ value consists of $-3.3 \pm 8.7\text{‰}$ (2σ) and indicates that isotopic equilibrium
47 between omphacite and amphibole is not globally reached during partial retrogression, even
48 if mineral pairs may be locally in equilibrium (Table 3).
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58 **Li elemental and isotopic composition in the rocks from the Ile de Groix**

59 *Whole rocks*

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3 The metabasites of the Ile de Groix have Li abundances of 16–124 ppm (Table 4). These
4 values are significantly higher than those of fresh MORB and Limousin UHP eclogite. Even if
5 they cover a large range of values, the Li concentrations of the metabasites of the Ile de
6 Groix do not vary according to the different metamorphic facies (Fig. 5) but are controlled by
7 the mineral assemblage (Fig. 5). The studied micaschists have Li contents of 15–52 ppm, in
8 agreement with the values measured in subducted metasediments (2–78 ppm, Bouman et
9 al., 2004; Chan et al., 2006). No change of Li concentration is observed between blueschist
10 and greenschist facies micaschists.

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12 The metabasites have $\delta^7\text{Li}$ values of -4.8 ± 0.5 to $+3.2 \pm 0.6\text{‰}$ (2σ SE) (Fig. 6a; Table
13 4) that are generally lower than those of fresh MORB ($+3.4 \pm 1.4\text{‰}$, 2σ ; Tomascak et al.,
14 2008). Most samples have $\delta^7\text{Li}$ within the range of data for heavy-Li low-T altered oceanic
15 crust (-1.7 to $+20.8\text{‰}$; Chan et al., 2002; Coogan et al., 2017). Even if Li abundances do not
16 show any correlation with the metamorphic facies, the $\delta^7\text{Li}$ values of the metabasites vary
17 between the metamorphic stages (Figs. 6a and b). The $\delta^7\text{Li}$ values of blueschists vary from $-$
18 0.6 ± 0.3 to $+0.7\text{‰}$ (2σ SE), i.e. from MORB-like values to lower negative values. Eclogites
19 have negative $\delta^7\text{Li}$ values ranging from -4.8 to -2.5‰ , which are lower than those of the low-
20 T altered oceanic crust (Fig. 6; Table 4). Greenschists show a larger range of $\delta^7\text{Li}$ values
21 from -4.5 ± 0.5 to $+3.2 \pm 0.6\text{‰}$ (2σ SE). Greenschists that underwent restricted fluid rock
22 interactions during retrogression (GR23 and 25b) display negative values (-4.5 ± 0.5 to $-0.1 \pm$
23 0.5‰). Greenschists displaying a higher degree of retrogression and rehydration (GR06 and
24 albite-bearing greenschist GROA52) have positive values of $+1.5 \pm 0.4$ to $+3.2 \pm 0.6\text{‰}$ (Fig.
25 6; Table 4). Micaschists have $\delta^7\text{Li}$ values of -1.7 ± 0.7 to $+0.2 \pm 0.4\text{‰}$ (2σ SE), consistent
26 with the $\delta^7\text{Li}$ values of subducted sediments (mean value: $+3.01\text{‰}$, Chan et al. (2006); -2.3
27 to $+6.8\text{‰}$, Penniston-Dorland et al., 2012; -6 to $+14.5\text{‰}$, Romer & Meixner, 2014) and upper
28 continental crust ($0 \pm 2\text{‰}$; Teng et al., 2004).

57 *Minerals*

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3 The Li contents in the minerals from the Ile de Groix (from this study and El Korh et al., 2009)
4 are reported in Fig. 5 and Table 5. In blueschists and eclogites, main Li-hosting minerals are
5 glaucophane (48–319 ppm), omphacite (27–145 ppm) and phengite (4.4–39 ppm).
6 Retrograde barroisite and actinolite formed after glaucophane have lower Li contents of 3.1–
7 9.6 ppm. Epidote, garnet and accessory titanite have Li abundances of 0.67–41, 0.47–1.5
8 and 1.3–17 ppm, respectively. In the retrograde greenschists, Li is mainly hosted by chlorite
9 (13–182 ppm), phengite (5.8–46 ppm), and epidote (1.3–31 ppm) (see also El Korh et al.,
10 2009). Retrograde albite also host significant amounts of Li (41–212 ppm). Values are
11 consistent with the values reported by Marschall et al. (2006) for HP metamorphic rocks of
12 the Greek island of Syros (Cyclades). In micaschists, main Li-hosting minerals are white
13 micas (phengite + paragonite; 28–61 ppm) and retrograde chlorite (150–180 ppm).
14 Accessory tourmaline (detrital) also contains high amounts of Li (19–47 ppm), while Li
15 abundances are low in garnet, chloritoid, epidote, and accessory titanite and apatite (<5
16 ppm) (Fig. 5; Table 5).

17
18 These results point out the importance of glaucophane and omphacite for the Li
19 budget and isotopic fractionation during prograde and HP–LT metamorphic stages. The Li
20 isotopic composition of glaucophane and omphacite are scattered within each sample, and
21 vary on average from one sample to the other (Fig. 7; Table 6).

22
23 Glaucophane in blueschists has positive mean $\delta^7\text{Li}$ values of $+1.3 \pm 8.5$ and $+1.3 \pm$
24 4.3% (2σ SD) (Fig. 7a; Table 6). However, $\delta^7\text{Li}$ variations are observed within glaucophane
25 grains. Glaucophane core parts have generally positive MORB-like $\delta^7\text{Li}$ values ($+2.5 \pm 3.4$ to
26 $+3.8 \pm 6.1\%$; 2σ SD), while the $\delta^7\text{Li}$ values decrease rimwards up to negative values ($-2.6 \pm$
27 4.9 to $-0.1 \pm 3.6\%$; 2σ SD) (Figs. 7b and c; Table 6). No core-to-rim zonation of Li
28 abundances is observed in blueschist GR02. Blueschist GR25a shows a relatively good
29 correlation between individual Li abundances and $\delta^7\text{Li}$ values, suggesting kinetic diffusion of
30 Li during glaucophane crystallisation.

31
32 In eclogites, glaucophane has negative mean $\delta^7\text{Li}$ values of -4.8 ± 2.3 to $-2.3 \pm 4.4\%$
33 (2σ SD) (Fig. 7a; Table 6). Contrary to glaucophane from blueschists, glaucophane core

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3 have negative $\delta^7\text{Li}$ values. $\delta^7\text{Li}$ values in glaucophane generally decrease from core ($-4.5 \pm$
4 2.9 to $-1.1 \pm 3.4\%$; 2σ SD) to rim (-6.6 ± 2.8 to $-3.8 \pm 3.8\%$; 2σ SD). Lithium abundances do
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6 not vary from core to rim (Figs. 7d–f; Table 6). The absence of core-to-rim zonation of Li
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8 abundances and the absence of correlation between the Li contents and Li isotopic
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10 compositions indicates that no late Li diffusion along grain boundaries occurred. Omphacite
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12 have negative mean $\delta^7\text{Li}$ varying from -15.6 ± 9.4 to $-3.5 \pm 5.2\%$ (2σ SD) (Fig. 7a; Table 6),
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14 contrasting with the positive $\delta^7\text{Li}$ recorded by omphacite in the UHP eclogite from the
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16 Limousin ophiolite. No distinct rimward zonation of Li abundances and $\delta^7\text{Li}$ values is
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18 observed (Fig. 7d–f), excepting omphacite from eclogite GR24a, where $\delta^7\text{Li}$ values lower
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20 than -20% are measured in rim parts (Fig. 7e).
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25 Despite the large 2σ SD uncertainties of the mean $\delta^7\text{Li}$ values obtained on the
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27 different phases, due to mineral heterogeneities and core-to-rim zonation, fractionation
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29 factors between glaucophane, omphacite and whole rock were calculated using these mean
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31 $\delta^7\text{Li}$ values to determine if the main Li-hosting minerals show isotopic equilibrium with their
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33 respective whole rocks. Glaucophane is a major contributor for the whole rock isotopic
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35 budget, with $\Delta^7\text{Li}_{\text{WR-gln}}$ values ranging from -1.9 ± 4.3 to $+0.0 \pm 2.3\%$ (2σ) (Table 6). In
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37 eclogites GR21 and 29, omphacite display $\delta^7\text{Li}$ values close to its host rock, with $\Delta^7\text{Li}_{\text{WR-omph}}$
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39 values varying between -0.6 ± 5.2 and $-0.2 \pm 6.9\%$ (2σ), and with bulk glaucophane [$\Delta^7\text{Li}_{\text{gln-}}$
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41 omph values of -0.2 ± 7.3 to $-0.1 \pm 8.3\%$ (2σ)] (Table 6), and thus can be considered at isotopic
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43 equilibrium, despite large uncertainties due to mineral heterogeneities. However, considering
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45 that omphacite have crystallised at the same time as glaucophane rims, the two minerals do
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47 not appear to be at isotopic equilibrium with $\Delta^7\text{Li}_{\text{gln rim-omph}}$ values from $-3.1 \pm 5.9\%$ to $-0.5 \pm$
48
49 5.9% (2σ), suggesting Li isotope fractionation under HP–LT conditions. At the opposite,
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51 omphacite from eclogite GR24a shows isotopic disequilibrium with whole rock and
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53 glaucophane, as evidenced by $\Delta^7\text{Li}_{\text{WR-omph}}$, $\Delta^7\text{Li}_{\text{gln-omph}}$ and $\Delta^7\text{Li}_{\text{gln rim-omph}}$ values of $+13.1 \pm$
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55 9.4 , $+13.2 \pm 10.4\%$ and $+11.7 \pm 8.3\%$ (2σ) (Table 6). Retrograde barrosite formed along
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57 omphacite rims have mean $\delta^7\text{Li}$ values within the same range as omphacite (-15.4 ± 18.2 to -
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3 5.6 ± 6.5‰; 2σ SD), but exhibits a large spread of δ⁷Li values, resulting in large 2σ
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5 uncertainties on the Δ⁷Li_{omph-barr} values [-0.1 ± 20.5 to +1.0 ± 9.5‰; (2σ); Table 6].
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9 **CALCULATION OF THE FLUID LI ISOTOPIC COMPOSITION**

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11 The fluid δ⁷Li_{fluid} composition is sensitive to temperature variations in the subduction zone
12 (Marschall et al., 2007; Penniston-Dorland et al., 2012). Mineral-fluid fractionation factors
13 obtained from experimental studies on Li fractionation between silicates (clinopyroxene:
14 spodumene, staurolite, Li-amphibole and Li-mica) and H₂O indicate that fluids generally
15 display a higher δ⁷Li_{fluid} relative to rocks (Wunder et al., 2006, 2007, 2011). In our study, we
16 have employed fractionation factors determined for clinopyroxene (Δ⁷Li_{spudomene-fluid} = -4.61 ×
17 (1000/T) + 2.48; Wunder et al., 2006), assuming a similar Li partition behaviour in
18 clinopyroxene and amphiboles (inosilicates) relative to fluid (see also Penniston-Dorland et
19 al., 2012). We have also employed the same fractionation factors to calculate the δ⁷Li_{fluid} of
20 the fluid in equilibrium with the whole rocks from the Ile de Groix. The δ⁷Li_{fluid} of the fluid in
21 equilibrium with serpentine (phyllosilicate) was calculated using the fractionation factor
22 determined for micas (phyllosilicates) (Δ⁷Li_{mica-fluid} = -4.52 × (1000/T) + 4.74; Wunder et al.,
23 2007, 2010). However, the large range of temperature at which the different minerals were
24 formed is a major source of uncertainty on the fluid isotopic composition.
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43 **Limousin**

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45 The temperature of hydrothermal of oceanic basalts and serpentine formation is rather poorly
46 defined (Mével, 2003). Ocean-floor serpentinites in ophiolites commonly follow a retrograde
47 reaction and often display the crystallisation sequence antigorite > chrysotile > lizardite with
48 decreasing temperature (O'Hanley, 1996). Hydrothermal alteration of ultrabasic rocks is
49 assumed to have occurred between 350 and 500°C, because of the presence of tremolitic
50 amphibole and absence of talc in the mineral assemblage (Berger et al., 2005). In
51 serpentinite LAU2, δ⁷Li_{fluid} calculated for Mg-rich serpentine and altered Fe-richer serpentine
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3 yield undistinguishable negative values of -7.8 to -6.4‰ and -7.6 to -6.2‰, respectively, for
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5 temperatures decreasing from 500°C to 350°C (Fig. 8a; Table 7).
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8 Formation of the second generation of serpentine in samples FLOT2a and CLUZ6,
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10 evidenced by a rimward increase in MgO, may result from changes in hydrothermal alteration
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12 temperature conditions. This may correspond to the formation of different serpentine species:
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14 transition from antigorite to chrysotile/lizardite is typical of a temperature decrease during
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16 hydrothermal alteration (e.g. Evans et al., 1976; Mével, 2003; Wunder et al., 2010). XRD
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18 measurements in sample FLOT 2b have shown that the three serpentine species are
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20 present. Variation in the Mg# may also reflect the incorporation of various small-size minerals
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22 within serpentine layers (Viti & Mellini, 1998; Früh-Green et al., 2004; Bach et al., 2006): Fe-
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24 oxides, hydroxides or clay minerals in equilibrium with the first generation of serpentine and
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26 Mg-hydroxides (brucite) in equilibrium with the second generation. Fe-rich serpentine in
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28 serpentinite CLUZ6 has totally replaced olivine, and yield a $\delta^{7}\text{Li}_{\text{fluid}}$ value of -1.1 to +0.4‰ for
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30 temperatures decreasing from 500°C to 350°C. The $\delta^{7}\text{Li}_{\text{fluid}}$ of the fluid in equilibrium with the
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32 Mg-richer serpentine (rimming the Fe-rich serpentine) and amphibole (tremolite to Mg-
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34 hornblende) have been estimated to be +5.3 to +6.7‰ and +10.1‰, respectively (Fig. 8a;
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36 Table 7). A $\delta^{7}\text{Li}_{\text{fluid}}$ value varying between -1.4 and 0.0‰ has been calculated for the Mg-rich
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38 serpentine rimming olivine in the serpentinite FLOT2a, at a temperature decreasing from
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40 500°C to 350°C (Table 7).
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44 Based on thermometric calculations, Berger et al. (2005) have determined the
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46 temperature of equilibration of amphibole and plagioclase in amphibolites to vary between
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48 572 and 749°C. For this range of temperatures, the $\delta^{7}\text{Li}_{\text{fluid}}$ of the fluid in equilibrium with
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50 hornblende in sample CLUZ1 varies from +5.5 to +6.4‰ (Fig. 8a; Table 7). The altered
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52 zones in amphibole appear to have equilibrated with a heavy-Li fluid ($\delta^{7}\text{Li}_{\text{fluid}} = +11.8$ to
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54 +12.7‰). Amphibolite CLUZ4 yields a high $\delta^{7}\text{Li}_{\text{fluid}}$ value of +14.5 to +15.5‰ (Table 7).
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57 The UHP zoisite-eclogite L04-143 has recorded peak metamorphic P–T conditions of
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59 3.0 GPa and 600°C (Berger et al., 2010a). The fluid in equilibrium with omphacite has a high
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 $\delta^{7}\text{Li}$ value of +24.7‰ (Fig. 8a; Table 7). Secondary pargasitic amphibole crystallisation

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3 occurred during partial retrogression of the rock (Berger et al., 2010a). A $\delta^7\text{Li}_{\text{fluid}}$ was
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5 calculated to be +21.5‰ at 600°C and +22.1‰ at 500°C.
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9 **Ile de Groix**

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11 The $\delta^7\text{Li}$ of the fluid in equilibrium with the metabasites and blueschist-facies micaschists can
12
13 be calculated using the peak metamorphic temperature conditions for blueschist and eclogite
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15 facies rocks (500 and 550°C, respectively; El Korh et al., 2009). In blueschists, the $\delta^7\text{Li}$ of the
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17 fluid in equilibrium with the whole rocks have been calculated at 500°C to be +2.9 to +4.2‰
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19 (Fig. 8b; Table 8). The detailed calculation of the $\delta^7\text{Li}$ values of the fluid in equilibrium with
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21 glaucophane cores ($T \sim 450^\circ\text{C}$) and glaucophane rim ($T \sim 500^\circ\text{C}$) shows that the $\delta^7\text{Li}$ values
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23 of the fluids decreased from +6.4–7.7 to +0.9–3.4‰ with increasing temperature during
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25 glaucophane formation, i.e. during the prograde metamorphism. The $\delta^7\text{Li}_{\text{fluid}}$ of the fluid in
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27 equilibrium with the blueschist-facies micaschists have been calculated to vary between +1.8
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29 to +3.7‰, at a temperature assumed to be 500°C (Table 8). These values are typical of
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31 subduction fluids with a mixed composition between altered oceanic crust and Global
32
33 Subducting Sediment (GLOSS) ($+7 \pm 5\%$; Simons et al., 2010).
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37 In eclogites, the $\delta^7\text{Li}_{\text{fluid}}$ of fluids in equilibrium with whole rocks are -1.6 to +0.7‰,
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39 indicating equilibrium with a fluid with a heavier Li isotopic composition than with blueschists
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41 (Fig. 8b; Table 8). The fluid in equilibrium with glaucophane cores ($T \sim 500^\circ\text{C}$) has $\delta^7\text{Li}_{\text{fluid}}$
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43 values of -1.1 to +2.4‰. The $\delta^7\text{Li}_{\text{fluid}}$ of fluids in equilibrium with glaucophane rims ($\delta^7\text{Li}_{\text{fluid}}$ -
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45 3.5 to -0.7‰) becomes Li-heavier with increasing temperature up to 550°C. The $\delta^7\text{Li}$ of fluids
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47 in equilibrium with omphacite vary between -1.4 and -0.4‰ for eclogites GR21 and 29 (Fig.
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49 8b; Table 8). Omphacite GR24a in eclogite yields a negative $\delta^7\text{Li}_{\text{fluid}}$ of -12.4‰, which is
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51 lower than that of whole rock (-2.5‰; Table 4), suggesting intensive fluid migration and
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53 metasomatism under HP conditions and quartz vein formation (El Korh et al., 2011; see also
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55 Fig. 2f).
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59 Retrogression in the greenschist facies occurred under P–T conditions lower than 1.0
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61 GPa and 450°C (El Korh et al., 2011, 2013). In greenschists, the $\delta^7\text{Li}_{\text{fluid}}$ was calculated to be

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3 -0.6 to +7.1‰ at a temperature of 450°C (Fig. 8b; Table 8). In the most retrogressed sample
4 (albitic greenschist GROA52), the $\delta^{7}\text{Li}_{\text{fluid}}$ was estimated to be +5.8‰ at 400°C. The results
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6 highlight heavy-Li fluid migration during retrogression.
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10 DISCUSSION

11 **Lithium behaviour and fractionation during hydrothermal alteration of the ocean crust:** 12 **the case of Limousin ophiolite**

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18 The studied serpentinites from the Limousin ophiolite have low Li concentrations (0.9–4.6
19 ppm), as commonly observed for ocean floor serpentinites and serpentinitised peridotites
20 (Decitre et al., 2002; Scambelluri et al., 2004; Vils et al., 2008). In the studied serpentinites
21 from Saint-Laurent (probably deriving from dunites), the Li content in serpentine increases in
22 the Fe-rich serpentine generation, while the $\delta^{7}\text{Li}$ values remain constant (c. -8.9‰). Even if
23 lithium in abyssal serpentinites is generally heavy with positive whole rock $\delta^{7}\text{Li}$ values,
24 serpentinitised oceanic peridotites may display a large range of $\delta^{7}\text{Li}$ values from -19 to +28‰
25 (Decitre et al., 2002; Benton et al., 2004). Serpentine formed early during hydrothermal
26 alteration of oceanic peridotites preferentially incorporates ^6Li (Decitre et al., 2002). The low
27 Li abundances in serpentinites and negative $\delta^{7}\text{Li}$ values recorded by serpentine indicate that
28 hydrothermal alteration occurred in equilibrium with a Li-poor fluid during the early stages of
29 hydrothermal alteration, such as seawater or hydrothermal vent fluids (Chan et al., 1988).
30 Hence, Li is leached from the basic oceanic crust by the passing fluid, resulting in a Li
31 recycling during hydrothermal alteration of ultrabasic rocks (Decitre et al., 2002). At a
32 constant temperature, Mg-rich serpentine and Fe-richer altered zones should have
33 equilibrated with a fluid with a similar $\delta^{7}\text{Li}$, varying from -7.6 to -6.4‰ (Fig. 8a).
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51 The studied serpentinites from La Flotte and Le Cluzeau (deriving from harzburgites
52 or troctolites) have Li contents slightly lower than MORB suggesting only a minor Li loss
53 during hydrothermal alteration. Lithium is mainly distributed between olivine, serpentine and
54 amphibole (Fig. 3). During hydrothermal alteration, Li abundances slightly increase from
55 olivine to the replacing Fe-rich serpentine and decrease in the Mg-rich serpentine generation,
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3 i.e. with decreasing temperature. The $\delta^7\text{Li}$ values also vary during hydrothermal alteration. In
4 serpentinite FLOT2a, the $\delta^7\text{Li}$ values decreased from olivine relicts to Mg-rich serpentine
5 from +6.3 to -2.5‰ (Fig. 4a). In sample CLUZ6, the Fe-rich serpentine that has totally
6 replaced olivine has a value similar to Mg-rich serpentine in sample FLOT2a (-2.16‰). In
7 sample CLUZ6, the $\delta^7\text{Li}$ values increase in the second generation of serpentine (Mg-rich
8 serpentine: +4.2‰) and amphibole (+6.6‰), while the Li abundances decrease.
9 Consequently, the chemistry of serpentine does not seem to be the only factor controlling Li
10 fractionation.
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20 The negative $\delta^7\text{Li}$ recorded by serpentine formed after olivine indicates that
21 hydrothermal alteration occurred in equilibrium with a fluid with a $\delta^7\text{Li}_{\text{fluid}}$ value between -1.4
22 to +0.4‰ at a temperature lower than 500°C (Fig. 8a). The low $\delta^7\text{Li}$ of serpentine formed
23 after olivine can be explained by fluid-induced kinetic fractionation during the early stage of
24 hydrothermal alteration (Decitre et al., 2002). ^6Li is preferentially diffusing from the fluid
25 phase to the rock during fluid-rock interactions due to its higher diffusivity compared to ^7Li
26 (Richter et al., 2003). The higher $\delta^7\text{Li}$ values and lower Li abundances recorded by the Mg-
27 rich serpentine and amphibole in sample CLUZ6 may reflect a change in the
28 physicochemical conditions of fluid-rock interactions (e.g. fluid source, temperature, redox
29 conditions). According to Decitre et al. (2002), the higher $\delta^7\text{Li}$ values recorded by serpentine
30 formed during a later stage of hydrothermal alteration reflect derivation from more evolved
31 hydrothermal fluids, the latter becoming heavier during their passage through the oceanic
32 crust.
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47 In amphibolites from the Limousin ophiolite, hornblende is the main Li-bearing phase.
48 Thus, its mean $\delta^7\text{Li}$ value mirrors the whole rock $\delta^7\text{Li}$ value. Hornblende display $\delta^7\text{Li}$ values
49 of +3.5 to +12.5‰, typical of Li isotopic compositions of hydrothermally altered deep oceanic
50 basic rocks (sheeted dykes and gabbros: -1.7 to +7.9‰; Chan et al., 2002). Hornblende in
51 the metamorphosed dyke CLUZ1 is isotopically lighter than in metagabbro CLUZ4. This result is
52 in agreement with data obtained on the Troodos ophiolite (Cyprus), which show that the
53 uppermost part of the altered oceanic crust is isotopically lighter than the deeper part, and
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3 probably reflect variable secondary mineral precipitation with depth during hydrothermal
4 alteration (Coogan et al., 2017). The $\delta^7\text{Li}_{\text{fluid}}$ values of the fluid in equilibrium with
5 amphibolites range from +5.5 to 15.5‰, indicating interaction with heavy-Li fluids – seawater
6 or upwelling hydrothermal fluids – under high-T to low-T hydrothermal conditions. Actually,
7 samples that have incorporated a seawater Li component during low-T hydrothermal
8 alteration have a $\delta^7\text{Li}$ value of c. $+10 \pm 2\%$ (Coogan et al., 2017). However, the MORB-like Li
9 abundances in amphibolites (3.1–8.2 ppm) reflect limited fluid-rock interactions during
10 hydrothermal alteration (Chan et al., 2002).

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20 Even if serpentinites play a major role in fluid-mobile element recycling processes
21 during subduction (Scambelluri et al., 2004; Kodolányi et al., 2012), our results support that
22 abyssal serpentinites are not significant Li-carrier rocks in the subduction zone. Serpentinites
23 dehydration would release Li-poor fluids with variable $\delta^7\text{Li}$, and does not constitute an
24 important Li source for Li-rich HP–LT metamorphic rocks (see also Marschall et al., 2007;
25 Halama et al., 2011). Dehydrating altered amphibolites would release Li-richer fluids with
26 higher $\delta^7\text{Li}$ than serpentinitised rocks. Therefore, the high Li content in subducted metabasites
27 can only be explained if a Li-rich sedimentary source is involved (Halama et al., 2011).

28 29 30 31 32 33 34 35 36 37 38 39 **Lithium fractionation during subduction zone metamorphism**

40 41 *Early subduction hydrothermal processes in the samples from the Ile de Groix*

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43 The high whole rock Li contents in the metabasic rocks of the Ile de Groix (16–124 ppm)
44 compared to fresh MORB (3–8 ppm; Niu & Batiza, 1997) indicates that Li enrichment results
45 from fluid overprint during pre-HP low-T hydrothermal processes. Lithium concentrations in
46 the metabasites of the Ile de Groix are significantly higher than those of the Limousin
47 ophiolite (altered oceanic crust) or altered MORB (ODP Sites 504B and 896A; 1–35 ppm;
48 Chan et al., 2002) (Fig. 5). However, Li contents of metabasites are similar to those of
49 altered oceanic crust in the Troodos ophiolite (Cyprus), which range from 3 to 119 ppm
50 (Coogan et al., 2017). The uppermost part of the altered oceanic crust, i.e. the part in contact
51 with the overlying sediments (mostly composed of limestones), shows the highest Li contents
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3 and lighter $\delta^7\text{Li}$. The changes in Li compositions were interpreted as the result of changes in
4 the secondary minerals with depth, rather than interaction with sediment-derived pore fluids
5 (Coogan et al., 2017).
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9 By contrast, the high Li abundances in the metabasites of the Ile de Groix, as well as
10 the large volume of metapelites in contact with the metabasites, would suggest a
11 sedimentary source in addition to seawater for Li. Subducted sediments (such as the
12 GLOSS) contain high amounts of Li (2–75 ppm; Bouman et al., 2004) and may release Li-
13 rich fluids in the subduction zone due to the prograde breakdown of Li-rich chlorite into
14 garnet + H_2O (Bebout et al., 2007; Halama et al., 2011). The high Li abundances measured in
15 glaucophane indicates Li enrichment during the early stages of subduction, i.e. until the
16 lawsonite-blueschist facies were reached at P–T conditions lower than 1.0–2.0 GPa and
17 350–450°C (El Korh et al., 2009). Contrary to the Fe isotope data from the same series of
18 samples, which only show slight Fe isotope fractionation during low-temperature
19 hydrothermal alteration (El Korh et al., 2017a), Li is strongly sensitive to hydrothermal
20 processes. However, the Li compositions of the metabasites of the Ile de Groix do not follow
21 the common fractionation trend of low-temperature hydrothermal alteration observed in the
22 altered oceanic crust (increase of Li contents and increase of the $\delta^7\text{Li}$ value; e.g. Chan et al.,
23 2002; Woodland et al., 2002).
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43 *Blueschist to eclogite facies metamorphism in the samples from the Ile de Groix: effects of*
44 *kinetic isotope fractionation*
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47 The $\delta^7\text{Li}$ decrease from the blueschist to the eclogite facies metabasites of the Ile de Groix
48 do not correlate with the large range of Li abundances (Figs. 6a, and b), indicating that Li
49 may have fractionated during the subduction zone metamorphism. Enrichment of Li coupled
50 to a $\delta^7\text{Li}$ decrease in orogenic eclogites and HP–LT rocks after the onset of subduction is a
51 common feature (Zack et al., 2003; Marschall et al., 2006, 2007; Agostini et al., 2008;
52 Penniston-Dorland et al., 2010, 2012; Simons et al., 2010; Halama et al., 2011; Xiao et al.,
53 2011; Romer & Meixner, 2014). The pioneering study of Zack et al. (2003) argued that light
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3 Li signatures of eclogites from Trescolmen (Adula nappe, Central Alps, Switzerland) do not
4 originate from the surrounding metasediments, but follow a Rayleigh distillation during
5 dehydration of clays and/or chlorite during the early stages of subduction zone
6 metamorphism. However, based on experimental and natural data, Marschall et al., (2007)
7 have shown that the high Li concentrations coupled to negative $\delta^7\text{Li}$ values observed in most
8 eclogites do not follow a Rayleigh dehydration process. Thus, Li isotope fractionation is the
9 result of kinetic fractionation during eclogitisation and/or exhumation (Marschall et al., 2007;
10 Halama et al., 2011). The changes in the Li isotope ratios in the subducted rocks is coupled
11 to a significant mobilisation of Li during dehydration reactions, with a loss of 40 to 60% of
12 the initial whole rock Li content (Marschall et al., 2007; Beinlich et al., 2010).

23
24 During dehydration reactions, the fluid regime and rock porosity evolves continuously.
25 First, fluids migrate in small scale and form dehydration veins (= closed system; slow and low
26 fluid fluxes). With increasing rock porosity during metamorphic reactions, the fluid regime
27 evolves to channelised fluid flow (or transport veins; fast and high fluid fluxes) carrying
28 externally derived fluids in open system on the outcrop scale (John et al., 2008; Taetz et al.,
29 2018). The change in the fluid regime allows diffusive transport of Li from the unfractured
30 rocks to the wall rock and vein, and thus kinetic isotope fractionation during fluid-induced
31 eclogitisation (John et al., 2012; Jonas et al., 2014; Taetz et al., 2018).

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41 Fluids released by dehydration processes of pelitic sediments and basic rocks of the
42 Ile de Groix were channelised during the HP–LT event, as shown by the large vein network
43 developed in the metamorphic rocks (El Korh et al., 2011). Fluid-rock interactions mainly
44 involved internally-derived fluids, or fluids derived from the deeper part of the subducted
45 crust and equilibrated with their host rocks. Most of the studied massive blueschists and
46 eclogites do not crop in contact with large veins, and did not interact with the passing fluids
47 owing to their low permeability and porosity (El Korh et al., 2011, 2013). Consequently, the
48 whole rock $\delta^7\text{Li}$ decrease from MORB-like values in blueschists to negative values in
49 eclogites (Fig. 6a) during HP–LT metamorphism may be interpreted as the result of
50 progressive fluid-induced Li kinetic diffusion and isotope fractionation during dehydration
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3 reactions already under prograde epidote-blueschist facies P–T conditions, without involving
4 high fluid fluxes (Fig. 6a). The importance of the transition from blueschist facies to eclogite
5 facies is also evidenced by the results of Halama et al. (2011), who showed that zoisite-
6 eclogites from the Raspas Complex (Ecuador) experienced more intensive metasomatic
7 effects than blueschists. Li diffusion on the intragrain scale and along grain boundaries is
8 triggered by mineral appearance and disappearance related to metamorphic reactions and
9 fluid-related dissolution–precipitation processes (Jonas et al., 2014; Taetz et al., 2018). In
10 blueschists, the $\delta^7\text{Li}$ decreases from MORB-like values in glaucophane core to negative
11 values in rims (Figs. 7b and c). Thus, the metabasites were able to conserve a MORB-like
12 isotopic signature after the onset of subduction, i.e. until blueschist facies conditions were
13 reached, even if Li was enriched during the pre-HP hydrothermal processes.

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The metamorphic minerals (glaucophane and omphacite) carry high Li contents in the
subduction zone, owing to their large stability field during the prograde metamorphism, from
lawsonite-blueschist facies (1.0–2.0 GPa, 350–450°C; El Korh et al., 2009) to eclogite facies
P–T conditions (1.6–2.5 GPa, 500–600°C; El Korh et al., 2009). The high Li content in
glaucophane indicate that glaucophane is the main mineral controlling Li fractionation during
prograde blueschist facies metamorphism up to HP–LT peak metamorphic conditions.
Lithium isotope fractionation occurred during the prograde dehydration with increasing
temperature conditions, probably at the transition from the lawsonite-blueschist facies (=
glaucophane core crystallisation) to the epidote-garnet-blueschist facies (= glaucophane rim
formation). The blueschists from the Ile de Groix contain frequent lawsonite pseudomorphs.
Lawsonite breakdown during prograde metamorphism produces large amounts of fluids,
which may trigger fluid-induced Li kinetic diffusion and isotope fractionation already under
lower grade conditions (transition from lawsonite-blueschist to epidote-blueschist facies). The
decrease of the $\delta^7\text{Li}$ values may be associated to Li enrichment in glaucophane rims (sample
GR25a; Fig. 7c) during metasomatic processes.

Omphacite and glaucophane in eclogites have lower $\delta^7\text{Li}$ values than MORB. The
rimward $\delta^7\text{Li}$ decrease in glaucophane indicates that fluid-induced kinetic Li diffusion still

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3 went on during eclogitisation (Figs. 7d–f). As observed for blueschists, the $\Delta^7\text{Li}_{\text{WR-gln}}$, $\Delta^7\text{Li}_{\text{WR-}}$
4 omph values and $\Delta^7\text{Li}_{\text{gln-omph}}$ of -0.6 ± 5.2 to $0.0 \pm 2.3\text{‰}$ in eclogites GR21 and 29 indicate that
5 bulk glaucophane and bulk omphacite are relatively at isotopic equilibrium with their host
6 rock. However, the negative $\Delta^7\text{Li}_{\text{gln rim-omph}}$ values from -3.1 ± 5.9 to -0.5 ± 5.9 reveal Li
7 isotope fractionation under peak metamorphic P–T conditions. For only one sample (eclogite
8 GR24a), omphacite has a low $\delta^7\text{Li}$ compared to the whole rock and glaucophane, resulting
9 from metasomatic processes under eclogite facies P–T conditions, as suggested by the
10 presence of HP quartz veins (El Korh et al., 2011). Retrograde barroisite formed along
11 omphacite rims have a mean $\delta^7\text{Li}$ value similar to that of omphacite, but exhibits a large
12 spread of $\delta^7\text{Li}$ values, suggesting localised Li mobilisation and isotope fractionation during
13 early retrogression. The calculated mean $\delta^7\text{Li}_{\text{fluid}}$ of fluids in equilibrium with dehydrating
14 metabasic and metapelitic rocks decrease from +8 to -2‰ with increasing P–T conditions,
15 i.e. from the lawsonite-blueschist facies (1.0–2.0 GPa, 350–450°C) to the eclogite facies
16 (1.6–2.5 GPa, 500–600°C) (Fig. 8b), even if the $\delta^7\text{Li}_{\text{fluid}}$ values remain higher than the
17 corresponding $\delta^7\text{Li}_{\text{solid}}$ (see also Marschall et al., 2007; Penniston-Dorland et al., 2012).
18 Consequently, our study argues that the $\delta^7\text{Li}$ decrease during subduction zone prograde
19 metamorphism results from cumulative effects of dehydration and fluid-induced Li kinetic
20 diffusion and isotope fractionation.
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41 Our data agree with the $\delta^7\text{Li}_{\text{fluid}}$ decrease in dehydrating metasediments of high
42 metamorphic grade (lawsonite-blueschist and epidote-amphibolite facies; 275–750°C; 0.5–
43 1.2 GPa; Bebout & Barton, 1993) from the Catalina Schist (Penniston-Dorland et al., 2012).
44 The highest $\delta^7\text{Li}_{\text{fluid}}$ (+6.4 to +7.7 ‰; Fig. 8b) at equilibrium with glaucophane cores in
45 blueschists (lawsonite-blueschist facies) plot within the field of the $\delta^7\text{Li}_{\text{fluid}}$ recorded by
46 lawsonite-blueschist and amphibolite facies metabasites from the Catalina Schist (+7 to
47 +13‰; Penniston-Dorland et al., 2012). However, the $\delta^7\text{Li}_{\text{fluid}}$ of fluids in equilibrium with the
48 metabasites and metapelites of the Ile de Groix of higher metamorphic grade (epidote-
49 blueschist to eclogite facies; $\delta^7\text{Li}_{\text{fluid}}$ of -3.5 to +4.2‰; Fig. 8b) are generally lower than the
50 $\delta^7\text{Li}_{\text{fluid}}$ of the fluids derived from the metasedimentary and metabasic rocks of the Catalina
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3 Schist (c. +5–18‰; Penniston-Dorland et al., 2012), but plot within the field of kinetically
4 altered amphibolites (0 to +4‰; Penniston-Dorland et al., 2012). The heavy-Li fluids in
5 equilibrium with blueschist-facies metabasites and micaschists are typical of subduction
6 fluids with a mixed composition between altered oceanic crust and GLOSS (+7 ± 5‰;
7 Simons et al., 2010). The release of these fluids will result in a decrease of the $\delta^7\text{Li}_{\text{solid}}$, and
8 could be at the origin of the low $\delta^7\text{Li}$ values of eclogites and fluids at equilibrium with them.

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Fluids in equilibrium with eclogites have a lower $\delta^7\text{Li}_{\text{fluid}}$ than subduction zone fluids. It
is suggested that the low $\delta^7\text{Li}_{\text{fluid}}$ under eclogite facies conditions may not reflect their real
 $\delta^7\text{Li}_{\text{fluid}}$ value, and would result from kinetic isotope fractionation that becomes predominant
over equilibrium fractionation with increasing metamorphic grade and temperature (Richter et
al., 2003; Marschall et al., 2007).

Li isotope fractionation during greenschist facies retrograde metamorphism related to exhumation of the Ile de Groix

During exhumation of the rocks from the Ile de Groix, the degree of retrogression of
metabasites is directly related to the free fluid phase, i.e. to the porosity. During the early
stages of exhumation (<1.6 GPa, 450–500°C; El Korh et al., 2009), retrograde reactions
occurred under restricted fluid-rock interactions and involved internally-derived fluids (El Korh
et al., 2013). The similar Li abundances and $\delta^7\text{Li}$ values of blueschists and eclogites (-4.8 to
+0.7‰) and greenschists (-4.5 to -0.1‰) that underwent restricted fluid-rock interactions
during retrogression ($\delta^7\text{Li}_{\text{fluid}}$ of -0.6 and +3.8‰ for samples GR23 and 25b, respectively; Fig.
8b), indicate that fluid-induced metasomatism was not able to reset the Li isotope
distribution. During the advanced stages of retrogression, the permeability and porosity of the
metabasites increase with the decrease of the P–T conditions (<1.0 GPa, <400–450°C),
allowing migration of higher amounts of fluids derived from the dehydrated metabasites (El
Korh et al., 2011, 2013). The increase of the $\delta^7\text{Li}$ values toward positive values in the most
retrogressed samples (+3.2 and +1.5‰ for samples GR06a and GROA52, respectively)
highlights a Li mineral/fluid isotopic exchange and migration of fluids with a heavier-Li

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3 composition (+5.8 to +7.6‰; Fig. 8b) during rehydration reactions. Our results agree with
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5 Penniston-Dorland et al. (2010), who observed retrograde reactions related to an infiltration
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7 of an aqueous fluid with high $\delta^7\text{Li}_{\text{fluid}}$ in HP rocks from the Franciscan Complex (California,
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9 USA). Similarly, Xiao et al. (2011) observed heavier Li isotopic compositions in retrograde
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11 amphibolites (-0.4 ± 0.3 to $+0.9 \pm 0.2\text{‰}$) compared to neighbouring UHP eclogites (-6.9 ± 0.2
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13 to $-6.5 \pm 0.1\text{‰}$) from the Chinese Continental Scientific Drilling Program (Sulu, East China).
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15 The authors suggest that Li budget and isotope fractionation is mostly controlled by the
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17 mineral assemblage, as significant fractionation occur both in closed and open fluid-rock
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19 systems (Xiao et al., 2011).
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22 Our data confirm that Li isotopes are strongly sensitive to retrograde fluid-rock
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24 interactions related to exhumation of HP rocks. Significant Li isotope fractionation during
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26 rehydration reactions in open system result in apparent Li compositions that do not reflect the
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28 subduction signature anymore. A similar behaviour has also been reported for Ge isotopes
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30 (El Korh et al., 2017b): rehydration reactions triggered Ge isotope fractionation towards
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32 heavier compositions in the most retrogressed greenschists, while the least retrogressed
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34 samples (closed system) can retain the Ge isotope signature of high grade facies
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36 metabasites.
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39 40 41 *Li isotope fractionation in the Limousin UHP zoisite-eclogite*

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43 The Li abundances and isotopic data in the UHP zoisite-eclogite from the Limousin
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45 significantly contrast with the results obtained for the Ile de Groix. The UHP zoisite eclogite,
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47 deriving from an iron-rich plagioclase cumulate such as those emplaced in continental
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49 intrusions or forming Fe-Ti oceanic gabbros (Berger et al., 2010a), has a Li abundance
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51 slightly lower than MORB (Fig. 3). Garnet and zoisite are the most abundant minerals, but do
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53 not play an important role in the Li budget due to their low Li contents (Fig. 3). Omphacite
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55 and pargasitic amphibole are the main hosts for Li, but display lower Li contents than in
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57 eclogites from the Ile de Groix. However, they show a heavy-Li signature typical of low-
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59 temperature altered oceanic crust (Chan et al., 2002), with $\delta^7\text{Li}$ values considerably higher
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3 than those of the Ile de Groix (Figs. 4 and 6).
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5 The positive $\delta^7\text{Li}$ value recorded by omphacite agrees with the model of Li
6 fractionation determined by Marschall et al (2007) predicting that deeply subducted eclogites
7 have a heavier Li signature than the mantle. However, the abnormally high $\delta^7\text{Li}$ recorded by
8 omphacite probably reflects an interaction with a heavy-Li fluid migrating in the subduction
9 zone (Fig. 8a). Zoisite-eclogites have been intensively metasomatised during the UHP event,
10 by interaction with a fluid derived from dehydrating subducted sediments at the interface
11 slab/mantle (Berger et al., 2010a). Extremely heavy-Li isotopic signatures related to high Li
12 mobility are characteristic of upwelling fluids and sediments in subduction zone decollements
13 (Chan & Kastner, 2000). However, the low Li abundances do not argue for any Li transport
14 and enrichment from the fluid phase, but may reflect Li leaching and preferential ^6Li transfer
15 towards the passing fluid. The decrease of the $\delta^7\text{Li}$ value in secondary pargasitic amphibole
16 (from +21.9‰ in omphacite to +18.7‰ in amphibole) indicates interaction with a Li-richer and
17 lighter fluid during partial retrogression (Figs. 4b and 8a).
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32 Muscovite and quartz in pegmatites from Black Hills (South Dakota, USA) also exhibit
33 heavy-Li isotopic signatures (up to +21.3‰) and result from crystal melt fractionation (Teng
34 et al., 2006). The high $\delta^7\text{Li}$ values in omphacite from the UHP zoisite-eclogite may also
35 reflect interaction with crustal-derived fluids during subduction or, more unlikely a crustal
36 contamination during differentiation of the magmatic protolith (see Berger et al., 2010a for
37 discussion of the protolith origin). In any case, the zoisite-eclogite L04-143 derives from a
38 protolith of a different composition than the MORB-derived rocks of the Ile de Groix, and
39 have undergone a different metamorphic history during subduction.
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51 **SYNTHESIS AND CONCLUSIONS**

52 This study provides bulk and in-situ analyses to reconstruct Li behaviour and isotope
53 fractionation during the various stages of fluid-rock interactions occurring in the ancient
54 Variscan oceanic lithosphere, including seafloor high-T and low-T hydrothermal alteration,
55 subduction and exhumation processes.
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5 1) In the Limousin ophiolite, high-T hydrothermal alteration of ultrabasic rocks produces
6 serpentinities with a Li concentration lower than 5 ppm during interaction with hydrothermal
7 fluids and/or seawater. Serpentine formed during the early stages of alteration has a low
8 $\delta^7\text{Li}$. The $\delta^7\text{Li}$ increase in serpentine formed during the late stages of hydrothermal alteration
9 indicates changes in the fluid $\delta^7\text{Li}_{\text{fluid}}$ composition and, probably, a temperature decrease
10 from high-T to low-T conditions. Amphibolites display Li contents and isotopic compositions
11 typical of hydrothermally altered sheeted dykes and gabbros. The high $\delta^7\text{Li}$ values of
12 amphibolites indicate an interaction with heavy-Li fluids – seawater or upwelling
13 hydrothermal fluids – under high-T conditions. These results confirm that Li-poor abyssal
14 serpentinities do not constitute an important source of Li for Li-rich metabasic rocks during
15 subduction zone metamorphism.
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30 2) Li concentrations in the metabasites of the Ile de Groix are significantly higher than in
31 fresh MORB. The elevated Li content in the subducted metabasites of the Ile de Groix can
32 only be explained by a metasomatic overprint of fluids derived from Li-rich sediments during
33 the early stages of subduction, as observed in other orogenic eclogites. Lithium abundances
34 remain high in the metabasites of the Ile de Groix during subduction zone metamorphism,
35 owing to the large stability field of Li-hosting minerals from the lawsonite-blueschist to the
36 eclogite facies, and in retrograde greenschist facies rocks. Lithium is mainly hosted by 1)
37 glaucophane and omphacite in blueschists and eclogites; 2) chlorite and albite in retrograde
38 greenschists; 3) phengite and chlorite in micaschists.
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51 3) The metabasites of the Ile de Groix have whole rock $\delta^7\text{Li}$ values decreasing from
52 blueschists to eclogites. Both bulk and in-situ $\delta^7\text{Li}$ data clearly demonstrate that Li isotopes
53 fractionate under blueschist facies conditions in metabasic rocks, i.e. before eclogite facies
54 conditions are reached in the subduction zone. Glaucophane in blueschists have $\delta^7\text{Li}$ values
55 decreasing rimwards from positive $\delta^7\text{Li}$ values to negative values, indicating that significant Li
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3 isotope fractionation in the metabasites of the Ile de Groix occurred at the transition from the
4 lawsonite-blueschist facies to the epidote-garnet-blueschist facies. Lawsonite breakdown
5 releases high amounts of fluids, which can trigger fluid-induced kinetic fractionation of Li. In
6 the eclogites facies metabasites from the Ile de Groix, omphacite and glaucophane have
7 lower $\delta^7\text{Li}$ values than glaucophane in blueschists, indicating that fluid-induced kinetic Li
8 diffusion carried on during eclogitisation. However the calculated $\delta^7\text{Li}_{\text{fluid}}$ at equilibrium may
9 be not representative, because of the possible predominance of kinetic isotope fractionation
10 compared to equilibrium fractionation.
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20 Calculation of the fluid $\delta^7\text{Li}$ values in equilibrium with the metabasites and metapelites
21 of the Ile de Groix reveals that the dehydrating metabasites release heavy-Li fluids typical of
22 subduction fluids. The fluid $\delta^7\text{Li}$ values in equilibrium with metabasites decrease with
23 increasing metamorphic grade up to eclogite facies conditions. Overprint of a fluid under HP
24 conditions with an extremely low $\delta^7\text{Li}$ value is evidenced by omphacite in one eclogite
25 sample. However, the $\delta^7\text{Li}$ of fluids under epidote-blueschist and eclogite facies may not be
26 representative of the real composition because of the predominance of kinetic isotope
27 fractionation compared to equilibrium fractionation with increasing temperature conditions.
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39 4) The low Li abundances and high $\delta^7\text{Li}$ values recorded by omphacite and pargasitic
40 amphibole in the UHP zoisite-eclogite from the Limousin significantly contrast with the results
41 obtained for the Ile de Groix. This probably reflects Li leaching and Li isotopic fractionation
42 during intensive metasomatism by a fluid derived from dehydrating sediments. It may also
43 reflect crustal contamination in the protolith composition.
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51 5) Retrograde greenschists from the Ile de Groix have whole rock Li abundance and $\delta^7\text{Li}$
52 values within the same range as blueschists and eclogites. Therefore, the increase of the
53 $\delta^7\text{Li}$ values toward positive values in the most retrogressed samples highlight a Li
54 mineral/fluid isotopic exchange during rehydration reactions and interaction with a Li-heavy
55 fluid.
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5 6) Lithium isotope fractionation in blueschists and in the most retrogressed greenschists from
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7 the Ile de Groix highlights the migration of heavy-Li fluids along the oceanic crust-mantle
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9 interface in the subduction zone. As predicted by former models of Li fractionation in
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11 subduction zones (Elliott et al., 2004, 2006; Marschall et al., 2007; Halama et al., 2011), our
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13 data suggest that migration of heavy-Li fluids along the crust-mantle wedge may be
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15 responsible for an enrichment of the fore-arc mantle wedge along the subduction channel.
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52 53 **REFERENCES**

54
55 Agostini, S., Ryan, J. G., Tonarini, S. & Innocenti, F. (2008). Drying and dying of a subducted
56
57 slab: coupled Li and B isotope variations in Western Anatolia Cenozoic Volcanism. *Earth*
58
59 *and Planetary Science Letters* **272**, 139–147.
60

- 1
2
3 Audren, C., Triboulet, C., Chauris, L., Lefort, J.-P., Vignerresse, J.-L., Audrain, J.,
4 Thiéblemont, D., Goyallon, J., Jégouzo, P., Guennoc, P., Augris, C. & Carn, A. (1993).
5 Notice explicative de la feuille Ile de Groix à 1/25000, carte géologique. BRGM, Orléans.
6
7
8
9 Bach, W., Paulick, H., Garrido, C. J., Ildefonse, B., Meurer, W. P. & Humphris, S. E. (2006).
10 Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry,
11 and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophysical*
12 *Research Letters* **33**, L13306, doi:10.1029/2006GL025681.
13
14
15
16
17 Ballèvre, M., Martínez Catalán, J.R., López-Carmona, A., Pitra, P., Abati, J., Díez
18 Fernández, R., Ducassou, C., Arenas, R., Bosse, V., Castiñeiras, P., Fernández-Suárez,
19 J., Gómez Barreiro, J., Paquette, J.-L., Peucat, J.-J., Pujol, M., Ruffet, G. & Sánchez
20 Martínez, S. (2014). Correlation of the nappe stack in the Ibero-Armorican arc across the
21 Bay of Biscay: a joint French–Spanish project. In: Schulmann, K., Martínez Catalán, J. R.,
22 Lardeaux, J. M., Janousek, V., Oggiano, G. (eds), "The Variscan orogeny: extent,
23 timescale and the formation of the European crust". *Geological Society of London Special*
24 *Publications* **405**, 77–113.
25
26
27
28
29
30
31
32
33
34 Ballèvre, M., Pitra, P. & Bohn, M. (2003). Lawsonite growth in the epidote blueschists from
35 the Ile de Groix (Armorican massif, France): a potential geobarometer. *Journal of*
36 *Metamorphic Geology* **21**, 723–735.
37
38
39
40 Barrientos, X. & Selverstone, J. (1993). Infiltration vs. thermal overprinting of epidote
41 blueschists, Ile de Groix, France. *Geology* **21**, 69–72.
42
43
44
45 Bebout, G. E. & Barton, M. D. (1993). Metasomatism during subduction: products and
46 possible paths in the Catalina Schist, California. *Chemical Geology* **108**, 61–92.
47
48
49 Bebout G. E., Bebout A. E. & Graham C. M. (2007). Cycling of B, Li, and LILE (K, Cs, Rb,
50 Ba, Sr) into subduction zones: SIMS evidence from micas in high-P/T metasedimentary
51 rocks. *Chemical Geology* **239**, 284–304.
52
53
54
55 Bebout, G. E., Ryan, J. & Leeman, W. (1993). B-Be systematics in subduction-related
56 metamorphic rocks: Characterization of the subducted component. *Geochimica et*
57 *Cosmochimica Acta* **57**, 2227–2237.
58
59
60

- 1
2
3 Bellot, J. P. & Roig, J. Y. (2007). Episodic exhumation of HP rocks inferred from structural
4 data and P–T paths from the Southwestern Massif Central (Variscan belt, France).
5 *Journal of Structural Geology* **29**, 1538–1557.
6
7
8
9 Benton, L. D., Ryan, J. G. & Savov, I. P. (2004). Lithium abundance and isotope systematics
10 of forearc serpentinites, Conical Seamount, Mariana forearc: Insights into the mechanics
11 of slab-mantle exchange during subduction, *Geochemistry Geophysics Geosystems* **5**,
12 Q08J12, doi:10.1029/2004GC000708.
13
14
15
16
17 Berger, J., Féménias, O., Mercier, J. C. C. & Demaiffe, D. (2005). Ocean-floor hydrothermal
18 metamorphism in the Limousin ophiolites (western French Massif Central): evidence of a
19 rare preserved Variscan oceanic marker. *Journal of Metamorphic Geology* **23**, 795–812.
20
21
22
23
24 Berger, J., Féménias, O., Mercier, J. C. C. & Demaiffe, D. (2006). A Variscan slow-spreading
25 ridge (MOR-LHOT) in Limousin (French Massif Central): magmatic evolution and tectonic
26 setting inferred from mineral chemistry. *Mineralogical Magazine* **70**, 175–185.
27
28
29
30
31 Berger, J., Féménias, O., Ohnenstetter, D., Bruguier, O., Plissart, G., Mercier, J. C. C. &
32 Demaiffe, D. (2010a). New occurrence of UHP eclogites in Limousin (French Massif
33 Central): Age, tectonic setting and fluid–rock interactions. *Lithos* **118**, 365–382.
34
35
36
37 Berger, J., Féménias, O., Ohnenstetter, D., Plissart, G. & Mercier, J. C. C. (2010b). Origin
38 and tectonic significance of corundum–kyanite–sapphirine amphibolites from the Variscan
39 French Massif Central. *Journal of Metamorphic Geology* **28**, 341–360.
40
41
42
43
44 Bernard-Griffiths, J., Carpenter, M. S. N., Peucat, J.-J. & Jahn, B. M. (1986). Geochemical
45 and isotopic characteristics of blueschist facies rocks from the Ile de Groix, Armorican
46 Massif (northwest France). *Lithos* **19**, 235–253.
47
48
49
50 Berthelsen, A. (1992). Mobile Europe. In Blundell, D., Freeman, R. & Mueller, S. (eds) *A*
51 *continent revealed. The European geotraverse*, Cambridge University Press, Cambridge,
52 UK, 11–32.
53
54
55
56 Bosse, V., Ballèvre, M. & Vidal, O. (2002). Ductile thrusting recorded by the garnet isograd
57 from blueschist-facies metapelites of the Ile de Groix, Armorican Massif, France. *Journal*
58 *of Petrology* **43**, 485–510.
59
60

- 1
2
3 Bosse, V., Féraud, G., Ballèvre, M., Peucat, J.-J. & Corsini, M. (2005). Rb-Sr and $^{40}\text{Ar}/^{39}\text{Ar}$
4 ages in blueschists from the Ile de Groix (Armorican Massif, France): Implications for
5 closure mechanisms in isotopic systems. *Chemical Geology* **220**, 21–45.
6
7
8
9 Bouman, C., Elliott, T. & Vroon, P. Z. (2004). Lithium inputs to subduction zones. *Chemical*
10 *Geology* **212**, 59–79.
11
12
13 Bouvier, A.-S., Métrich, N. & Deloule, E. (2008). Slab-derived fluids in magma sources of St.
14 Vincent (Lesser Antilles Arc): Volatile and light element imprints. *Journal of Petrology* **49**,
15 1427–1448.
16
17
18
19 Brenan, J. M., Ryerson, F. J. & Shaw, H. F. (1998). The role of aqueous fluids in the slab-to-
20 mantle transfer of boron, beryllium, and lithium during subduction: Experiments and
21 models. *Geochimica et Cosmochimica Acta* **62**, 3337–3347.
22
23
24
25 Carignan, J., Hild, P., Mevelle, G., Morel, J. & Yeghicheyan, D. (2001). Routine analyses of
26 trace elements in geological samples using flow injection and low pressure on-line liquid
27 chromatography coupled to ICP-MS: A study of geochemical reference materials BR, DR-
28 N, UB-N, AN-G and GH. *Geostandard Newsletters* **25**, 187–198.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Carpenter, M. S. N. (1976). Petrogenetic study of the glaucophane schists and associated
rocks from the Ile de Groix, Brittany, France. Unpublished PhD Thesis, Oxford University,
271 pp.
Chan, L. H., Alt, J. C. & Teagle, D. A. H. (2002). Lithium and lithium isotope profiles through
the upper oceanic crust: a study of seawater–basalt exchange at ODP sites 504b and
896a. *Earth and Planetary Science Letters* **201**, 187–201.
Chan, L. H. & Edmond, J. M. (1988). Variation of lithium isotope composition in the marine
environment: A preliminary report, *Geochimica et Cosmochimica Acta* **52**, 1711–1717.
Chan, L. H. & Kastner, M. (2000). Lithium isotopic compositions of pore fluids and sediments
in the Costa Rica subduction zone: implications for fluid processes and sediment
contribution to the arc volcanoes. *Earth and Planetary Science Letters* **183**, 275–290.
Chan, L. H., Leeman, W. P. & Plank, T. (2006). Lithium isotopic composition of marine
sediments. *Geochemistry Geophysics Geosystems* **7**, Q06005.

- 1
2
3 Chan, L. H., Leeman, W. P. & You, C. F. (1999). Lithium isotopic composition of central
4 American volcanic arc lavas: implications for modification of subarc mantle by slab-
5 derived fluids. *Chemical Geology* **160**, 255–280.
6
7
8
9
10 Coogan, L. A., Gillis, K. M., Pope, M. & Spence, J. (2017). The role of low-temperature (off-
11 axis) alteration of the oceanic crust in the global Li-cycle: Insights from the Troodos
12 ophiolite. *Geochimica et Cosmochimica Acta* **203**, 201–215.
13
14
15
16 Decitre, S. E., Deloule, E., Reisberg, L., James, R., Agrinier, P. & Mevel, C. (2002). Behavior
17 of Li and its isotopes during serpentinization of oceanic peridotites. *Geochemistry*
18 *Geophysics Geosystems* **3**, doi.org/10.1029/2001GC000178.
19
20
21
22 Demange, M. (1994). Anteviariscan evolution of the Montagne Noire (France): from a passive
23 margin to a foreland basin. *Comptes Rendus de l'Académie des Sciences de Paris* **318**
24 **(II)**, 921–933.
25
26
27
28 Dubuisson, G., Mercier, J.-C. C., Girardeau, J. & Frison, J.Y. (1989). Evidence for a lost
29 ocean in Variscan terranes of the Western Massif Central, France. *Nature* **337**, 729–732.
30
31
32
33 El Korh, A. (2010). Geochemical fingerprints of devolatilisation reactions in the high-pressure
34 rocks of Ile de Groix, France. PhD thesis, University of Geneva, Terre et Environnement
35 99, 361 pp.
36
37
38
39 El Korh, A., Luais, B., Boiron, M.-C., Deloule, E. & Cividini, D. (2017b). Investigation of Ge
40 and Ga exchange behaviour and Ge isotopic fractionation during subduction zone
41 metamorphism. *Chemical Geology* **449**, 165–181.
42
43
44
45 El Korh, A., Luais, B., Deloule, E. & Cividini, D. (2017a). Iron isotope fractionation in
46 subduction-related high-pressure metabasites (Ile de Groix, France). *Contributions to*
47 *Mineralogy and Petrology* **172**, 41.
48
49
50
51 El Korh, A., Schmidt, S. Th., Ballèvre, M., Ulianov, A. & Bruguier, O. (2012). Discovery of an
52 albite gneiss from the Ile de Groix (Armorican Massif, France): geochemistry and LA-ICP-
53 MS U–Pb geochronology of its Ordovician protolith. *International Journal of Earth*
54 *Sciences* **101**, 1169–1190.
55
56
57
58
59
60

- 1
2
3 El Korh, A., Schmidt S. Th., Ulianov, A. & Potel, S. (2009). Trace element partitioning in HP–
4 LT metamorphic assemblages during subduction-related metamorphism, Ile de Groix,
5 France: a detailed LA-ICP-MS study. *Journal of Petrology* **50**, 1107–1148.
6
7
8
9 El Korh, A., Schmidt, S. Th., Vennemann, T. & Ballèvre, M. (2013). Trace element and
10 isotopic fingerprints in HP–LT metamorphic rocks as a result of fluid-rock interactions (Ile
11 de Groix, France). *Gondwana Research* **23**, 880–900.
12
13
14 El Korh, A., Schmidt, S. Th., Vennemann, T. & Ulianov, A. (2011). Trace element and O-
15 isotope composition of polyphase metamorphic veins of the Ile de Groix (Armorican
16 Massif, France): implication for fluid flow during HP subduction and exhumation
17 processes. In: Dobrzhinetskaya, L., Faryad, W., Wallis, S., Cuthbert, S. (eds), "Ultrahigh
18 Pressure Metamorphism: 25 years after discovery of coesite and diamond". Elsevier,
19 Amsterdam, Netherlands, 243–291.
20
21
22 Elliott, T., Jeffcoate, A. & Bouman, C. (2004). The terrestrial Li isotope cycle: light-weight
23 constraints on mantle convection. *Earth and Planetary Science Letters* **220**, 231–245.
24
25
26 Elliott, T., Thomas, A., Jeffcoate, A. & Niu, Y. (2006). Lithium isotope evidence for
27 subduction-enriched mantle in the source of mid-ocean-ridge basalts. *Nature* **443**, 565–
28 568.
29
30
31 Evans, B. W., Johannes, W., Otterdoom, H. & Trommsdorff, V. (1976). Stability of chrysotile
32 and antigorite in the serpentine multi-system, *Schweizerische Mineralogische*
33 *Petrographische Mitteilungen* **50**, 481–492.
34
35
36 Faure, M., Lardeaux, J. M. & Ledru, P. (2009). A review of the pre-Permian geology of the
37 Variscan French Massif Central. *Comptes Rendus Geosciences* **341**, 202–213.
38
39
40 Franke, W. (1992). Phanerozoic structures and events in Central Europe. In Blundell, D.,
41 Freeman, R. & Mueller, S. (eds) *A continent revealed. The European geotraverse*,
42 Cambridge University Press, Cambridge, UK, 164–180.
43
44
45 Früh-Green, G. L., Connolly, J. A. D., Plas, A., Kelley, D. S. & Grobéty, B. (2004).
46 Serpentinization of oceanic peridotites: Implications for geochemical cycles and biological
47 Activity. In: Wilcock, W. S. D., Delong, E. F., Kelley, D. S., Baross, J. A., & Craig Cary, S.
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (eds) *The Subseafloor Biosphere at Mid-Ocean Ridges*, American Geophysical Union,
4 Washington, D. C.

5
6
7 Gao, Y., Snow, J. E., Casey, J. F. & Yu, J. (2011). Cooling-induced fractionation of mantle Li
8 isotopes from the ultraslow-spreading Gakkel Ridge. *Earth and Planetary Science Letters*,
9 **301**, 231–240.

10
11
12 Girardeau, J., Dubuisson, G. & Mercier, J.-C. C. (1986). Cinématique de mise en place des
13 ophiolites et nappes crystallophiliennes du Limousin, Ouest du Massif Central français.
14 *Bulletin de la Société Géologique de France* **2**, 849–860.

15
16
17 Halama, R., John, T., Harms, P., Hauff, F. & Schenk, V. (2011). A stable (Li, O) and
18 radiogenic (Sr, Nd) isotope perspective on metasomatic processes in a subducting slab.
19 *Chemical Geology* **281**, 151–166.

20
21
22 James, R. H. & Palmer, M. R. (2000). The lithium isotope composition of international rock
23 standards. *Chemical Geology* **166**, 319–326.

24
25
26 Jeffcoate, A. B., Elliott, T., Kasemann, S. A., Ionov, D., Cooper, K. & Brooker, R. (2007). Li
27 isotope fractionation in peridotites and mafic melts. *Geochimica et Cosmochimica Acta* **71**,
28 202–218.

29
30
31 John, T., Gussone, N., Podladchikov, Y. Y., Bebout, G. E., Dohmen, R., Halama, R., Klemd,
32 R., Magna, T., Seitz, H.-M. (2012). Volcanic arcs fed by rapid pulsed fluid flow through
33 subducting slabs. *Nature Geosciences* **5**, 489–492.

34
35
36 John, T., Klemd, R., Gao, J. & Garbe-Schönberg C.D. (2008). Trace-element mobilization in
37 slabs due to non steady-state fluid–rock interaction: Constraints from an eclogite-facies
38 transport vein in blueschist (Tianshan, China), *Lithos* **103**, 1–24.

39
40
41 Jonas, L., John, T., King, H. E., Geisler, T., Putnis, A. (2014). The role of grain boundaries
42 and transient porosity in rocks as fluid pathways for reaction front propagation. *Earth*
43 *Planetary Science Letters* **386**, 64–74.

44
45
46 Kasemann, S. A., Jeffcoate, A. B. & Elliott, T. (2005). Lithium isotope composition of basalt
47 glass reference material. *Analytical Chemistry* **77**, 5251–5257.

- 1
2
3 Kodolányi, J., Pettke, T., Spandler, C., Kamber, B. S. & Gméling, K. (2012). Geochemistry of
4 ocean floor and fore-arc serpentinites: constraints on the ultramafic input to subduction
5 zones. *Journal of Petrology* **53**, 235–270.
6
7
8
9 Kohn, M. J., Valley, J. W., Elsenheimer, D. & Spicuzza, M. J. (1993). Oxygen isotope zoning
10 in garnet and staurolite. *American Mineralogist* **78**, 988–1001.
11
12
13 Kretz, R. (1983). Symbols for rock-forming minerals. *American Mineralogist* **68**, 277–279.
14
15
16 Kroner, U. & Romer, R. L. (2013). Two plates—many subduction zones: the Variscan
17 orogeny reconsidered. *Gondwana Research* **24**, 298–329.
18
19
20 Lackey, J. S., Valley, J. W., Chen, J. H. & Stockli, D. F. (2008). Dynamic magma systems,
21 crustal recycling, and alteration in the Central Sierra Nevada Batholith: the oxygen isotope
22 record. *Journal of Petrology* **49**, 1397–1426.
23
24
25
26 Ledru, P., Autran, A. & Santallier, D. (1994). Lithostratigraphy of Variscan terranes in the
27 French Massif Central: a basis for paleogeographical reconstructions. In Keppie, J.D. (ed)
28 *Pre-mesozoic geology in France and related areas*, Springer-Verlag, Berlin Heidelberg,
29 276–288.
30
31
32
33
34 Ledru, P., Lardeaux, J. M., Santallier, D., Autran, A., Quenardel, J. M., Floc'h, J. P., Lerouge,
35 G., Maillet, N., Marchand, J. & Ploquin, A. (1989). Où sont les nappes dans le Massif
36 Central Français? *Bulletin de la Société Géologique de France* **3**, 605–618.
37
38
39
40
41 Longerich, H. P., Jackson, S. E. & Günther, D. (1996). Laser ablation inductively coupled
42 plasma mass spectrometric transient signal data acquisition and analyte concentration
43 calculation. *Journal of Analytical Atomic Spectrometry* **11**, 899–904.
44
45
46
47 Marignac, C. & Cuney, M. (1999). Ore deposits of the French Massif Central: insight into the
48 metallogenesis of the Variscan collision belt. *Mineralium Deposita* **34**, 472–504.
49
50
51
52 Marschall, H. R., Altherr, R., Ludwig, T., Kalt, A., Gméling, K. & Kasztovszky, Zs. (2006).
53 Partitioning and budget of Li, Be and B in high-pressure metamorphic rocks. *Geochimica*
54 *et Cosmochimica Acta* **70**, 4750–4769.
55
56
57
58
59
60

- 1
2
3 Marschall, H. R., Pogge von Strandmann, P. A. E., Seitz, H.-M., Elliott, T. & Niu, Y. (2007).
4
5 The lithium isotopic composition of orogenic eclogites and deep subducted slabs. *Earth*
6
7 *and Planetary Science Letters* **262**, 563–580.
8
- 9 Matte, P. (2001). The Variscan collage and orogeny (480–290 Ma) and the tectonic definition
10
11 of the Armorica microplate: a review. *Terra Nova* **13**, 122–128.
12
- 13 Melleton, J., Cocherie, A., Faure, M. & Rossi, P. (2010). Precambrian protoliths and early
14
15 Paleozoic magmatism in the French Massif Central: U–Pb data and the North Gondwana
16
17 connection in the west European Variscan belt. *Gondwana Research* **17**, 13–25.
18
- 19 Mével, C. (2003). Serpentinization of abyssal peridotites at mid-ocean ridges. *Comptes*
20
21 *Rendus Geoscience* **335**, 825–852.
22
- 23 Millot, R., Guerrot, C. & Vigier, N. (2004). Accurate and high- precision measurement of
24
25 lithium isotopes in two reference materials by MC-ICP-MS. *Geostandards Geoanalytical*
26
27 *Research* **28**, 153–159.
28
- 29 Nance, R. D., Gutiérrez-Alonso, G., Keppie, J. D., Linnemann, U., Murphy, J. B., Quesada,
30
31 C., Strachan, R. A. & Woodcock, N. H. (2010). Evolution of the Rheic Ocean. *Gondwana*
32
33 *Research* **17**, 194–222.
34
- 35 Niu, Y. & Batiza, R. (1997). Trace element evidence from seamounts for recycled oceanic
36
37 crust in the eastern Pacific mantle. *Earth and Planetary Science Letters* **148**, 471–483.
38
- 39 O'Hanley, D.S. (1996). *Serpentinities*, Oxford University Press, New York, 277 pp.
40
- 41 Paquette, J. L., Ballèvre, M., Peucat, J. J. & Cornen, G. (2017). From opening to subduction
42
43 of an oceanic domain constrained by LA-ICP-MS U-Pb zircon dating (Variscan belt,
44
45 Southern Armorican Massif, France). *Lithos* **294–295**, 418–437.
46
47
- 48 Penniston-Dorland S. C., Bebout, G. E., Pogge von Strandmann, P. A. E., Elliott, T. &
49
50 Sorensen, S. S. (2012). Lithium and its isotopes as tracers of subduction zone fluids and
51
52 metasomatic processes: Evidence from the Catalina Schist, California, USA. *Geochimica*
53
54 *et Cosmochimica Acta* **77**, 530–545.
55
- 56 Penniston-Dorland, S. C., Liu, X.-M. & Rudnick, R. L. (2017). Lithium isotope geochemistry.
57
58 *Reviews in Mineralogy and Geochemistry* **82**, 165–217.
59
60

- 1
2
3 Penniston-Dorland, S. C., Sorensen, S. S., Ash, R. D. & Khadke, S. V. (2010). Lithium
4 isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA.
5
6 *Earth and Planetary Science Letters* **292**, 181–190.
7
8
9 Qiu, L., Rudnick, R. L., Ague, J. J. & McDonough, W. F. (2011). A lithium isotopic study of
10 sub-greenschist to greenschist facies metamorphism in an accretionary prism, New
11 Zealand. *Earth and Planetary Science Letters* **301**, 213–221.
12
13
14 Quinquis, H. (1980). Schistes bleus et déformation progressive: l'exemple de l'île de Groix.
15 Thèse de 3ème cycle, Université de Rennes, 145 pp.
16
17
18 Quinquis, H. & Choukroune, P. (1981). Les schistes bleus de l'île de Groix dans la chaîne
19 Variscenne: implications cinématiques. *Bulletin de la Société Géologique de France* (7)
20 **XXIII**, 409–418.
21
22
23
24 Richter, F. M., Davis, A. M., DePaolo, D. J. & Watson, E. B. (2003). Isotope fractionation by
25 chemical diffusion between molten basalt and rhyolite. *Geochimica et Cosmochimica Acta*
26 **67**, 3905–3923.
27
28
29
30
31
32 Romer, R. L. & Meixner, A. (2014). Lithium and boron isotopic fractionation in sedimentary
33 rocks during metamorphism – The role of rock composition and protolith mineralogy.
34 *Geochimica et Cosmochimica Acta* **128**, 158–177.
35
36
37
38
39 Ryan, J. G. & Langmuir, C. H. (1987). The systematics of lithium abundances in young
40 volcanic rocks. *Geochimica et Cosmochimica Acta* **51**, 1727–1741.
41
42
43
44 Santallier, D., Briand, B., Ménot, R. P. & Piboule, M. (1988). Les complexes leptyno-
45 amphiboliques (C.L.A.): revue critique et suggestions pour un meilleur emploi de ce
46 terme. *Bulletin de la Société Géologique de France* **8 (IV)**, 3–12.
47
48
49
50 Scambelluri, M., Müntener, O., Ottolini, L., Pettke, T. T. & Vanucci, R. (2004). The fate of B,
51 Cl and Li in subducted oceanic mantle and in the antigorite breakdown fluids. *Earth and*
52 *Planetary Science Letters* **222**, 217–234.
53
54
55
56 Simons, K. K., Harlow, G. E., Brueckner, H. K., Goldstein, S. L., Sorensen, S. S., Hemming,
57 N. G. & Langmuir, C. H. (2010). Lithium isotopes in Guatemalan and Franciscan HP–LT
58
59
60

1
2
3 rocks: insights into the role of sediment-derived fluids during subduction. *Geochimica et*
4
5 *Cosmochimica Acta* **74**, 3621–3641.

6
7 Siron, G., Baumgartner, L. P., Bouvier, A.-S., Putlitz, B. & Vennemann, T. (2017). Biotite
8
9 reference materials for secondary ion mass spectrometry $^{18}\text{O}/^{16}\text{O}$ measurements.
10
11 *Geostandards and Geoanalytical Research* **41**, 243–253.

12
13 Siron, G., Baumgartner, L. P., Bouvier, A.-S. & Vennemann, T. (2018). Accurate
14
15 Measurements of H_2O , F and Cl Content in Biotite using Secondary Ion Mass
16
17 Spectrometry. *Geostandards and Geoanalytical Research*, doi: 10.1111/ggr.12235

18
19 Spandler, C. & Hermann, J. (2006). High-pressure veins in eclogite from New Caledonia and
20
21 their significance for fluid migration in subduction zones. *Lithos* **89**, 135–153.

22
23 Stampfli, G. M., von Raumer, J. F., Wilhem, C. (2011) The distribution of Gondwana derived
24
25 terranes in the early Paleozoic. In: Gutiérrez Marco JC, Rábano I, García-Bellido I (eds)
26
27 The ordovician of the world. *Instituto Geológico y Minero de España, Madrid, Cuadernos*
28
29 *del Museo Geominero* **14**, 567–574.

30
31 Su, B.-X., Gu, X.-Y., Deloule, E., Zhang, H.-F., Li, Q.-L., Li, X.-H., Vigier, N., Tang, Y.-J.,
32
33 Tang, G.-Q., Liu, Y., Pang, K.-N., Brewer, A., Mao, Q. & Ma, Y.-G. (2015). Potential
34
35 orthopyroxene, clinopyroxene and olivine reference materials for *in situ* lithium isotope
36
37 determination. *Geostandards and Geoanalytical Research* **39**, 357–369.

38
39 Taetz, S., John, T., Bröcker, M., Spandler, C. (2016). Fluid–rock interaction and evolution of
40
41 a high-pressure/low-temperature vein system in eclogite from New Caledonia: insights
42
43 into intraslab fluid flow processes. *Contributions to Mineralogy and Petrology* **171**, 90.

44
45 Taetz, S., John, T., Bröcker, M., Spandler, C. & Stracke, A. (2018). Fast intraslab fluid-flow
46
47 events linked to pulses of high pore fluid pressure at the subducted plate interface. *Earth*
48
49 *and Planetary Science Letters* **482**, 33–43.

50
51 Tang, Y. J., Zhang, H. F., Deloule, E., Su, B. X., Ying, J. F., Xiao, Y. & Hu, Y. (2012). Slab-
52
53 derived lithium isotopic signatures in mantle xenoliths from northeastern North China
54
55 Craton. *Lithos* **149**, 79–90.

- 1
2
3 Tang Y. J., Zhang H. F., Deloule, E., Su, B. X., Ying J. F., Santosh, M. & Xiao Y. (2014).
4
5 Abnormal lithium isotope composition from the ancient lithospheric mantle beneath the
6
7 North China Craton. *Scientific Reports* **4**, 4274.
8
- 9 Tang, Y. J., Zhang, H. F., Nakamura, E., Moriguti, T., Kobayashi, K. & Ying, J. F. (2007).
10
11 Lithium isotopic systematics of peridotite xenoliths from Hannuoba, North China Craton:
12
13 implications for melt-rock interaction in the considerably thinned lithospheric mantle.
14
15 *Geochimica et Cosmochimica Acta* **71**, 4327–4341.
16
- 17 Tang, Y. J., Zhang, H. F. & Ying, J. F., 2010. A brief review of isotopically light Li – a feature
18
19 of the enriched mantle? *International Geology Review* **52**, 964–976.
20
- 21 Teng, F.-Z., McDonough, W. F., Rudnick, R. L., Dalpé, C., Tomascak, P. B., Chappell, B. W.
22
23 & Gao, S. (2004). Lithium isotopic composition and concentration of the upper continental
24
25 crust. *Geochimica et Cosmochimica Acta* **68**, 4167–4178.
26
27
- 28 Teng, F.-Z., McDonough, W. F., Rudnick, R. L. & Walker, R. J. (2006). Lithium isotopic
29
30 systematics of granites and pegmatites from the Black Hills, South Dakota. *American*
31
32 *Mineralogist* **91**, 1488–1498.
33
- 34 Tomascak, P. B., 2004. Developments in the understanding and application of lithium
35
36 isotopes in the Earth and Planetary Sciences. In: Johnson, C.M., Beard, B.L., Albarède, F.
37
38 (Eds.), *Geochemistry of non-traditional stable isotopes*: Mineralogical Society of America,
39
40 *Reviews in Mineralogy and Geochemistry* **55**, 153–195.
41
42
- 43 Tomascak, P. B., Langmuir, C. H., Le Roux, P. J. & Shirey, S. B. (2008). Lithium isotopes in
44
45 global mid-ocean ridge basalts. *Geochimica et Cosmochimica Acta* **72**, 1626–1637.
46
- 47 Tomascak, P. B., Ryan, J. G. & Defant, M. J. (2000). Lithium isotope evidence for light
48
49 element decoupling in the Panama subarc mantle. *Geology* **28**, 507–510.
50
- 51 Tomascak, P. B., Widom, E., Benton, L. D., Goldstein, S. L. & Ryan, J. G. (2002). The
52
53 control of lithium budgets in island arcs. *Earth and Planetary Science Letters* **196**, 227–
54
55 238.
56
57
58
59
60

- 1
2
3 Vielzeuf, D., Veschambre, M., Brunet, F. (2005). Oxygen isotope heterogeneities and
4 diffusion profile in composite metamorphic–magmatic garnets from the Pyrenees.
5 *American Mineralogist* **90**, 463–472.
6
7
8
9 Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S. & France-Lanord, C. (2008).
10 Quantifying Li isotope fractionation during smectite formation and implications for the Li
11 cycle. *Geochimica et Cosmochimica Acta* **72**, 780–792.
12
13
14
15 Vils, F., Pelletier, L., Kalt, A., Müntener, O. & Ludwig, T. (2008). The Lithium, Boron and
16 Beryllium content of serpentinized peridotites from ODP Leg 209 (Sites 1272A and
17 1274A): Implications for lithium and boron budgets of oceanic lithosphere. *Geochimica et*
18 *Cosmochimica Acta* **72**, 5475–5504.
19
20
21
22
23
24 Viti, C. & Mellini, M. (1998). Mesh textures and bastites in the Elba retrograde
25 serpentinites. *European Journal of Mineralogy* **10**, 1341–1359.
26
27
28
29 von Raumer, J., Bussy, F., Schaltegger, U., Schulz, B., & Stampfli, G. M. (2013). Pre-
30 Mesozoic Alpine basements – their place in the European Paleozoic framework.
31 *Geological Society of America Bulletin* **125**, 89–108.
32
33
34
35 Von Raumer, J., Stampfli, G. M., Arenas, R. & Martínez, S. S. (2015). Ediacaran to Cambrian
36 oceanic rocks of the Gondwana margin and their tectonic interpretation. *International*
37 *Journal of Earth Sciences* **104**, 1107–1121.
38
39
40
41
42
43
44
45
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50
51
52
53
54
55
56
57
58
59
60
- Wan, H., Sun, H., Liu, H. & Xiao, Y. (2017). Lithium isotopic geochemistry in subduction
zones: retrospects and prospects. *Acta Geologica Sinica* **91**, 688–710.
- Woodland, A. B., Seitz, H.-M., Altherr, R., Olker, B., Marschall, H. & Ludwig, T. (2002).
Lithium abundances in eclogite minerals: a clue to a crustal or mantle origin?
Contributions to Mineralogy and Petrology **144**, 128–129.
- Wunder, B., Deschamps, F., Watenphul, A., Guillot, S., Meixner, A., Romer, R. & Wirth, R.
(2010). The effect of chrysotile nanotubes on the serpentine-fluid Li-isotopic fractionation.
Contributions to Mineralogy and Petrology **159**, 781–790.

- 1
2
3 Wunder, B., Meixner, A., Romer, R. L. & Heinrich, W. (2006) Temperature-dependent
4 isotopic fractionation of lithium between clinopyroxene and high-pressure hydrous fluids.
5 *Contributions to Mineralogy and Petrology* **151**, 112–120.
6
7
8
9 Wunder, B., Meixner, A., Romer, R. L. & Jahn, S. (2011). Li-isotope fractionation between
10 silicates and fluids: pressure dependence and influence of the bonding environment.
11 *European Journal of Mineralogy* **23**, 333–342.
12
13
14 Wunder, B., Meixner, A., Romer, R. L., Feenstra, A., Schettler, G. & Heinrich, W. (2007).
15 Lithium isotope fractionation between Li-bearing staurolite, Li-mica and aqueous fluids: an
16 experimental study. *Chemical Geology* **238**, 277–290.
17
18
19
20
21
22 Xiao, Y., Hoefs, J., Hou, Z., Simon, K. & Zhang, Z. (2011). Fluid/rock interaction and mass
23 transfer in continental subduction zones: constraints from trace elements and isotopes (Li,
24 B, O, Sr, Nd, Pb) in UHP rocks from the Chinese Continental Scientific Drilling Program,
25 Sulu, East China. *Contributions to Mineralogy and Petrology* **162**, 797–819.
26
27
28
29
30
31 You, C. F., Castillo, P. R., Gieskes, J. M., Chan, L. H. & Spivack, A. J. (1996). Trace element
32 behavior in hydrothermal experiments: Implications for fluid processes at shallow depths
33 in subduction zones. *Earth and Planetary Science Letters* **140**, 41–52.
34
35
36
37
38 Zack, T., Tomascak, P. B., Rudnick, R. L., Dalpe, C. & McDonough, W. F. (2003). Extremely
39 light Li in orogenic eclogites: the role of isotope fractionation during dehydration in
40 subducted oceanic crust. *Earth and Planetary Science Letters* **208**, 279–290.
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Figure 1. (a) General sketch of the Variscan Belt in Western Europe (after Berger et al., 2005; Ballèvre et al., 2014). The Limousin ophiolite and the Ile de Groix HP terrane are parts of the Middle Allochthon domain and belong to the series of ophiolites recognised along the Galicia-Brittany-French Massif Central suture zone. The latter was interpreted as the remnant of a narrow ocean between Gondwana and Armorica (Matte, 2001) or a late-Cambrian active margin setting along the Gondwana (von Raumer et al., 2015). (b) Geological map of the studied area in the Limousin ophiolite (modified after Berger et al., 2005, 2010a, 2010b). (c) Geological map of the Ile de Groix (after Audren et al., 1993; Bosse et al., 2002; El Korh et al., 2009, 2013). *The beach “Plage des Grands Sables” has moved with the oceanic currents. FMC: French Massif Central; VM: Vosges Massif; BF: Black Forest; LC: Lizard Complex; AM: Armorican Massif; Py: Pyrénées; ECM: External Crystalline Massifs of the Alps; RM: Rhenish Massif; RHZ: Rheno-Hercynian zone; STZ: Saxo-Thuringian zone; MZ: Moldanubian zone.

Figure 2. Photomicrographs of studied samples from the Limousin ophiolite (a–d) and Ile de Groix HP–LT terrane (e–f) in plane-polarised light. (a) Typical assemblage of serpentine, spinel, chlorite and tremolite in the serpentinite LAU2 from Saint-Laurent; (b) Serpentinite CLUZ6 from Le Cluzeau composed of serpentine, spinel, chlorite and tremolite, with relicts of olivine and pyroxene; (c) Fine grained and slightly foliated amphibolite CLUZ1 consisting of hornblende and plagioclase; (d) Plagioclase–amphibole symplectite around a hornblende aggregate in isotropic amphibolite CLUZ 4; (e) Garnet–omphacite–glaucophane–clinozoisite assemblage in eclogite GR 29. Partial retrogression is evidenced by titanite overgrowths around rutile, barroisite overgrowths on the rims of glaucophane and by the presence of barroisite–albite symplectites on the rims of omphacite; (f) Retrogression is more pronounced in eclogite GR 24a: rutile is totally replaced by titanite, barroisite–albite symplectites along omphacite are well developed and garnet is partially altered in chlorite + iron hydroxides.

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3 Quartz veins parallel to the main schistosity are also present. Mineral abbreviations are from
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5 Kretz (1983). "SympI" = Albite and barroisite symplectites.
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9 Figure 3. Variation in Li abundances in whole rocks and minerals from the Limousin ophiolite.
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11 The Li composition of fresh MORB is from Ryan & Langmuir (1987) and Niu & Batiza (1997).
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13 WR: whole rock
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17 Figure 4. Variation of the mean $\delta^7\text{Li}$ values relative to Li abundances in the minerals from the
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21 tremolite and hornblende, while amphibole in the UHP eclogite L04-143 is pargasite. Error
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23 bars are 2σ SD. The Li elemental composition of fresh MORB is from Ryan & Langmuir
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25 (1987) and Niu & Batiza (1997). The Li isotopic composition is from Chan et al. (2002),
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27 Bouman et al. (2004) and Tomascak et al. (2008).
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32 Figure 5. Variation in Li abundances in whole rocks and minerals from the Ile de Groix HP
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34 terrane. The Li composition of fresh MORB is from Ryan & Langmuir (1987) and Niu & Batiza
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36 (1997). The Li composition of altered MORB is from Chan et al. (2002), Bouman et al.,
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38 (2004) and Coogan et al. (2017). BS: blueschists; Ecl: eclogites; GS: greenschists; MS:
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40 micaschists; Micas: phengite + paragonite
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45 Figure 6. (a) Li isotopic composition of the metabasites and micaschists of the Ile de Groix.
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47 The $\delta^7\text{Li}$ values decrease from the blueschist facies to the eclogite facies. During
48
49 retrogression, the $\delta^7\text{Li}$ values increase with the intensity of rehydration. (b) $\delta^7\text{Li}$ values vs. Li
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51 abundances. No correlation is observed with the variation of the metamorphic facies. Error
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53 bars for $\delta^7\text{Li}$ values are 2σ SE, as the whole rock $\delta^7\text{Li}$ is calculated by averaging replicate
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55 analyses of the same sample solution.
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3 Figure 7. Variations in Li content and isotopic composition of glaucophane and omphacite
4 from the metabasites of the Ile de Groix. (a) Mean $\delta^7\text{Li}$ vs. Lithium contents. Mean Li
5 abundances were calculated using the LA-ICPMS data. Mean $\delta^7\text{Li}$ values correspond to
6 unweighted average of all in-situ $\delta^7\text{Li}$ values measured by SIMS in each sample. Error bars
7 are 2σ SD. The dark grey field represents the Li composition of fresh MORB (Ryan &
8 Langmuir, 1987; Niu & Batiza, 1997; Chan et al., 2002; Bouman et al., 2004; Tomascak et
9 al., 2008) (b–f) Core-to-rim variations of the $\delta^7\text{Li}$ values and Li contents in (b–c) blueschists
10 and, (d–f) eclogites. The dotted lines and grey field give the corresponding whole rock and
11 2σ SE values. Individual Li abundances were calculated based on the mean Li contents
12 obtained by LA-ICPMS and ^{6+7}Li intensities, as follows:

$$C(\text{Li})_i^{\text{SIMS}} = [I(\text{Li})_i^{\text{SIMS}} \times C(\text{Li})_{\text{mean}}^{\text{LA-ICPMS}}] / C(\text{Li})_{\text{mean}}^{\text{SIMS}}$$

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28 Figure 8. Calculated Li isotope composition of fluids in equilibrium with rocks and minerals in
29 the rocks from: (a) the Limousin ophiolite and, (b) the Ile de Groix. $\delta^7\text{Li}_{\text{fluid}}$ calculations were
30 made using the clinopyroxene-fluid fractionation factors for amphiboles, omphacite and
31 whole rocks, and the mica-fluid fractionation factor for serpentine (Wunder et al., 2006,
32 2011): $\delta^7\text{Li}_{\text{fluid}} = \delta^7\text{Li}_{\text{sample}} - \Delta^7\text{Li}_{\text{mineral-fluid}}$. The 2σ uncertainties, represented by the error bars,
33 are identical to those of the mean $\delta^7\text{Li}$ of minerals and whole rocks employed for calculation.
34 (a) The $\delta^7\text{Li}$ values of the fluids in equilibrium with serpentine were calculated for 350°C and
35 500°C, as the temperature of hydrothermal alteration is not precisely constrained. (b) It is
36 assumed that glaucophane rims have formed at a temperature 50°C higher than
37 glaucophane core.
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Table 1. Provenance and mineral assemblage of the studied rocks

Sample	Rock type	Locality*	Mineralogical assemblage**	Ref.***
<i>Limousin</i>				
LAU-1	Serpentinite (dunite)	Saint-Laurent	Serp-chl-spl-± ol-± amph (tr)-Fe ox	-
LAU-2	Serpentinite (dunite)	Saint-Laurent	Serp-chl-spl-± amph (tr)-Fe ox	-
CLUZ-6	Serpentinite (harzburgite or troctolite)	Le Cluzeau	Serp-amph-chl-spl-ol-opx-Fe ox-Fe sulf	-
FLOT-1	Serpentinite (harzburgite or troctolite)	La Flotte	Serp-amph (tr)-chl-± ol-Fe ox	-
FLOT-2a	Serpentinite (harzburgite or troctolite)	La Flotte	Serp-spl-ol-Fe ox	-
FLOT-2b	Serpentinite (harzburgite or troctolite)	La Flotte	Serp-chl-Fe ox	-
CLUZ-1	Amphibolite	Le Cluzeau	Amph-plag-chl-Fe ox	-
CLUZ-1a	Amphibolite	Le Cluzeau	Amph-plag-chl-Fe ox	-
CLUZ-4	Amphibolite	Le Cluzeau	Amph-plag-chl-ttn-Fe ox-Fe sulf	-
CLUZ-5	Amphibolite	Le Cluzeau	Amph-plag-chl-Fe ox	-
L04-143	Eclogite	E of Saint-Laurent	Grt-omph-zo-amph-rt-ilim	[1]
<i>Île de Groix</i>				
GR 02	Blueschist	Les Sables Rouges	Grt-gln-barr-ep-phe-qtz-ttn-rt-ap-◇ lws	[2]
GR 04	Blueschist	Beg er Skeul	Grt-gln-barr-ep-phe-qtz-ttn-rt-ap-◇ lws	[3]
GR 11b	Blueschist	Les Saisies	Grt-gln-barr-ep-phe-chl-ab-ttn-Fe ox (mt)-◇ lws	[2]
GR 12b	Blueschist	Porh Roëd	Grt-act-ep-phe-chl-ab-ttn-ap-qtz-Fe ox (hm)-◇ lws	[2]
GR 25a	Blueschist	Port Lay	Grt-gln-ep-phe-act-qtz-chl-ttn-Fe ox (mt)-◇ lws	[2]
GROA 56	Blueschist	Lumiaret	Grt-gln-barr-ep-phe-qtz-ttn-chl-ap-Fe ox (hm, mt)	[3]
GR 21	Eclogite	Poskedoul	Grt-gln-omph-barr-ep-phe-chl-qtz-Fe ox (hm)	[2]
GR 24a	Eclogite	Plage du Rolaz	Grt-gln-barr-ep-omph-phe-chl-qtz-Fe ox (hm, mt)	[2]
GR 29	Eclogite	Porh Giguéou	Grt-gln-omph-barr-ep-phe-chl-qtz-ap-rt-ttn-± ◇ lws	[2]
GR 06a	Greenschist	S of Locqueltas	Chl-ep-ab-phe-barr-qtz-Fe ox (mt)-Fe hydrox	[3]
GR 23	Greenschist	Côte d'Héno	Grt-ep-chl-ab-barr-phe-act-gln-ttn-rt-Fe ox (mt) - ◇ lws	[2]
GR 25b	Greenschist	Port Lay	Grt-ep-chl-gln-barr-act-ab-qtz-ap-ttn-rt-Fe ox (mt)	[2]
GROA 43	Ab-/cc-greenschist	Biléric	Chl-Ab-cc-phe-ilim-czo-Fe ox (mt)	[3]
GROA 52	Ab-/cc-greenschist	Gadoéric	Ab-chl-qtz-ep-act-barr-cc-ttn-Fe ox (mt)	[4]
GROA 110	Micaschist (BS)	W of Porh Morvil	Cld-grt-phe-qtz-ap-pg-rt-chl-Fe ox (hm)-tur	[3]
GROA 111a	Micaschist (BS)	Les Saisies	Gln-ep (± piemt)-phe-pg-qtz-ap-± ab-± ilm	[3]
GR 26b	Micaschist (GS)	Port Melin	Grt-phe-ep-qtz-chl-ab-ttn-ap-Fe ox (mt)-tur	[2]
GROA 104	Micaschist (GS)	Côte d'Héno	Grt-phe-pg-gln-chl-qtz-ap-act-rt -ilm	[4]

BS: blueschist; GS: greenschist; ◇ lws: pseudomorphs after lawsonite

* see Figure 1

** The mineral abbreviations are from Kretz (1983)

*** [1] Berger et al., 2010; [2] El Korh et al., 2009; [3] El Korh et al., 2013; [4] El Korh et al., 2011

1
2
3 Table 2. Lithium abundances
4 in the rocks from the Limousin
5 ophiolite (in ppm)

6 Samples	7 Li
8 <i>Serpentinites</i>	
9 LAU-1	2.4
10 LAU-2	4.6
11 CLUZ-6	1.9
12 FLOT-2a	3.0
13 FLOT-2b	0.9
14 <i>Amphibolites</i>	
15 CLUZ-1	5.5
16 CLUZ-1a	8.2
17 CLUZ-4	3.1
18 CLUZ-5	6.6
19 <i>UHP zoisite-eclogite</i>	
20 L04-143	2.3

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Table 3. In-situ SIMS measurements of mineral Li contents (in ppm) and isotopic composition (in ‰) for the Limousin ultrabasic and basic rocks. Calculated Li fractionation factors ($\Delta^7\text{Li}$, in ‰) are given for mineral-mineral pairs.

	Li (ppm)				$\delta^7\text{Li}$					$\Delta^7\text{Li}$			
	min-max	mean	2 σ	SD	n	min	max	mean	2 σ	SD	n	mean	2 σ^*
<i>Serpentinite LAU2</i>													
chl	0.67–1.0	0.83	0.32		6								
spl	0.27–2.6	1.5	3.4		2								
Fe-rich serp	1.3–6.7	3.2	3.4		13	-10.4	-6.7	-8.7	3.1		7		
Mg-rich serp	0.7–2.5	1.4	0.9		19	-12.4	-3.5	-8.9	5.2		10		
Fe-rich serp–Mg-rich serp												+0.2	6.0
<i>Serpentinite CLUZ6</i>													
chl	0.45–0.75	0.54	0.29		2								
amph	1.4–3.5	2.5	3.0		4	+4.5	+9.5	+6.6	4.6		4		
Fe-rich serp	1.2–8.2	4.5	4.5		10	-4.2	+1.3	-2.2	3.0		12		
Mg-rich serp	0.76–3.6	2.0	1.2		22	-0.7	+7.0	+4.2	3.5		21		
Fe-rich serp–Mg-rich serp												-6.3	4.6
Fe-rich serp–amph												-8.8	5.5
Mg-rich serp–amph												-2.5	5.8
<i>Serpentinite FLOT1</i>													
amph	1.1–1.9	1.3	0.8		4								
chl	0.24–0.60	0.42	0.51		2								
Fe-rich serp	4.2	4.2	–		1								
Mg-rich serp	0.77–2.2	1.2	1.0		9								
<i>Serpentinite FLOT2a</i>													
ol	1.5–3.0	2.4	0.8		10	+3.1	+8.8	+6.3	2.9		24		
Mg-rich serp	0.33–1.2	0.5	0.4		27	-9.6	+2.8	-2.5	5.5		22		
spl	2.1–2.3	2.2	0.3		2								
Mg-rich serp–ol												-8.8	6.3
<i>Amphibolite CLUZ1</i>													
amph	1.7–8.4	5.3	3.5		14	-0.2	+6.9	+3.5	4.4		17		
altered amphib	1.3–3.5	2.4	3.1		2	+9.4	+10.1	+9.8	0.9		2		
plag	0.11–1.0	0.44	1.02		3								
<i>Amphibolite CLUZ4</i>													
amph	1.4–11	3.5	6.2		8	+2.9	+18.2	+12.5	9.6		13		
plag	0.09–0.94	0.39	0.60		8								
<i>UHP eclogite L04-143</i>													
amph	1.2–25	9.5	12.6		12	+12.2	+24.2	+18.7	7.2		13		
omph	1.5–10	4.2	6.6		19	+16.7	+26.3	+21.9	5.0		21		
grt	0.15–0.90	0.36	0.39		8								
zo	0.03–0.38	0.11	0.19		12								
rt	0.19–5.7	3.0	7.8		2								
amph–omph												-3.3	8.7

* Propagated 2 σ uncertainties

Table 4. Lithium contents (in ppm) and MC-ICPMS isotopic data (in ‰) of the rocks from the Ile de Groix

	Li	$\delta^7\text{Li}$	2σ SE*	n**
<i>Blueschists</i>				
GR 02	45	0.74	–	1
GR 04	16.2	n.a.	–	
GR 11b	70	-0.60	0.23	3
GR 12b	124	n.a.	–	
GR 25a	39	-0.60	0.10	3
GROA 56	55	n.a.	–	
<i>Eclogites</i>				
GR 21	18	-4.12	0.38	3
GR 24a	28	-2.46	0.12	3
GR 29	102	-4.75	0.26	3
<i>Greenschists</i>				
GR 06a	74	3.16	0.59	3
GR 23	58	-4.51	0.51	3
GR 25b	37	-0.14	0.52	3
GROA 43	62	n.a.	–	
GROA 52	45	1.45	0.39	2
<i>Micaschists</i>				
GROA 110	15	0.18	0.43	3
GROA 111a	48	-1.68	0.73	3
GR 26b	50	n.a.	–	
GROA 104	52	n.a.	–	

* 2σ standard error (i.e. 2σ standard deviations of the mean) calculated on the basis of replicate analyses of the same sample solution

** n = number of replicates for Li isotope measurements;

Table 5. Lithium abundances in the metamorphic minerals from the rocks of the Ile de Groix measured by LA-ICPMS (in ppm)

Mineral	Sample	Li abundances		mean	2 σ SD
		this study	[1, 2]*		
<i>Prograde minerals in metabasites</i>					
ap	GR29	–	2.6	2.6	–
ap	GR25b	–	0.49–0.58	0.53	0.12
ep	GR02	–	0.78–3.4	2.3	19
ep	GR11b	–	4.8–9.4	6.6	4.9
ep	GR12b	2.0–41	0.67–26	9.9	22
ep	GR25a	–	1.6–9.7	5.8	7.4
ep	GR21	–	1.2–5.1	3.1	2.7
ep	GR24a	–	2.6–5.7	4.1	2.7
ep	GR29	1.3–10	5.6	3.9	17
ep	GR23	17–31	1.3–22	7.9	14
ep	GR25b	–	2.2–7.2	3.7	3.5
grt	GR02	–	0.47–1.1	0.72	0.52
grt	GR21	–	0.49–0.63	0.57	0.15
grt	GR29	1.5	–	1.5	–
grt	GR23	–	0.86–1.3	1.1	0.5
grt	GR25b	–	0.57–1.5	0.95	1.03
gln	GR02	84–103	–	94	28
gln	GR11b	–	209–319	270	106
gln	GR12b	295–401	–	360	253
gln	GR25a	67–90	–	77	35
gln	GR21	–	81–215	115	91
gln	GR24a	88–113	48–74	72	46
gln	GR29	110–295	–	179	142
gln	GR25b	77–252	121–129	144	119
omph	GR21	–	41–61	47	14
omph	GR24a	32–33	27–31	31	5
omph	GR29	111–145	90–118	107	28
phe	GR02	–	16	16	–
phe	GR11b	–	26–39	32	8.0
phe	GR12b	–	9–33	23	25
phe	GR21	–	21–33	26	9.2
phe	GR24a	–	4.4–9.1	6.8	3.9
phe	GR23	25–27	41–46	37	20
phe	GR25b	–	5.8–7.1	6.5	1.8
ttn	GR02	–	1.3–8.2	4.6	6.1
ttn	GR11b	–	7.3	7.4	–
ttn	GR12b	–	17	17	–
ttn	GR25a	1.6–10	–	5.9	12
ttn	GR24a	–	4.8–7.0	5.9	1.8
ttn	GR23	–	14–15	15	1
ttn	GR25b	–	2.9	2.9	–
<i>Retrograde minerals in metabasites</i>					
ab	GR29	174–212	–	193	53
ab	GR25b	–	41	41	–
act	GR12b	5.7–8.1	–	6.7	2.3
act	GR25b	–	2.0–19	7.7	11.8
barr	GR11b	–	5.1–9.4	7.3	6.1
barr	GR21	–	9	9	–
barr	GR24a	–	3.1–9.6	6.4	9.2
chl	GR11b	–	69–182	107	87
chl	GR12b	106–126	126–127	119	17
chl	GR25a	27–33	–	30	8
chl	GR25b	13–50	46–61	43	33
<i>Minerals in micaschists</i>					
cld	GROA110	–	0.31–1.2	0.75	1.24
phe	GROA110	–	20–26	22	4.0
phe	GR26b	33–52	38–61	45	15
pg	GROA110	–	28	28	–
grt	GR26b	–	3.1–5.0	3.9	2.0
chl	GR26b	180	150–185	170	28
ep	GR26b	–	4.2	4.2	–
ap	GR26b	–	2.8	2.8	–
ttn	GR26b	–	3.6	3.6	–
tur	GR26b	47	19–27	29	25

* Data from: [1] El Korh et al. (2009); [2] El Korh (2010)

Table 6. Lithium isotopic composition measured by SIMS in the metabasites of the Ile de Groix (in ‰). Calculated Li fractionation factors ($\Delta^7\text{Li}$, in ‰) are given for mineral-mineral and whole rock–mineral pairs. WR: whole rock

	bulk $\delta^7\text{Li}^*$					core			rim			$\Delta^7\text{Li}$	
	min	max	mean	2 σ SD	n	mean	2 σ SD	n	mean	2 σ SD	n	mean	2 σ
SIMS data													
<i>Blueschist GR02</i>													
gln	-7.1	+8.8	+1.3	8.5	33	+3.8	6.1	20	-2.6	4.9	13		
WR–gln												-0.5	8.5
<i>Blueschist GR25a</i>													
gln	-4.8	+5.2	+1.3	4.3	34	+2.5	3.4	18	-0.1	3.6	16		
WR–gln												-1.9	4.3
<i>Eclogite GR21</i>													
gln	-8.0	+0.8	-3.6	6.5	13	-1.1	3.4	7	-6.6	2.8	6		
omph	-7.2	+3.3	-3.5	5.2	17	-2.9	7.5	7	-3.9	3.0	10		
WR–gln												-0.5	6.5
WR–omph												-0.6	5.2
gln–omph												-0.1	8.3
gln rim–omph												-3.1	5.9
<i>Eclogite GR24a</i>													
gln	-8.6	+1.4	-2.3	4.4	26	-1.1	3.2	14	-3.8	3.8	12		
omph	-22.4	-9.0	-15.6	9.4	12	-10.9	6.0	4	-17.9	7.0	8		
barr	-24.9	-6.7	-15.4	18.2	3	–	–		–	–			
WR–gln												-0.1	4.4
WR–omph												+13.1	9.4
gln–omph												+13.2	10.4
gln rim–omph												+11.7	8.3
omph–barr												-0.1	20.5
<i>Eclogite GR29</i>													
gln	-6.2	-1.9	-4.8	2.2	14	-4.5	2.9	7	-5.0	1.3	7		
omph	-11.2	+2.4	-4.5	6.9	15	-3.0	7.2	8	-6.2	5.5	6		
barr	-8.4	-2.0	-5.6	6.5	3	–	–		–	–			
WR–gln												+0.0	2.3
WR–omph												-0.2	6.9
gln–omph												-0.2	7.3
gln rim–omph												-0.5	5.9
omph–barr												+1.0	9.5
MC-ICPMS data													
<i>Eclogite GR29</i>													
gln			-4.8	0.6	4								
omph			-4.5	2.3	3								

* Mean $\delta^7\text{Li}$ values for bulk mineral correspond to unweighted average of all measured data, without considering core/rim proportion.

Table 7. Calculated Li isotopic composition of fluids in equilibrium with the minerals of the Limousin ultrabasic and basic rocks (in ‰)

	serp-H ₂ O		amph-H ₂ O		omph-H ₂ O									
	350°C	2σ	500°C	2σ	570°C	2σ	600°C	2σ	750°C	2σ	600°C	2σ		
<i>Serpentine LAU2</i>														
Fe-rich serp	-6.15	3.07	-7.55	3.07										
Mg-rich serp	-6.37	5.21	-7.77	5.21										
<i>Serpentine CLUZ6</i>														
amph			+10.12	4.63										
Fe-rich serp	+0.35	2.99	-1.05	2.99										
Mg-rich serp	+6.70	3.48	+5.30	3.48										
<i>Serpentine FLOT2a</i>														
Mg-rich serp	-0.01	5.51	-1.41	5.51										
<i>Amphibolite CLUZ1</i>														
amph			+6.44	4.38										
altered amph			+12.72	0.94										
<i>Amphibolite CLUZ4</i>														
amph			+15.45	9.63										
<i>UHP eclogite L04-143</i>														
amph			+22.13	7.18										
omph											+21.45	7.18	+24.72	4.99

2σ uncertainties correspond to the 2σ standard deviations calculated for the mean δ⁷Li values of the different mineral generations

Table 8. Calculated Li isotopic composition of fluids in equilibrium with glaucophane, omphacite and whole metabasic rocks from the Ile de Groix (in ‰)

	whole rock-H ₂ O			gln-H ₂ O			omph-H ₂ O		
	400°C	450°C	500°C	450°C	500°C	550°C	450°C	500°C	550°C
	2σ	2σ	2σ	2σ	2σ	2σ	2σ	2σ	2σ
<i>Blueschists</i>									
GR02			+4.2		+7.7		+0.9	4.9	
GR11b			+2.9		6.1				
GR25a			+2.9		6.1		+3.4	3.6	
			0.1		3.4				
<i>Eclogites</i>									
GR 21						-1.0	+2.4	3.4	-3.5
GR 24a						+0.7	+2.4	3.2	-0.7
GR 29						-1.6	-1.0	2.9	-1.9
						0.4			2.8
						0.1			3.8
						0.3			1.3
									-0.4
									5.2
									-12.4
									9.4
									-1.4
									6.9
<i>Greenschists</i>									
GR 23		-0.6	0.6						
GR 25b		+3.8	0.5						
GR 06a		+7.1	0.5						
GROA 52	+5.8	0.4							
<i>Micaschists</i>									
GROA 110			+3.7						
GROA 111a			+1.8						
			0.4						
			0.7						

2σ uncertainties correspond to the 2σ standard deviations calculated for the mean δ⁷Li values of the different mineral generations for fluids in equilibrium with glaucophane and omphacite, and to the 2σ standard error of the whole rock δ⁷Li values for fluids in equilibrium with the whole rock.

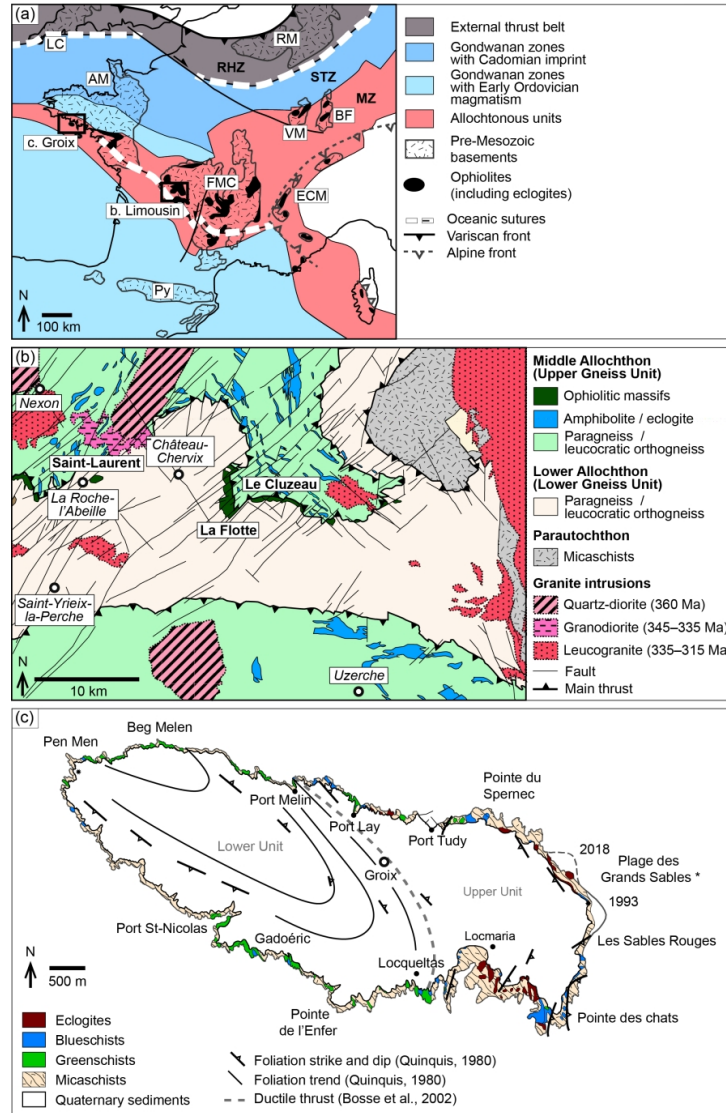


Figure 1. (a) General sketch of the Variscan Belt in Western Europe (after Berger et al., 2005; Ballèvre et al., 2014). The Limousin ophiolite and the Ile de Groix HP terrane are parts of the Middle Allochthon domain and belong to the series of ophiolites recognised along the Galicia-Brittany-French Massif Central suture zone. The latter was interpreted as the remnant of a narrow ocean between Gondwana and Armorica (Matte, 2001) or a late-Cambrian active margin setting along the Gondwana (von Raumer et al., 2015). (b) Geological map of the studied area in the Limousin ophiolite (modified after Berger et al., 2005, 2010a, 2010b). (c) Geological map of the Ile de Groix (after Audren et al., 1993; Bosse et al., 2002; El Korh et al., 2009, 2013). *The beach "Plage des Grands Sables" has moved with the oceanic currents. FMC: French Massif Central; VM: Vosges Massif; BF: Black Forest; LC: Lizard Complex; AM: Armorican Massif; Py: Pyrénées; ECM: External Crystalline Massifs of the Alps; RM: Rhenish Massif; RHZ: Reno-Hercynian zone; STZ: Saxo-Thuringian zone; MZ: Moldanubian zone.

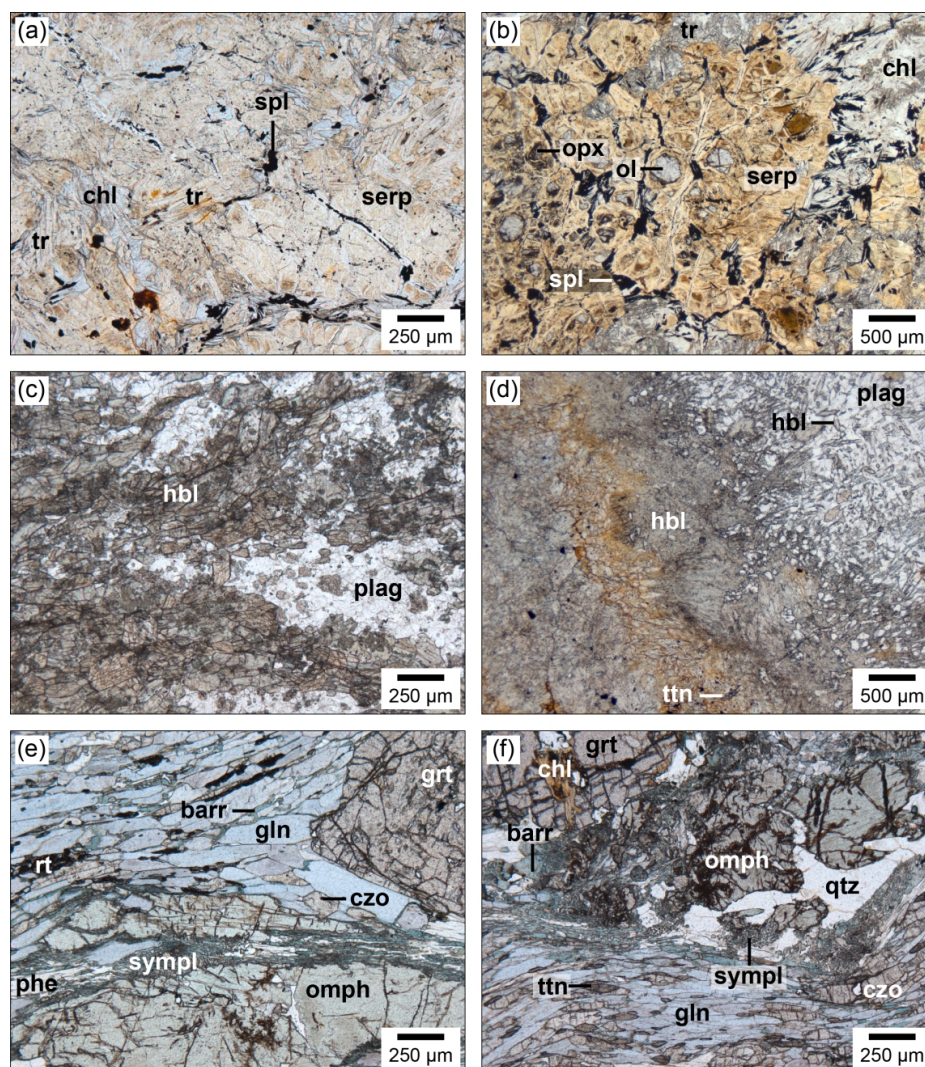


Figure 2. Photomicrographs of studied samples from the Limousin ophiolite (a–d) and Ile de Groix HP–LT terrane (e–f) in plane-polarised light. (a) Typical assemblage of serpentine, spinel, chlorite and tremolite in the serpentinite LAU2 from Saint-Laurent; (b) Serpentinite CLUZ6 from Le Cluzeau composed of serpentine, spinel, chlorite and tremolite, with relicts of olivine and pyroxene; (c) Fine grained and slightly foliated amphibolite CLUZ1 consisting of hornblende and plagioclase; (d) Plagioclase–amphibole symplectite around a hornblende aggregate in isotropic amphibolite CLUZ 4; (e) Garnet–omphacite–glaucophane–clinozoisite assemblage in eclogite GR 29. Partial retrogression is evidenced by titanite overgrowths around rutile, barrosite overgrowths on the rims of glaucophane and by the presence of barrosite–albite symplectites on the rims of omphacite; (f) Retrogression is more pronounced in eclogite GR 24a: rutile is totally replaced by titanite, barrosite–albite symplectites along omphacite are well developed and garnet is partially altered in chlorite + iron hydroxides. Quartz veins parallel to the main schistosity are also present. Mineral abbreviations are from Kretz (1983). "SympI" = Albite and barrosite symplectites.

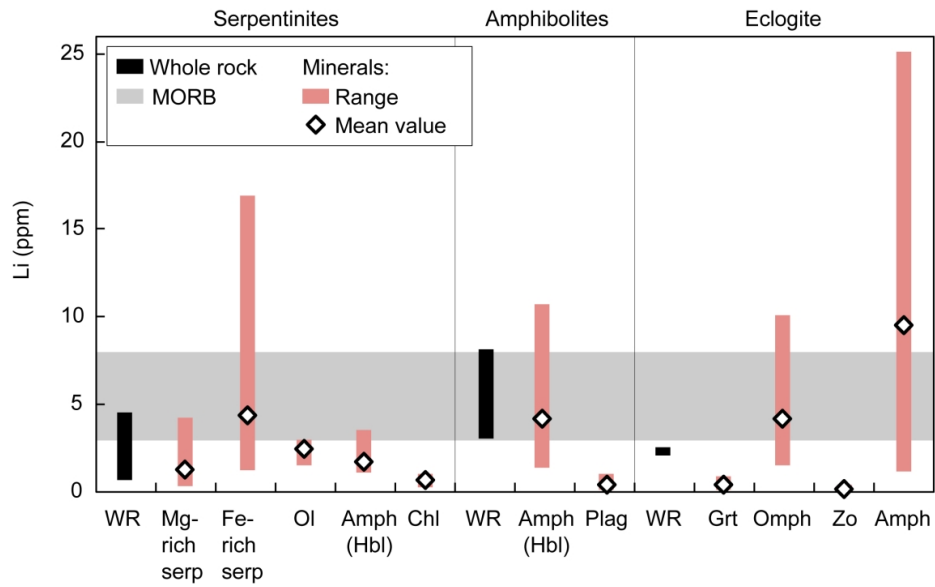


Figure 3. Variation in Li abundances in whole rocks and minerals from the Limousin ophiolite. The Li composition of fresh MORB is from Ryan & Langmuir (1987) and Niu & Batiza (1997). WR: whole rock

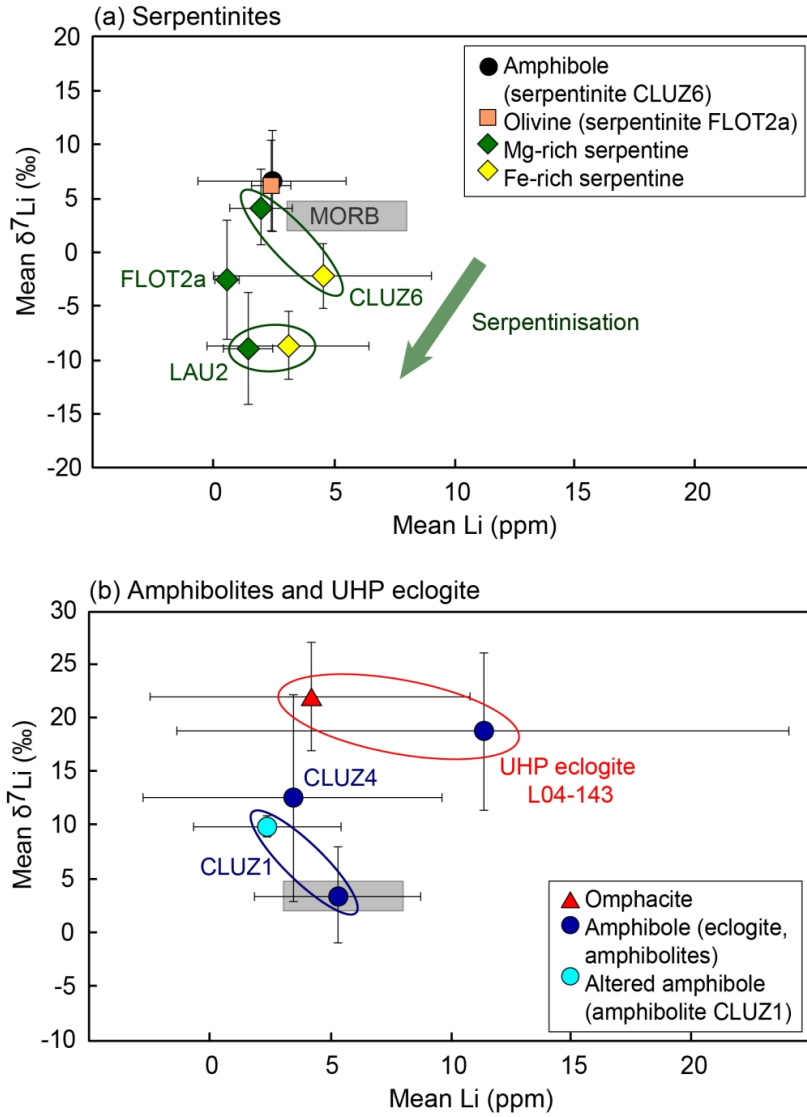


Figure 4. Variation of the mean $\delta^7\text{Li}$ values relative to Li abundances in the minerals from the rocks of the Limousin ophiolite. Amphibole in serpentinites and amphibolites is mainly tremolite and hornblende, while amphibole in the UHP eclogite L04-143 is pargasite. Error bars are 2σ SD. The Li elemental composition of fresh MORB is from Ryan & Langmuir (1987) and Niu & Batiza (1997). The Li isotopic composition is from Chan et al. (2002), Bouman et al. (2004) and Tomascak et al. (2008).

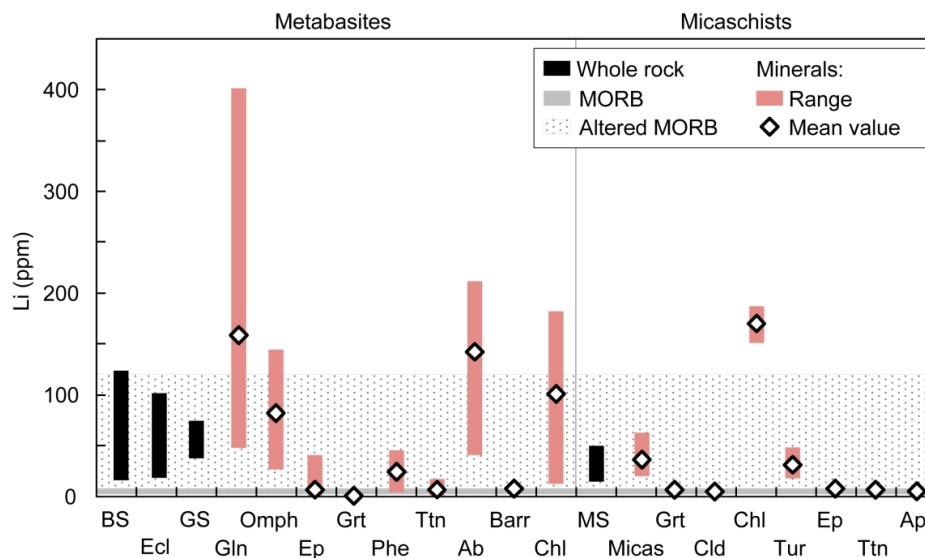


Figure 5. Variation in Li abundances in whole rocks and minerals from the Ile de Groix HP terrane. The Li composition of fresh MORB is from Ryan & Langmuir (1987) and Niu & Batiza (1997). The Li composition of altered MORB is from Chan et al. (2002), Bouman et al., (2004) and Coogan et al. (2017). BS: blueschists; Ecl: eclogites; GS: greenschists; MS: micaschists; Micas: phengite + paragonite

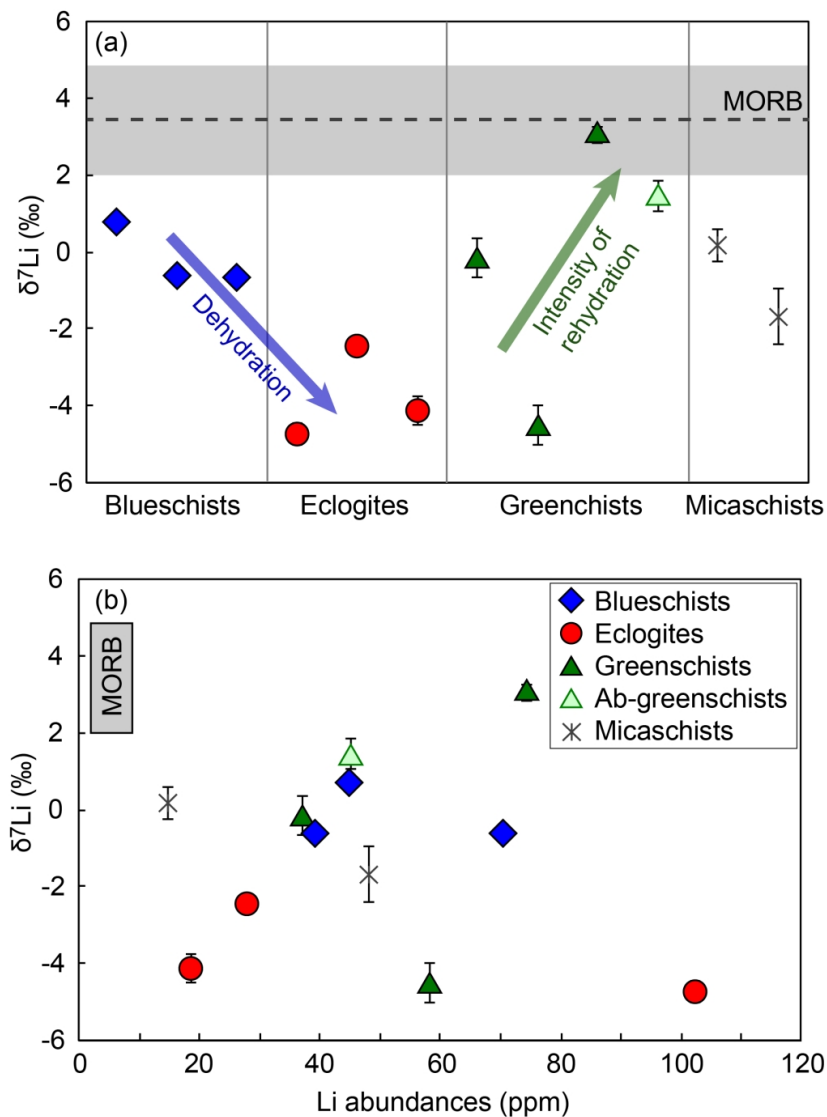


Figure 6. (a) Li isotopic composition of the metabasites and micaschists of the Ile de Groix. The $\delta^7\text{Li}$ values decrease from the blueschist facies to the eclogite facies. During retrogression, the $\delta^7\text{Li}$ values increase with the intensity of rehydration. (b) $\delta^7\text{Li}$ values vs. Li abundances. No correlation is observed with the variation of the metamorphic facies. Error bars for $\delta^7\text{Li}$ values are 2σ SE, as the whole rock $\delta^7\text{Li}$ is calculated by averaging replicate analyses of the same sample solution.

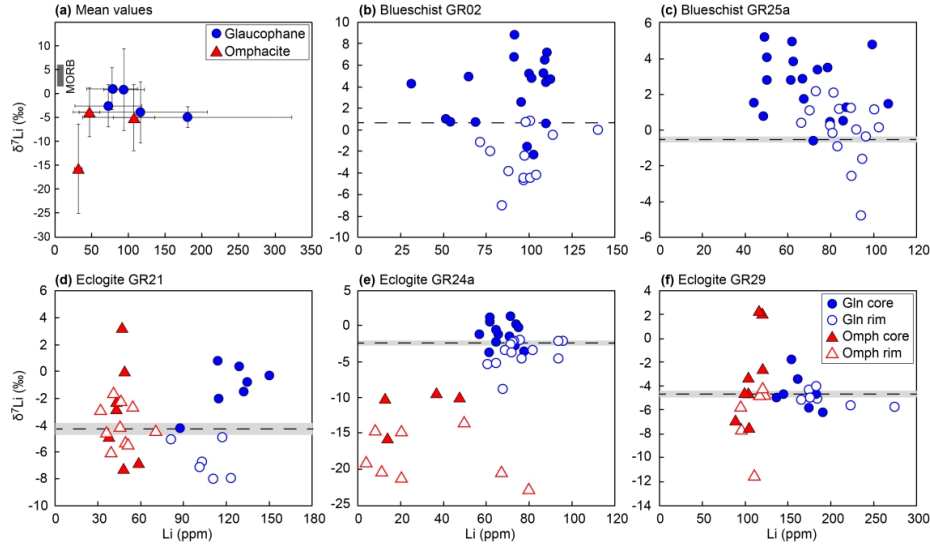


Figure 7. Variations in Li content and isotopic composition of glaucophane and omphacite from the metabasites of the Ile de Groix. (a) Mean $\delta^7\text{Li}$ vs. Lithium contents. Mean Li abundances were calculated using the LA-ICPMS data. Mean $\delta^7\text{Li}$ values correspond to unweighted average of all in-situ $\delta^7\text{Li}$ values measured by SIMS in each sample. Error bars are 2σ SD. The dark grey field represents the Li composition of fresh MORB (Ryan & Langmuir, 1987; Niu & Batiza, 1997; Chan et al., 2002; Bouman et al., 2004; Tomascak et al., 2008) (b–f) Core-to-rim variations of the $\delta^7\text{Li}$ values and Li contents in (b–c) blueschists and, (d–f) eclogites. The dotted lines and grey field give the corresponding whole rock and 2σ SE values. Individual Li abundances were calculated based on the mean Li contents obtained by LA-ICPMS and ^{6+7}Li intensities, as follows: $C(\text{Li})_i^{\text{SIMS}} = [I(\text{Li})_i^{\text{SIMS}} \times C(\text{Li})_{\text{mean}}^{\text{LA-ICPMS}}] / C(\text{Li})_{\text{mean}}^{\text{SIMS}}$

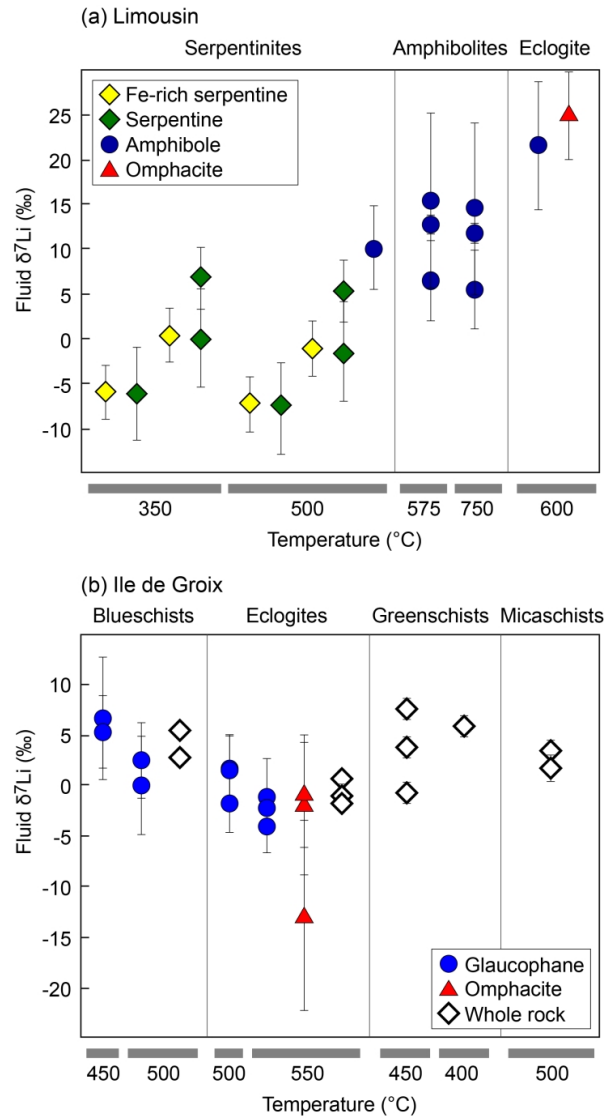


Figure 8. Calculated Li isotope composition of fluids in equilibrium with rocks and minerals in the rocks from: (a) the Limousin ophiolite and, (b) the Ile de Groix. $\delta^7\text{Li}_{\text{fluid}}$ calculations were made using the clinopyroxene-fluid fractionation factors for amphiboles, omphacite and whole rocks, and the mica-fluid fractionation factor for serpentine (Wunder et al., 2006, 2011): $\delta^7\text{Li}_{\text{fluid}} = \delta^7\text{Li}_{\text{sample}} - \Delta^7\text{Li}_{\text{mineral-fluid}}$. The 2σ uncertainties, represented by the error bars, are identical to those of the mean $\delta^7\text{Li}$ of minerals and whole rocks employed for calculation. (a) The $\delta^7\text{Li}$ values of the fluids in equilibrium with serpentine were calculated for 350°C and 500°C, as the temperature of hydrothermal alteration is not precisely constrained. (b) It is assumed that glaucophane rims have formed at a temperature 50°C higher than glaucophane core.