**Investigation of Ge and Ga exchange behaviour and Ge isotopic fractionation during
subduction zone metamorphism**

**Affé El Korh^{1*}, Béatrice Luais¹, Marie-Christine Boiron², Etienne Deloule¹, Damien
Cividini¹**

¹Centre de Recherches Pétrographiques et Géochimiques (CRPG), UMR 7358 CNRS-
Université de Lorraine, 15 rue Notre Dame des Pauvres, BP 20, F-54501 Vandœuvre-lès-
Nancy Cedex, France

²GeoRessources, Université de Lorraine, CNRS, UMR 7359, Boulevard des Aiguillettes, BP
70239, F-54506 Vandœuvre-lès-Nancy, France

*Corresponding author: elkorh@crpg.cnrs-nancy.fr;

Tel: + 33 3 83 59 42 00; Fax: + 33 3 83 51 17 98

Keywords: germanium; gallium; Ge isotopes; subduction; fluid-rock interactions; HP–LT
metamorphism

ABSTRACT

Germanium (Ge) and gallium (Ga) are slightly to moderately incompatible trace elements during magmatic processes and may be indicators of the nature of the mantle source. Because of their solubility in fluids, Ge and Ga are also geochemical tracers of various hydrothermal processes. Understanding high-pressure/low-temperature (HP–LT) recycling processes of Ge and Ga through fluid-mediated mass transfers in subduction zones can then allow discussing whether they can be source of geochemical heterogeneities in the mantle wedge. We have analysed Ge and Ga abundances and Ge isotope composition of a series of well-characterised HP–LT metabasites of mid-ocean ridge basalt (MORB) affinity and pelitic micaschists from the Ile de Groix (France), to determine Ge and Ga behaviour and Ge isotope fractionation during subduction zone metamorphism (SZM). Metabasites have Ge and Ga contents of 1.2–2.1 ppm and 17–22 ppm, respectively, typical of tholeiitic basalts. Garnet-bearing blueschists and eclogites have $\delta^{74}\text{Ge}$ values (+0.42 to +0.65‰) similar within error to that of tholeiitic basalts (+0.55 to +0.57‰; Luais, 2012).

Our study shows that during the prograde metamorphism, Ge and Ga abundances and $\delta^{74}\text{Ge}$ values do not vary from blueschists to eclogites, owing to the large stability field of Ge- and Ga-hosting minerals (epidote, garnet, titanite, amphiboles and omphacite) under varying P–T conditions. During the retrograde metamorphism, the slight decrease of the Ga content of c. 8% in greenschists (19 ± 1 ppm; 2σ) compared to HP rocks (21 ± 1 ppm; 2σ) suggests Ga loss during retrogression, whereas Ge abundances remain within the same range as blueschists and eclogites. In the garnet-bearing greenschists (early stages of retrogression), the $\delta^{74}\text{Ge}$ values (+0.38 to +0.49‰) remain similar within error to HP rocks. However, albite- and calcite-bearing greenschists have higher $\delta^{74}\text{Ge}$ values (+0.84 to +0.98‰), showing evidence of Ge fractionation under intensive fluid-rock interactions (late stage of retrogression). Micaschists have Ge and Ga abundances within the same range as continental

crust and schists. Their variations in $\delta^{74}\text{Ge}$ (+0.29 to +0.70‰) reflect variations in the sedimentary source and protolith composition.

The relatively small variation of $\delta^{74}\text{Ge}$ values in metabasites compared to mantle rocks implies that the subducted oceanic crust cannot trigger Ge isotopic heterogeneities in the mantle through fluid-induced metasomatism or recycling in the deep mantle. However, during the late stages of retrogression, migration of oxidising fluids along the crust-mantle wedge may be responsible for a resolvable increase of the $\delta^{74}\text{Ge}$ value of the mantle wedge along the subduction channel. Besides, the larger range of Ge concentrations and $\delta^{74}\text{Ge}$ values in the micaschists suggests that recycling of subducted sediments may generate mantle Ge elemental and isotopic heterogeneities.

1. Introduction

During the last decades, the petrology of the high-pressure/low-temperature (HP–LT) rocks and volatile recycling processes involved in subduction zones were intensely investigated and provided significant information on fluid–rock interactions and mass transfers that occur within the subducting oceanic lithosphere (e.g. Sorensen and Grossman, 1989; Schmidt and Poli, 1998; Rüpke et al., 2004; Spandler et al., 2004; John et al., 2008; El Korh et al., 2009, 2013; Martin et al., 2011). During subduction, the hydrated oceanic crust (sediments + altered basic rocks) dehydrates continuously and releases a large portion of its H₂O content at a relatively shallow level (50–80 km), even if hydrous minerals are stable until depths of 200 km (Schmidt and Poli, 1998; Rüpke et al., 2004). Devolatilisation reactions trigger fluid- or melt-mediated mass transfers from the oceanic crust to the overlying mantle wedge, resulting in metasomatism of the latter (e.g. Schmidt and Poli, 1998; Plank and Langmuir, 1988, 1993). Dehydration fluids may mobilise large ion lithophile elements (LILE: Cs, Rb, Ba) and light rare-earth elements (LREE) from the host basic rocks, resulting in LILE- and LREE-depleted dry eclogites (e.g. John et al., 2008), and in LILE- and LREE-enriched arc magmas (Davidson, 1997).

Processes of oxidation of the mantle wedge are largely debated (e.g. Parkinson and Arculus, 1999; Malaspina et al., 2009; Rowe et al., 2009; Groppo and Castelli, 2010; Evans, 2012; Lee et al., 2012). Dehydration-redox reactions occurring in the subducting slab (altered oceanic crust, sediments, serpentinitised lithosphere) may trigger the oxidation of the metasomatised mantle wedge above subduction zones (Evans, 2012; and references therein). The response of stable isotopes (e.g. Ge isotopes) to redox-mediated fluid released is thus to be investigated. Redox-sensitive elements (Fe, C or S) from subducted sediments and altered oceanic crust added to the fore-arc mantle directly controls the redox state of volcanic products such as arc magmas, with long-term (>1 Ga) consequences for the bulk mantle

(Evans, 2012). While the role of water as oxidising agents is discussed (Brandon and Draper, 1996, 1998; Frost and Ballhaus, 1998), silicate-rich C-bearing fluids could be effective oxidising agents (Malaspina et al., 2010). Based on pseudosection modelling, Groppo and Castelli (2010) have shown that prograde lawsonite and chlorite breakdown in FeTi-oxides metagabbros at a depth of about 65–70 km, release H₂O, as well as O₂. The blueschist to eclogite facies transition represents a redox-equilibrium boundary between a low-T oxidised assemblage, and a high-T more reduced assemblage (Groppo and Castelli, 2010). Galvez et al. (2013) have also highlighted the importance of reduced fluid migration in subduction zones for graphite formation in subducted sediments overlying hydrothermally altered rocks.

Fluid migration in subduction zones induces mantle melting and directly controls arc magma chemistry. Deconvolution of geochemical signals from both elemental recycling processes and fore-arc mantle melting, implies 1) to use mildly compatible/incompatible elements that will not be strongly fractionated during partial melting, to interpret their variation in terms of fluid-mediated processes, and 2) to compare the behaviour of fluid-mobile vs. fluid-immobile elements. Germanium (Ge) and gallium (Ga) are slightly to moderately incompatible elements during partial melting of mantle peridotites, with bulk partition coefficient slightly less than unity (Malvin et Drake, 1987; Davis et al., 2013). Therefore, because of their mobility in fluids (see section 2), Ga and Ge can be useful tracers to examine if and how recycling processes can modify the fore-arc mantle Ge and Ga concentrations and generate mantle heterogeneities through fluid-mediated mass transfer in subduction zones.

This study investigates the behaviour of Ge and Ga in HP–LT metamorphic rocks of blueschist, eclogite and retrograde greenschist facies of the Ile de Groix, a well-known late-Palaeozoic HP–LT terrane. In this study, we aim to determine a model for Ga and Ge mobility/immobility and Ge isotopic fractionation during the successive fluid-rock

interactions related to subduction and exhumation processes. We first identify the main host minerals for Ge and Ga in a series of metabasites and metapelites rocks. The dataset allows characterising Ge and Ga behaviour and partition between the mineral phases during devolatilisation and rehydration reactions generated by the variable metamorphic conditions. Then, we measure the Ge isotope composition of a series of metabasites representative of the different metamorphic facies, as well as in a series of micaschists, in order to determine the Ge isotopic signature of the subducted basic rocks and their pelitic sedimentary cover. We also consider the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the studied samples in order to determine whether Ge isotope fractionation is constrained by changes in Fe redox state during the different stages of fluid-rock interactions related to subduction and exhumation processes. The results will allow the Ge cycle in the subduction zone to be evaluated, with inferred consequences for the composition of deeply subducted slabs and fore-arc mantle wedge.

2. Ge and Ga geochemical behaviour and mobility during fluid-rock interactions

Ge and Ga mobility and solubility in fluids in natural hydrothermal systems, as well as during fluid-related experiments, have been quantified with regards to varying thermodynamical conditions (such as temperature, pH, fluid composition, speciation of Ge and Ga) (Mortlock and Froelich, 1986; Pokrovski and Schott, 1998; Wood and Samson, 2006). Variations in Ge and Ga could trace of reaction processes between seawater and ocean floor basalts during high-temperature (high-T; $>350^{\circ}\text{C}$) and low-temperature (low-T; $<350^{\circ}\text{C}$) hydrothermal processes (e.g. Mortlock and Froelich, 1986; Mortlock et al., 1993; Luais, 2012; Escoube et al., 2015).

In the Earth's crust, Ga has lithophile characteristics in the absence of metallic phases (Malvin and Drake, 1987). Ga has an oxidation state of 3^{+} and shares a strong affinity with Al (e.g. de Argollo and Schilling, 1978b). Thus, Ga is a common trace element in Al-rich rock-

forming minerals (Burton et al., 1959). Micas, feldspars and Al-oxides have generally high Ga contents, while amphiboles and pyroxenes often display lower Ga concentrations. Al-poor phases such as quartz and olivine are poor in Ga (Burton et al., 1959; Malvin and Drake, 1987). High-pressure experiments of Ga partitioning have highlighted Ga compatibility in high-pressure Al-rich minerals (zoisite, lawsonite) compared to fluid (Martin et al., 2011). Experimental studies have shown that Ga is transported as hydroxides and, to a lesser extent, as fluoride complexes in hydrothermal fluids (Wood and Samson, 2006).

Ge behaviour varies from lithophile to moderately siderophile or chalcophile according to mantle-crust geological environments (Bernstein, 1985; Höll et al., 2007). Ge shares a strong affinity with Si, owing to their similar oxidation state of 4^+ , and similar ionic and covalent radii (de Argollo and Schilling, 1978b; Bernstein, 1985; Pokrovski and Schott, 1998; Höll et al., 2007). In magmatic or metamorphic mineral assemblages, germanium partitioning depends on the crystallographic structure: Ge is preferentially incorporated into the less polymerised silicates, such as nesosilicates (garnet, titanite), sorosilicates (epidote), inosilicates (amphiboles, pyroxenes) and/or phyllosilicates. Tectosilicates (quartz, feldspars) generally show the lowest Ge concentrations (Bernstein, 1985). For this reason, normalisation of Ge to Si and, likewise, of Ga to Al in minerals cancels out the effects of Ge and Ga variations related to crystallographic substitutions and allows evaluating whether they may be mobile during fluid-rock interactions related to subduction zone metamorphism (SZM). Aqueous Ge and Si have a relatively similar speciation distribution in fluids (Wood and Samson, 2006). With increasing temperature, the preferential dissociation of $\text{Si(OH)}_4(\text{aq})$ species, owing to a lower enthalpy and heat capacity than $\text{Ge(OH)}_4(\text{aq})$ species, results in an increase of the Ge/Si ratio in fluids in equilibrium with Ge-rich silicates (quartz, biogenic opals) (Pokrovski and Schott, 1998; Evans and Derry, 2002). Therefore, Pokrovsky et al. (2006, 2014) have shown that adsorption of Ge by goethite at ambient temperature (25°C)

may result in a decoupling of Ge and Si: due to its strong affinity with Fe hydroxides, Ge can co-precipitate with Fe during Fe^{2+} oxidation or Fe^{3+} hydrolysis, with a maximal Ge/Fe molar ratio of 0.5 in the solid. Thus, physico-chemical conditions of hydrothermal processes may result in: 1) Ge depletion of the basaltic crust in the presence of hydrothermal sulphides during high-T alteration along hydrothermal vents or; 2) Ge enrichment of the altered basaltic crust due to Ge adsorption by iron hydroxides (Prokrovsky et al., 2006, 2014; Escoube et al., 2015).

Ge has five stable isotopes (masses 70, 72, 73, 74 and 76) that could fractionate, with $\delta^{74}\text{Ge}$ ($= [({}^{74}\text{Ge}/{}^{70}\text{Ge})_{\text{sample}} / ({}^{74}\text{Ge}/{}^{70}\text{Ge})_{\text{NIST3120a}} - 1] * 1000$, relative to the NIST SRM 3120a Ge standard in all the following $\delta^{74}\text{Ge}$ notations) varying from -4.0 to +4.7‰ among meteorites and Earth reservoirs (Hirata et al., 1997; Rouxel et al., 2006; Luais, 2007, 2012; Qi et al., 2011; Escoube et al., 2012, 2015; Rouxel and Luais, 2017). Stable isotope fractionation is temperature dependant and decreases with increasing temperature and atomic mass (Bigeleisen and Mayer, 1947; Urey, 1947). Heavy isotopes are preferentially incorporated in species with a high oxidation state, short and strong bonds, and low coordinated sites (Schauble, 2004). Thermodynamic constraints on Ge partitioning and isotopic fractionation during the primitive core–silicate mantle segregation control the mantle Ge composition (Ge: 1.1 ppm; $\delta^{74}\text{Ge}$: +0.46 to +0.50‰) (McDonough and Sun, 1995; Luais, 2012). Recent studies have demonstrated that Ge isotope fractionation is low under high-T magmatic conditions (>800°C), with $\delta^{74}\text{Ge}$ from +0.37 to +0.68‰ in ultrabasic, basic and granitic rocks (Rouxel et al., 2006; Escoube et al., 2012, 2015; Luais, 2012). Thus, the variable $\delta^{74}\text{Ge}$ values recorded by tholeiitic and alkaline basalts (+ 0.37 to +0.62‰; Escoube et al., 2012; Luais, 2012) would reveal variations in the mantle source Ge isotopic composition.

By contrast, it has been shown that Ge isotope fractionation is strongly sensitive to low-T (<350°C) hydrothermal processes and to the nature of precipitated phases, yielding

large variations in $\delta^{74}\text{Ge}$ values: 1) marine hydrothermal Fe-rich deposits and sulfide deposits display $\delta^{74}\text{Ge}$ from -0.98 to +0.16‰ and from -4.71 to -2.98‰, respectively (Rouxel et al., 2006; Escoube et al., 2012, 2015); 2) a $\delta^{74}\text{Ge}$ of +0.61‰ was measured in serpentine (Luais, 2012) that could reflect interaction with heavy seawater (Escoube et al., 2015) and; 3) $\delta^{74}\text{Ge}$ values from -2.08 to +0.91‰ were measured in terrestrial hydrothermal sphalerite (Luais, 2012; Belissont et al., 2014). Thus, Ge isotopes were employed as geochemical tracers of various marine and hydrothermal processes in order to constrain the sources of Si and Ge in ancient and modern seawater (Siebert et al., 2006, 2011; Rouxel et al., 2006; Escoube et al., 2015; Rouxel and Luais, 2017). Li et al. (2009) and Li and Liu (2010) have established a theoretical basis for the quantification of equilibrium Ge isotopic fractionation between fluids and minerals. Their model predicts heavy $\delta^{74}\text{Ge}$ in fluids with respect to sulfide minerals, in agreement with the high $\delta^{74}\text{Ge}$ measured in hydrothermal vent fluids (+0.61 to +2.20‰; Escoube et al., 2015), and with the estimation of the seawater $\delta^{74}\text{Ge}$ to +3.00‰ (Escoube et al., 2015).

Because of Ge solubility and partitioning into fluid phase, Ge isotope fractionation can be expected at intermediate temperatures in conditions of SZM during slab dehydration (400–600°C; blueschist to eclogite facies). Our study aims to evaluate whether Ge isotopes can fractionate during SZM and trace fluid-rock interactions, and if the subducting oceanic crust may contribute to mantle Ge heterogeneities.

3. Geological setting and studied samples

The Ile de Groix (France) is a Variscan HP terrain, bearing well-preserved neighbouring eclogite, blueschist and retrograde greenschist facies rocks (Fig. 1). The mineralogy, petrology, geochemistry and P–T conditions of the metamorphic rocks of the Ile de Groix have been intensively studied during the last 50 years (e.g. Cogné et al., 1966; Triboulet,

1974; Carpenter, 1976; Quinquis, 1980; Quinquis & Choukroune, 1981; Bernard-Griffiths et al., 1986; Djro et al., 1989; Barrientos & Selverstone, 1993; Audren et al., 1993; Schulz et al., 2001; Bosse et al., 2002, 2005; Ballèvre et al., 2003; Philippon, 2009; El Korh et al., 2009, 2011, 2012, 2013). The metamorphic rocks of the Ile de Groix are composed of 20% metabasic rocks corresponding to former hydrothermally altered mid-ocean ridge basalts (MORB), intercalated with 80% pelitic micaschists (Bernard-Griffiths et al., 1986; Bosse et al., 2002; El Korh et al., 2009, 2013). The high-pressure rocks are interpreted as the remnants of the uppermost part of an oceanic lithosphere or of basaltic lavas, which were sheared off and imbricated in an accretionary prism with the metasediments during subduction (El Korh et al., 2012). Two metamorphic stages were recorded: 1) a prograde blueschist to eclogite facies metamorphism M1 related to subduction; and 2) a greenschist facies overprint M2 related to exhumation (e.g. Triboulet, 1974; Barrientos and Selverstone, 1993; Schulz et al., 2001; Bosse et al., 2002). The eastern part of the Ile de Groix is dominated by HP eclogites, and epidote-blueschist facies rocks, whereas retrograde greenschist facies rocks are dominant on the western part (Fig. 1). Based on P–T calculations using the NFMASH system in metapelites, Bosse et al. (2002) have determined two tectonic units: the Upper Unit (1.6–1.8 GPa, 450–500°C) in the eastern part of the island, and the Lower Unit (1.4–1.6 GPa, 400–450°C) in the West. In metabasites, the peak pressure–temperature (P–T) conditions (1.6–2.5 GPa, 500–600°C) (Fig. 1) correspond to a 60–70 km depth in a subduction zone with an intermediate thermal regime (El Korh et al., 2009).

Large-scale fluid-rock interactions in metabasites occurred as: 1) Hydration of rocks during seafloor low-T hydrothermal alteration and early-subduction metasomatism resulting from an interaction with pelite-derived fluids released during dehydration of micaschists; 2) Dehydration of metabasites during HP–LT metamorphic reactions related to subduction; 3)

Rehydration during retrogression in the greenschist facies resulting from an interaction with slab-derived fluids upwelling from deeply subducted metabasites (El Korh et al., 2013).

Metabasites are fine- to medium-grained massive rocks (Fig. 2). Peak metamorphic assemblages (blueschists and eclogites) are composed of garnet, glaucophane, epidote, phengite, apatite, quartz, titanite and/or rutile (Figs. 2a and b). Omphacite porphyroblasts are only present in eclogites. Blueschist facies rocks often contain pseudomorphs after lawsonite, mainly consisting of epidote, white mica (phengite, paragonite), actinolite and albite (Ballèvre et al., 2003; El Korh et al., 2009). The difference of mineral assemblages between eclogites and blueschists results from small variations in the protolith composition and/or from a difference of c. 50°C for the peak temperature conditions (El Korh et al., 2009, 2013).

Euhedral garnet poikiloblasts in eclogite and blueschist facies metabasites display a bell-shaped Mn-Fe zonation, typical of garnet formed under increasing P–T conditions, with cores enriched in the spessartine and depleted in almandine components compared to the rims (rimward X^{alm} increase from ~55% to ~65%; El Korh et al., 2009). Epidote grains in blueschists and greenschists are optically zoned and have core enriched in Fe^{3+} ($X_{\text{Fe}^{3+}}$ up to 33%; El Korh et al., 2009) compared to the rims, richer in the clinozoisite component ($X_{\text{Fe}^{3+}}$ 18–23%; El Korh et al., 2009). In eclogites, epidote is dominated by the (clino)zoisite component ($X_{\text{Fe}^{3+}}$ 19–25%; El Korh et al., 2009). Partial retrogression of eclogites and blueschists is revealed by (Fig. 2c): 1) a formation of barroisite + albite symplectites replacing omphacite, 2) barroisite and actinolite overgrowths along glaucophane rims, and 3) a partial replacement of garnet by chlorite and rutile by titanite.

Retrograde assemblages in greenschists consist of epidote, chlorite, actinolite, barroisite, albite, magnetite, and titanite. Greenschists also contain relicts of glaucophane rimmed by barroisite or actinolite. High-pressure garnet is partially to totally replaced by chlorite, actinolite and by a retrograde generation of epidote. "Albitic greenschists" are

characterised by the presence of large albite porphyroblasts and by the absence of garnet. Garnet-bearing greenschists result from retrogression under limited fluid–rock interactions at P–T conditions lower than 1.6 GPa and 450–500°C (El Korh et al., 2009). Albite- and calcite-bearing greenschists experienced intensive interactions with Na-Si-Ca-Al-rich fluids equilibrated with the metabasites at P–T conditions lower than 1 GPa and 400–450°C (El Korh et al., 2011, 2013). These fluids were transporting mobile trace elements, such as LILE, Sr and Pb (El Korh et al., 2011), and might possibly carry Ge and Ga. Some greenschist-facies metabasites also contain calcite formed during retrogression.

Micaschists are fine- to medium-grained foliated rocks. Main types of blueschist facies assemblages consist of: 1) Chloritoid-garnet micaschists, mainly composed of garnet, chloritoid, phengite, paragonite, with lesser abundances of Na-amphiboles, quartz, apatite, rutile ± accessory titanite and/or tourmaline; 2) Chloritoid-absent glaucophane-garnet micaschists; 3) Chloritoid-absent glaucophane-epidote micaschists and; 4) Garnet-epidote-chlorite micaschists. In the greenschist facies micaschists, garnet, chloritoid and glaucophane are partially replaced by chlorite, while epidote may still be stable. Greenschist-facies micaschists are also characterised by the retrograde formation of albite and ilmenite. The variable mineralogical assemblages of micaschists reflect variations in sedimentary sources (terrigenous/pelitic or volcanoclastic) and protolith composition (Bosse et al., 2002; El Korh et al., 2013).

During this study, thirteen massive metabasite samples were investigated, typical of each metamorphic facies (blueschists GR 02, 11b, 12b, 25a and GROA 56; eclogites GR 21, 24a and 29; greenschists GR 06a, 23 and 25b, GROA 43 and 52) (Table 1; Fig. 1). Parts that were subject to late surface weathering were carefully avoided. Eclogites and blueschists display the typical garnet-bearing assemblage of high-pressure rocks. Garnet-free blueschist GR 12b displays large pseudomorphs after lawsonite and high proportions of Fe³⁺-rich

epidote. The absence of garnet probably results from slight variations in the chemical composition compared to other blueschists, which result from an intensive hydrothermal alteration or from an interaction with sediment-derived fluids. Albite- and calcite- bearing greenschists GROA 43 and 52 (LOI: 5.7–11%; El Korh et al., 2011, 2013) have experienced a stronger rehydration than greenschists GR 06a, GR 23 and 25b (LOI: 1.9–3.7%; El Korh et al., 2009, 2013). Three micaschists were also studied to evaluate the Ga and Ge composition of the sedimentary cover (blueschist facies GROA 110; greenschist facies GR 26b and GROA 104). Mineralogical assemblages are summarised in Table 1.

4. Analytical techniques

4.1. Whole rock trace element analyses

The whole-rock trace element analyses were performed at the SARM (CRPG-Nancy) by inductively coupled plasma mass spectrometry (ICPMS), using a ThermoFisher X7 instrument (ThermoFisher Scientific, Germany and USA). 200 mg of powdered samples were fused with 600 mg LiBO₂ at 980°C, and dissolved in a mixture of HNO₃ (5%), H₂O₂ (0.5%) and glycerol (10%) prior to analysis, following the procedure described by Carignan et al. (2001). Uncertainties are generally <8% at 1 σ for the ICPMS data. In order to improve the accuracy of low Ge concentrations, supplementary measurements of Ge abundances in the metabasites were performed by standard addition method. The initial sample solutions were doped with the NIST SRM 3120a (Luais, 2012) Ge standard (10 ppb Ge) in 1:1, 2:1 and 3:1 ratios. The Ge abundances obtained by the two methods show an excellent correlation (R^2 coefficient of 0.94), so the final Ge concentrations are calculated by averaging the data obtained with and without standard additions. Uncertainties at 2 σ are 5.5–14%.

The FeO content of the studied rocks was measured by colorimetric method at the SARM (CRPG-Nancy) and allowed calculation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio based on the total Fe_2O_3 composition from El Korh et al. (2009, 2011, 2013) reported in Table 3.

4.2. Mineral trace element analysis using LA-ICPMS

The mineral trace element abundances were measured by laser ablation ICPMS (LA-ICPMS) at the GeoRessources laboratory, University of Lorraine (Vandœuvre-lès-Nancy, France). Analyses were performed using an Agilent 7500c quadrupole spectrometer interfaced to a GeoLas Pro 193 nm ArF excimer laser ablation system (Lambda Physik, Germany). The laser was operating using a 5 Hz repetition rate, a fluence of $\sim 10 \text{ J/cm}^2$, and a 44 μm pit size. Helium was used as the carrier gas (0.8 L/min) and was mixed with Ar prior to its introduction in the plasma (1.5 L/min). Peak hopping mode was employed, as well as dual (counting and analogue) secondary electron multiplier (SEM) detector mode. Dwell times were 10 ms for major elements and 20 ms for the measured isotopes ^{69}Ga and ^{74}Ge . During analysis of silicates, main interferences on ^{69}Ga are $^{138}\text{Ba}^{2+}$, $^{29}\text{Si}^{40}\text{Ar}^+$ and $^{53}\text{Cr}^{16}\text{O}^+$. Main polyatomic interferences on ^{74}Ge are $^{148}\text{Sm}^{2+}$, $^{148}\text{Nd}^{2+}$, $^{58}\text{Ni}^{16}\text{O}^+$, $^{40}\text{Ar}^{34}\text{S}^+$ (see also Belissont et al., 2014 for discussion on the selected isotopes). The ThO^+/Th^+ and $\text{Ca}^{2+}/\text{Ca}^+$ ratios were carefully optimised to about 0.3–0.7 and 0.3–0.5% respectively, by ablation of the National Institute of Standards and Technology standard reference material SRM 610, a synthetic glass doped with trace elements. The low oxide and doubly charged ion production rates prevented polyatomic interferences with $^{53}\text{Cr}^{16}\text{O}^+$, $^{58}\text{Ni}^{16}\text{O}^+$, $^{138}\text{Ba}^{2+}$, $^{148}\text{Sm}^{2+}$ and $^{148}\text{Nd}^{2+}$. The formation of $^{29}\text{Si}^{40}\text{Ar}$ interferences was monitored by plotting mean ^{29}Si vs. ^{69}Ga intensities of sample analyses for each session. The absence of a clear correlation suggests that no significant interferences occurred on mass 69. The $^{29}\text{Si}^{40}\text{Ar}^+$ interference is also minimised by the internal/external standardisation method, as both standards and samples are Si-rich.

Acquisition times for background and ablation signals were 60 and 40 s, respectively, allowing the measurement of duplicate spots per analysis.

The NIST 610 reference material was used for external standardisation, using the preferred values of average element abundances from the GeoRem database (Max Planck Institut für Chemie, Mainz, Germany; <http://georem.mpch-mainz.gwdg.de>). Typical analytical series consisted of 10–16 measurements of mineral samples, bracketed at the start and end of each analytical sequence by 2 measurements of the primary standard. Intensity vs. time data were reduced using the ratio-of-the-mean intensities method in an Excel spreadsheet, following the procedure defined in Longerich et al. (1996). Internal standards were ^{42}Ca (epidote, garnet, omphacite, actinolite, titanite, calcite), ^{29}Si (glaucophane/barroisite, albite, chlorite, phengite), ^{57}Fe (magnetite) and ^{49}Ti (rutile), based on the mineral major element compositions determined in El Korh et al., (2009). During data treatment, intervals of 45 and 25 s were selected for the background and the ablation signal, respectively, with an offset of 3 s from the beginning of the ablation to avoid unstable parts of the signal, resulting from large particle production and/or surface contamination. No correction for down-hole fractionation was applied. The instrumental mass bias was corrected using a linear regression function, considering an equal time interval between each analysis. The minimum detection limit, corresponding to three times the standard deviation of the background measurement, is based on the 99% confidence level over the Gaussian counting statistics. Limits of detection are lower than 1 ppm. Uncertainties on individual measurements at 1σ are 3.1-15% for Ga and Ge.

Measurements of the NIST SRM 610 external standard [Ga: 433 ± 13 ppm; Ge: 447 ± 78 ppm; 95% confidence level (CL); GeoRem database] yielded 2σ uncertainties of ± 1.8 and 1.6 ppm [2σ standard errors (SE)] for Ga and Ge, respectively, on the basis of replicate analyses ($n = 49$). The NIST SRM 612 glass was employed as secondary standard and yielded

Ga and Ge abundances of 36.98 ± 0.46 and 39.49 ± 0.47 ppm (2σ SE; $n = 12$), respectively, in agreement with the reference values (Ga: 36.9 ± 1.5 ppm; Ge: 36.1 ± 3.8 ppm; 95% CL; GeoRem database) (see Supplementary Table B1).

4.3. Ge isotope analyses using MC-ICPMS

The Ge isotope ratios in whole rocks were measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) using a Neptune Plus spectrometer (ThermoFisher Scientific, Germany and USA) at the CRPG-Nancy (Table 2). Details of Ge dissolution and chemistry steps are given in Luais (2007, 2012). About 300 mg of powdered samples were dissolved in a 3:1 mixture of HF (28 N) and HNO₃ (15 N) on a hot plate at 60–65°C to avoid any loss of volatile Ge, with alternating ultrasonic and hot plate steps, up to about eight days. Even if HP oxide minerals (i.e. rutile) would be difficult to dissolve, their very low percentage (1–2%) and Ge contents with respect to Ge mineral hosts (<0.5 ppm in rutile, see next section) would not bias the Ge elemental and isotopic signature of the rocks. Total dissolution of the samples was examined visually, and confirmed when obtaining a solution free of any dark particles. Several steps of centrifugation and leaching with HF lead to complete Ge recovery in the supernatant fraction (Luais, 2012). Ge was isolated through two steps resin-exchange chromatography columns. The sample solution was first introduced through an AG 1-X8 anion exchange resin (chloride form, 200–400 mesh, 2 ml) with HF (1 N), and the Ge fraction was collected with HNO₃ (0.2 N). Ge was then purified through an AG 50W-X8 (hydrogen form, 200–400 mesh, 2 ml) cationic-exchange resin, and eluted with HNO₃ (0.5 N) (Luais, 2012). Chemistry blanks were less than 6 pg of Ge. Ge isotope measurements were performed on 25–100 ppb diluted Ge standards and samples in HNO₃ (0.01 N). Standards and samples were doped with the NBS SRM 994 Ga reference

international isotopic standard ($^{69}\text{Ga}/^{71}\text{Ga} = 1.50676$; Machlan et al., 1986), in a 10:1 ratio to monitor mass bias accuracy and stability during the analytical session.

Analyses performed in February 2014 employed a standard nebuliser and cyclonic chamber, then using the Apex nebuliser from June 2014 to September 2014 in order to increase the sensitivity meanwhile reducing the quantity of Ge to be analysed. The MC-ICPMS instrument was operating in static mode at a medium resolution ($M/\Delta M = 6000$). The cup configuration consisted of: Low 3 (^{68}Zn), Low 2 (^{69}Ga), Low 1 (^{70}Ge), Axial (^{71}Ga), High 1 (^{72}Ge), High 2 (^{73}Ge), High 3 (^{74}Ge). ^{68}Zn was used to correct the isobaric interference between ^{70}Ge and ^{70}Zn mathematically (Luais, 2012). ^{69}Ga and ^{71}Ga were measured to monitor the instrumental drift and mass fractionation. Fe and Ni oxide interferences, as well as argide interferences on Ge masses (Luais, 2012) were avoided following a careful procedure described in the Appendix A.

At the beginning of each analytical session, the gas flow rates, torch parameters and ion lenses were optimised using a solution of the NIST SRM 3120a Ge standard (Luais, 2012). The correction coefficients between the Faraday cups were obtained by a gain calibration before optimising the peak shapes and centring the peaks. Typical acquisition series consisted of an alternation of a measurement of the NIST SRM 3120a Ge standard and a measurement of a sample. 60 integration cycles were measured during 9 min, after a washout time of 200s in HNO_3 (0.6 N), 8+2 min in HNO_3 (0.01 N). This configuration allows calculating the Ge isotope ratio using the standard bracketing method as follows:

$$\text{‰ } \delta^x\text{Ge}_{\text{NIST3120a}} (\text{sample}) = [(^x\text{Ge}/^{70}\text{Ge})_{\text{sample}} / (^x\text{Ge}/^{70}\text{Ge})_{\text{NIST3120a}} - 1] * 1000$$

The JMC and Aldrich Ge standards (Luais, 2012) were used as secondary standards to evaluate the long-term stability of the ICP mass spectrometer, accuracy and precision of the

isotopic measurements. The BIR-1 basalt standard (USGS) was dissolved and submitted to the same chemical procedure as the studied samples and allows to estimate the long-term reproducibility of both chemistry and analysis of a complex matrix sample. The Aldrich and JMC secondary standard measurements ($n = 64, 70$, respectively) and BIR-1 data ($n = 4$) are reported in Table 5. They yield average $\delta^{72}\text{Ge}$, $\delta^{73}\text{Ge}$ and $\delta^{74}\text{Ge}$ values that are consistent with their respective reference values (Luais, 2007, 2012; Escoube et al., 2012).

5. Results

5.1. Whole rock Ga and Ge abundances and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios

The Ge and Ga contents and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in the metabasites from the Ile de Groix (eclogites, blueschists and greenschists) are given in Table 3 and reported on Figs. 3 and 4. The metabasites have Ge abundances of 1.2–2.1 ppm [average: 1.7 ± 0.1 ppm (2σ SE)] (Table 3), comparable to those of tholeiitic basalts [1.1–1.9 ppm, average: 1.53 ± 0.01 ppm (2σ SE, $n = 443$)] (Fig. 3a and reference therein). Ge abundances do display any correlation with the $\delta^{18}\text{O}$, fluid-mobile (e.g. Rb) or fluid-immobile (e.g. Y) element compositions (see Electronic Appendix; Fig. B1). The calculated Ge/Si ratios in metabasites vary between 5.25×10^{-6} and 8.68×10^{-6} (Table 3), with an average of $7.12 \pm 0.47 \times 10^{-6}$ (2σ SE; $n = 14$). These values are generally similar to that of ocean floor basalts (including both fresh and low-T hydrothermally altered basalts) [$5.23\text{--}8.15 \times 10^{-6}$, average: $6.48 \pm 0.05 \times 10^{-6}$ (2σ SE, $n = 429$); De Argollo and Schilling, 1978a, 1978b; Rouxel et al., 2006; Jenner and O'Neill, 2012; Escoube et al., 2015]. Metabasites have Ge/Fe ratios ranging from 1.37×10^{-5} to 2.16×10^{-5} (Table 3), [average: $1.87 \pm 0.12 \times 10^{-5}$ (2σ SE; $n = 14$)], which are identical to those of ocean floor basalts [$1.39\text{--}2.37 \times 10^{-5}$; average: $1.92 \pm 0.02 \times 10^{-5}$ (2σ SE, $n = 390$); Jenner and O'Neill, 2012].

Micaschists, representing former terrigenous sediments, have Ge contents of 2.0–3.2 ppm (Figs. 3a and 4; Table 3), within the range of the felsic rocks (granites and diorites: 0.56–3.5 ppm; Fig. 3a and reference therein) and of the schists (0.9–2.9 ppm; Burton et al., 1959), but higher than the bulk continental crust (1.3–1.6 ppm; Rudnick and Gao, 2003 and references therein). The calculated Ge/Si ratios for the micaschists vary from 5.92×10^{-6} to 9.91×10^{-6} , while the Ge/Fe ratio varies from 2.91 to 5.76×10^{-5} .

The Ga compositions of the metabasites (17–22 ppm; Table 3) are typical of tholeiitic basalts (14–23 ppm; average 18.03 ± 0.15 ppm (2σ SE); $n = 555$) (Fig. 3b and reference therein), with Ga abundances in greenschists (17–21 ppm) generally lower than in blueschists and eclogites (21–22 ppm). The Ga contents in the metabasites do not show any correlation with the $\delta^{18}\text{O}$ values, nor with Rb and Y contents (Electronic Appendix; Fig. B1).

The Ga contents in micaschists (23–29 ppm; Figs. 3b and 4; Table 3) are similar to the Ga abundances of the felsic igneous rocks (granites and diorites: 9.5–59 ppm Ga; Fig. 3b and reference therein) and of the schists (11.9–37.4 ppm; Burton et al., 1959). As observed for Ge, Ga abundances in micaschists are higher than those of the bulk continental crust (15–18 ppm; Rudnick and Gao, 2003 and references therein).

The metabasites have $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.20–0.64, which are higher than those of MORB (0.07–0.16; Christie et al., 1986; Bezos and Humler, 2005; Cottrell and Kelley, 2011). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio varies between 0.35 and 0.56 in garnet-bearing blueschists, with an average of 0.50 ± 0.10 (2σ SE, $n = 5$), while it is 0.64 in the garnet-free blueschist GR 12b. Eclogites have lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.32–0.43 (average of 0.37 ± 0.07 ; 2σ SE, $n = 3$). Garnet-bearing greenschists have $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.33–0.50 (average of 0.41 ± 0.10 ; 2σ SE, $n = 3$), whereas albite- and calcite-bearing greenschists are characterized by lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.20–0.23 (average of 0.21 ± 0.03 ; 2σ SE, $n = 2$). Micaschists display a range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.12 to 0.36.

458

459 **5.2. Ga and Ge partitioning between the metamorphic minerals**

460 Ge and Ga contents in minerals are reported in the Electronic Appendix (Supplementary
461 Table B1). The detailed compositions of the different generations of garnet and epidote are
462 summarised in Table 4. As Ge shares a close affinity for Si and Ga for Al (e.g. de Argollo and
463 Schilling, 1978b; Höll et al., 2007), Ge was normalised to Si and Ga to Al in order to decipher
464 variations due to metamorphic processes (Tables 4 and B1). Ge/Si and Ga/Al variations
465 between minerals are represented in Figure 6.

466 Ge partitioning according to the crystallographic structure and Ge $\leftrightarrow$ Si substitution in
467 the tetrahedral site can be debated (Wickman 1943; Bernstein, 1985; Malvin et Drake, 1987).
468 In the metamorphic rocks of the Ile de Groix, garnet (nesosilicates) and epidote (sorosilicates)
469 are indeed the main hosts for Ge, with higher abundances in micaschists (10–27 and 6.5–11
470 ppm, respectively) than in metabasites (3.3–8.2 and 2.4–12 ppm, respectively) (Fig. 5).
471 Accessory titanite (nesosilicates) can incorporate Ge (2.0–4.1 ppm) as well, while amphiboles
472 and omphacite (inosilicates) have lower Ge values (0.5–2.2 ppm). However, in the calcite-
473 bearing greenschist (GROA 43), free of garnet and containing rare epidote, Ge is mainly
474 hosted by magnetite (4.3–6.3 ppm) and retrograde chlorite (4.4–4.5 ppm). Ga-bearing
475 minerals are: epidote (33–112 ppm), phengite (61–162 ppm), garnet (2.6–8.6 ppm),
476 omphacite (14–19 ppm), glaucophane, barroisite and actinolite (2.1–24 ppm), chlorite (4.9–53
477 ppm), and accessory titanite (0.6–7.6 ppm). In micaschists, accessory tourmaline also hosts
478 Ga (10–26 ppm). The budget of Ge and Ga among the metamorphic minerals of three
479 metabasites (blueschist GR 02, eclogite GR 29 and greenschist GR 25b) confirms that Ge and
480 Ga are mainly distributed between garnet, epidote and, to a lesser extent, omphacite and
481 glaucophane (Fig. 6).

Partition coefficients for Ge and Ga between epidote, garnet, glaucophane and omphacite, represented in Figure 7, were calculated for the different mineral generations stable with varying P–T conditions. Paragenetic assemblages and mineral equilibria were determined by El Korh et al. (2009), based on petrological observations, major and trace element analyses and pseudosection modelling. Detailed partition coefficients for Ge and Ga between all mineral pairs in equilibrium in metabasites under varying P–T conditions are given in the Electronic Appendix (Supplementary Table B2). For Ge, $D^{\text{ep/gln}}$, $D^{\text{ep/omph}}$ are 3.0–9.4 and 2.7–2.8, respectively. The $D^{\text{grt/omph}}$ and $D^{\text{grt/gln}}$ values range from 4.2 to 4.8 and from 3.2 to 9.2, respectively. The results show that Ge is preferentially incorporated into epidote and garnet rather than into glaucophane and omphacite. Variations of epidote/garnet partition coefficients around unity ($D^{\text{ep/grt}} = 0.56$ to 2.4) within each sample reflect Ge exchange between the different generations of garnet and epidote stable under varying P–T conditions (Figs. 7a and 8; Tables 4 and B2). Even if Ge contents of omphacite and glaucophane are low, Ge is slightly partitioned into omphacite ($D^{\text{gln/omph}} = 0.46$ –0.59).

For Ga, $D^{\text{ep/gln}}$, $D^{\text{ep/omph}}$ and $D^{\text{ep/grt}}$ are 4.9–9.9, 5.0–6.5 and 12–16, respectively (Fig. 7b; Table B2). The results indicate that Ga is strongly partitioned into epidote. Ga is preferentially incorporated into omphacite and glaucophane compared to garnet: $D^{\text{grt/omph}}$ and $D^{\text{grt/gln}}$ values range from 0.36 to 0.50, and from 0.40 to 0.73, respectively. Ga is slightly partitioned into omphacite compared to glaucophane ($D^{\text{gln/omph}} = 0.50$ to 0.97). Similarly to Ge, variations of epidote/garnet partition coefficients for Ga within each sample result from Ga exchange between the different generations of garnet and epidote (Figs. 7b and 8; Tables 4 and B2).

The Ga/Al and Ge/Si ratios in garnet and epidote vary between the various generations, i.e. with the changing P–T conditions and co-existing mineral assemblages (Figs. 8a–f; Table 4). Garnet and epidote in eclogites have higher Ga/Al values than in blueschists

and greenschists, due to distinct coexisting Ge- and Ga-host minerals under HP conditions (e.g. lawsonite, omphacite).

5.3. Whole rock germanium isotope compositions

Although the metabasites behaved as a relatively closed system for Ge during SZM owing to Ge partitioning between minerals with a large stability field (garnet, epidote, titanite), Ge isotopic ratio varied between the various metamorphic rocks depending on whether garnet is stable (Table 5; Fig. 9). The studied metabasites have $\delta^{74}\text{Ge}$ values varying between +0.21 and +0.98‰. Garnet-bearing blueschists have $\delta^{74}\text{Ge}$ values from +0.52 to +0.65‰, while garnet-free blueschist GR 12b has a lower $\delta^{74}\text{Ge}$ value of +0.21‰. Eclogites display a restricted range of $\delta^{74}\text{Ge}$ values from +0.42 to +0.54‰. The $\delta^{74}\text{Ge}$ values of garnet-bearing greenschists vary between +0.38 and +0.49‰, while albite- and calcite-bearing greenschists have higher $\delta^{74}\text{Ge}$ values of +0.88 to +0.98‰. The $\delta^{74}\text{Ge}$ values for micaschists cover all the range for metabasites, scattering between +0.29 and +0.70‰.

6. Discussion: Ge and Ga behaviour in metabasites during subduction zone metamorphism

Ge and Ga partitioning in metabasites and variations in $\delta^{74}\text{Ge}$ values according to the various stages of metamorphism may be correlated to variations with P–T conditions and fluid-rock interactions.

6.1. Pre-subduction processes

6.1.1. Low-temperature hydrothermal alteration of metabasites

All metabasites of the Ile de Groix have undergone various degrees of pre-HP hydrothermal processes (El Korh et al., 2013). Pre- and early-subduction hydration of metabasites occurred

as open system large-scale fluid-rock interactions consisting of: 1) seafloor and sub-seafloor low-T hydrothermal alteration ($T < 250^{\circ}\text{C}$), and 2) early-subduction metasomatism resulting from an interaction with pelite-derived fluids released during dehydration of micaschists at shallow depths (< 20 km) (Fig. 10). Low-T hydrothermal alteration was responsible for an increase of the LILE content and $\delta^{18}\text{O}$ values (El Korh et al., 2009, 2013). Because of the high-pressure metamorphic overprint, the samples from the Ile de Groix do not contain any low-T hydrothermal products anymore.

The similar ranges of Ga and Ge abundances and Ge/Si and Ge/Fe ratios in metabasites compared to ocean floor basalts, as well as the absence of clear correlations with the O values and Rb concentrations (Fig. B1), suggest that the pre-HP low-T hydrothermal alteration did not have a significant effect on the Ge and Ga contents, Ge/Si and Ge/Fe values of the basaltic protoliths. Escoube et al. (2015) have reported that high-T and low-T hydrothermal alteration may be responsible for an increase of the Ge/Si ratios and $\delta^{74}\text{Ge}$ in altered basalts, due to high Ge/Si and $\delta^{74}\text{Ge}$ values in hydrothermal fluids (Rouxel et al., 2006; Siebert et al., 2006, 2011; Escoube et al., 2015). Low-T hydrothermal alteration of oceanic basalts may also result in abundant Fe hydroxides precipitation, especially during the first stages of alteration (e.g. Schramm et al., 2005). As Ge has a strong affinity with Fe hydroxides, adsorption of Ge by goethite is expected to increase the Ge/Si and Ge/Fe ratios and to trigger Ge isotope fractionation (Pokrovsky et al., 2006, 2014; Escoube et al., 2015). However, low-T hydrothermal alteration may result in Ge/Si and $\delta^{74}\text{Ge}$ typical of basalts if: 1) Si-rich minerals (quartz) do not precipitate during hydrothermal processes and/or, 2) subsequent enhanced fluid-rock interaction decrease the Ge/Si and $\delta^{74}\text{Ge}$ values toward basalt values (Escoube et al., 2015).

The $\delta^{74}\text{Ge}$ values of +0.38 to +0.65‰ (Figs. 9a, b; Table 5), recorded by garnet-bearing blueschists, eclogites and garnet-bearing greenschists are similar within error to the

$\delta^{74}\text{Ge}$ values of fresh tholeiitic and continental basalts ($+0.55 \pm 0.14$ to $+0.57 \pm 0.04\text{‰}$; Luais, 2012). These results argue that pre-HP low-T hydrothermal processes in geodynamic contexts of MOR and SZM have had probably only a minor effect on the $\delta^{74}\text{Ge}$ values of the basaltic protoliths, as well.

Thus, three scenarios can explain the apparent MORB-like Ge/Si, Ge/Fe and $\delta^{74}\text{Ge}$ values: 1) Ge remained immobile during low-T hydrothermal alteration and was not adsorbed by hydrothermal alteration products; 2) the Ge/Si, Ge/Fe and $\delta^{74}\text{Ge}$ values of the metabasites have been reset during the advanced stages of hydrothermal alteration; or 3) Ge compositions have been altered during the subsequent SZM [see section '6.2. Prograde metamorphism (subduction)'].

6.1.2. Ge and Ga partition in micaschists

Micaschists, representing the sedimentary cover of the subducting basic rocks, display heterogeneous Ge, Ga and $\text{Fe}^{3+}/\Sigma\text{Fe}$ compositions. Variations in mineral assemblages in micaschists reflect variations in sedimentary sources and protolith composition (Bosse et al., 2002; El Korh et al., 2013). Consequently, variations in the Ge and Ga contents and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios between micaschists directly result from variations in the sedimentary source, even if metamorphic processes may have been responsible for geochemical overprints. The highest Ge and Ga abundances and lowest $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio were measured in the chloritoid-bearing micaschist GROA 110 (pelitic source only), while chloritoid-free micaschists GR 26b and GROA 104 (minor volcanoclastic input mixed with the pelitic sediments) have lower Ga and lower Ge contents. Previous trace element analyses in a larger series of micaschists confirm the Ga decrease from the chloritoid-bearing samples to the chloritoid-free samples (El Korh et al., 2013). The pelite-derived micaschists have variable $\delta^{74}\text{Ge}$ values ($+0.29$ to $+0.70\text{‰}$), the highest value being comparable to those of the granites ($\delta^{74}\text{Ge}_{\text{NIST3120a}}$ of $+0.40$ to $+0.68\text{‰}$;

Luais, 2012; Escoube et al., 2012). In micaschists, the $\delta^{74}\text{Ge}$ is not correlated to the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (Fig.9). The well-defined correlation between the $\delta^{74}\text{Ge}$ and the Ge/Si ratio (Fig. 9a) indicates that Ge fractionation is constrained by the protolith composition, and consequently by variations in the sedimentary source (El Korh et al., 2013), rather than by the Fe redox state.

6.2. Prograde metamorphism (subduction)

During the prograde metamorphism up to the peak metamorphic conditions (1.6–2.3 GPa, 500–600°C), the basic oceanic crust dehydrates continuously. Metabasites release large amounts of fluids at the transition from epidote-blueschist to eclogite facies (60–70 km) (e.g. Schmidt and Poli, 1998). Fluids generated by the dehydration of blueschists may be channelised (John et al., 2008) and mainly interact with the channel boundaries (high-permeability pathways). However, fluids may remain trapped within rocks with a low permeability and porosity, and that did not undergo any strong deformation (Spandler and Hermann, 2006). Consequently, massive blueschists and eclogites did not interact with the passing fluid owing to their low permeability and porosity (El Korh et al., 2013). The similar Ge and Ga contents in blueschists and eclogites indicate that Ge and Ga were relatively immobile at the scale of a closed system during prograde metamorphism, allowing Ga and Ge to be exchanged between the various generations of metamorphic minerals through variations of P–T conditions. Besides, the lower Ga abundance in the garnet-free blueschist (GR 12b) containing numerous pseudomorphs after lawsonite, suggests that a part of Ga have left the rock with the fluid released by lawsonite breakdown.

Garnet and epidote in eclogites have higher Ga/Al values than in blueschists and greenschists, due to distinct coexisting Ga-host minerals under HP conditions (e.g. lawsonite, omphacite) (Fig. 8). During dehydration reactions related to the prograde metamorphism

(1.0–2.0 GPa, <450°C; El Korh et al., 2009), the Ge/Si ratio of epidote (Ep) increased between Ep I, formed in equilibrium with lawsonite (now present as pseudomorphs) and Ep II, formed at the transition from the lawsonite blueschist facies to the epidote–garnet blueschist facies (450–500°C) (Figs. 8a–c; Table 4). Even if lawsonite is now absent from the rocks of the Ile de Groix, it appears to have played an important role in the Ge and Ga cycle during the prograde path. Lawsonite can incorporate Ge and Ga contents of 1.9–3.5 and 18–49 ppm, respectively (El Korh et al., 2009; see Table B2 for comparison). Lawsonite breakdown resulted in the uptake of Ge and Ga into Ep II and garnet core (Figs. 7 and 8a–c). Ga is preferentially incorporated into epidote compared to garnet and glaucophane with $D^{\text{ep/grt}} \approx 14$ and $D^{\text{ep/gln}} \approx 7$, while Ge is nearly equitably partitioned between garnet and epidote with $D^{\text{ep/grt}} \approx 0.8–1.5$ (Fig. 7a and b). Our results agree with the decrease of Ga compatibility observed in lawsonite with increasing P–T conditions (Martin et al., 2011).

With increasing P–T conditions up to the peak metamorphic conditions from epidote–blueschist to eclogite facies (1.6–2.3 GPa, 500–600°C; El Korh et al., 2009), the Ge/Si ratio only weakly increased rimwards in garnet (Figs. 8d, e), whilst it decreased in peak metamorphic Ep III from blueschists and greenschists (Figs. 8a, c; Table 4). Garnet in blueschists crystallised in equilibrium with titanite and shared Ge and Ga with Ep III and titanite. For this reason, only a weak Ge and Ga rimward increase is observed (Fig. 8d). In eclogites, the breakdown of the prograde titanite into rutile under peak P–T conditions (El Korh et al., 2009) released Ge, which was reincorporated into epidote and garnet, as shown by the increase of the Ge/Si ratio in garnet rims and, to a lesser extent, in Ep III (Figs. 8b, e; Table 4). The weak Ge/Si and Ga/Al zonation in epidote in eclogites mirrors the weak zonation in major elements (El Korh et al., 2009). The Ga/Al ratio decrease in garnet rims results from the cogenetic formation of Ga-rich omphacite and Ga-rich Ep III. The epidote/garnet and epidote/glaucophane partition coefficients for Ga do not vary with the

temperature increase (Fig. 7b). The epidote/garnet and epidote/glaucophane partition coefficients for Ge decrease with the temperature increase, even if they remain within uncertainty with the partition coefficients calculated for lower temperature conditions (Fig. 7a).

The Ge/Si and Ge/Fe ratios in blueschists and eclogites do not vary from garnet-bearing blueschists ($6.72\text{--}8.68 \times 10^{-6}$ and $1.70\text{--}2.18 \times 10^{-5}$, respectively) to eclogites ($6.51\text{--}8.25 \times 10^{-6}$ and $1.64\text{--}1.92 \times 10^{-5}$, respectively). As Fe is relatively immobile in Cl-poor subduction fluids (Manning, 2004), the absence of Ge/Fe variation argues for Ge immobility during dehydration reactions from the blueschist to the eclogite facies (Table 3; Fig. 9). Even if the ranges of $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of garnet-bearing blueschists and eclogites overlap, the mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios appear to decrease from garnet-bearing blueschists (0.50 ± 0.10 ; 2σ SE, $n = 5$) to eclogites (0.37 ± 0.07 ; 2σ SE, $n = 3$) (Figs. 9a and c). Our data agree with Groppo and Castelli (2010), who have observed a transition from a low-T oxidised assemblage to a high-T more reduced assemblage during eclogitisation of metagabbros in the Monviso ophiolite in Western Alps.

The $\delta^{74}\text{Ge}$ values in blueschists and eclogites do not show any correlation with the Ge/Si or Ge/Fe elemental ratios or with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (Figs. 9a and c). However, the $\delta^{74}\text{Ge}$ values appear to decrease systematically from blueschists [$+0.52$ to $+0.65\text{‰}$; average: $+0.60 \pm 0.08\text{‰}$ (2σ SE)] to eclogites [$+0.42$ to $+0.54\text{‰}$; average: $+0.48 \pm 0.07\text{‰}$ (2σ SE)], even if they cannot be clearly resolvable at the level of 2σ . Germanium isotope fractionation during partial eclogitisation indicates that dehydration reactions at the transition from epidote-blueschist to eclogite facies ($500\text{--}600^\circ\text{C}$) may have released Ge-poor fluids with a slightly higher $\delta^{74}\text{Ge}$ value than the source rocks.

The lowest $\delta^{74}\text{Ge}$ value of the garnet-free blueschist GR 12b ($+0.21\text{‰}$) results from Ge isotope fractionation during fluid release by lawsonite breakdown at the transition from

lawsonite to epidote blueschist facies (2.0 GPa; 500–550°C; El Korh et al., 2009), concomitantly with Fe oxidation ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.64$) and, probably, with the release of a reducing fluid (Fig. 9c). Ge isotope fractionation toward lighter value was probably enhanced by the absence of garnet, a major host for Ge.

6.3. Retrogression (exhumation)

The decrease of Ga abundances of c. 8% in greenschists (17–21 ppm), compared to unretrogressed blueschists and eclogites (21–22 ppm), suggests that Ga was mobile during retrogression (Fig. 4). Blueschists with evidences of partial rehydration (GR 04, GR 12b, GROA 56) have Ga values (17–19 ppm) comparable to those of greenschists, indicating that Ga was already mobile during the early stages of retrogression (Fig. 4). In epidote, the Ga/Al ratio did not vary from Ep III to retrograde Ep IV (Fig. 9c; Table 4). Ga released by glaucophane alteration was mainly transferred to the replacing chlorite and to a lesser extent, to retrograde barroisite and/or actinolite, even if a part of Ga was mobilised by the passing fluid and was released during retrogression in the greenschist facies (Figs. 4 and 8f).

The similar range of Ge abundances in greenschists (1.2–1.9 ppm) and in eclogites and blueschists (1.5–2.0 ppm), as well as their similar range of Ge/Si and Ge/Fe ratios, suggests that Ge remained relatively immobile during retrogression. However, it is not clear whether the lowest Ge concentration measured in an albite-bearing greenschist (GROA 52) result from Ge depletion during retrogression, because of its redistribution in retrograde phases. During rehydration reactions related to retrogression in the greenschist facies (<1.6 GPa, <450–500°C; El Korh et al., 2009), garnet was partially altered to chlorite and released Ge, whilst the retrograde generation of epidote (Ep IV) grew in equilibrium with retrograde titanite. The Ge/Si values did not increase in Ep IV, as Ge was shared between retrograde epidote and accessory titanite (Figs. 5 and 8).

During the early stages of retrogression in the greenschist facies under limited fluid-rock interactions (El Korh et al., 2013), the $\delta^{74}\text{Ge}$ values weakly decreased in the garnet-bearing greenschists [$+0.38$ to $+0.49\text{‰}$; average: $+0.42 \pm 0.07\text{‰}$ (2σ SE); Fig. 10a], even if they remained indistinguishable from HP rocks at 2σ . By contrast, the garnet-bearing greenschists display a range of Fe redox state ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.33\text{--}0.50$; Fig. 9c) identical to that of HP rocks. The fluid-rock interactions responsible for the rehydration of the rocks have only slightly affected the Ge isotope signature, owing to the large stability field of epidote and titanite, and to the presence of Ge-rich garnet relicts.

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, $<400\text{--}450^\circ\text{C}$; El Korh et al., 2011). Large-scale fluid-rock interactions with upwelling Na-Si-rich fluids derived from the dehydrated metabasites were responsible for albitisation of the rocks and for the formation of a large network of retrograde albite, quartz and calcite veins (El Korh et al., 2011, 2013). In the $\delta^{74}\text{Ge}$ vs. Ge/Si and $\delta^{74}\text{Ge}$ vs. Ge/Fe diagrams (Fig. 9b), the retrograde albite- and calcite-bearing greenschists formed under intensive fluid-rock interactions plot outside the field defined by the blueschists, eclogites and garnet-bearing greenschists, indicating that the increase of their $\delta^{74}\text{Ge}$ values results from advanced retrograde processes. The high $\delta^{74}\text{Ge}$ values ($+0.88$ to $+0.98\text{‰}$) and low $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios ($0.20\text{--}0.23$) of retrograde albite- and calcite-bearing greenschists suggests that the Na-Si-rich fluid responsible for the advanced stages of retrogression has triggered Fe reduction and Ge isotope fractionation (Figs. 9 and 10), and became more oxidising. Our data agree with Siebert et al. (2006, 2011), who described migration of heavy-Ge fluids in terrestrial hydrothermal systems ($\pm 300^\circ\text{C}$), with $\delta^{74/72}\text{Ge}_{\text{fluid}}$ values from $+0.4$ to $+1.3\text{‰}$ relative to the Columbia River Basalt (BCR-1) standard (corresponding to $+0.8$ to $+1.6\text{‰}$ relative to NIST3120a). Mineral-fluid Ge partitioning and isotopic fractionation result in preferential incorporation of the heavy-Ge

isotopes in the less polymerised Ge-bearing minerals formed during the advanced stages of retrogression, i.e. epidote (sorosilicate), titanite (nesosilicate) and, to a lesser extent, chlorite (inosilicate).

7. Summary of processes controlling the Ge cycle in subduction zones

Prior to subduction, the oceanic crust is hydrated during hydrothermal alteration (e.g. Cartwright and Barnicoat, 1999). High-T hydrothermal alteration occurs along spreading ridges and upflow zones. Sulphide mineralisation may occur on the ocean floor in black-smoker-type deposits. Seafloor low-T hydrothermal alteration occurs in downflow zones in the upper part of the oceanic crust, further away from the ridges. During low-T hydrothermal alteration, Ge isotope fractionation is directly controlled by the mineral assemblage of secondary products, such as quartz and/or Fe-sulfides (Li et al., 2009; Escoube et al., 2015). For this reason, hydrothermal alteration may lead to variable Ge/Si, Ge/Fe ratios and $\delta^{74}\text{Ge}$ values (Li et al., 2009; Belissont et al., 2014; Escoube et al., 2015). In the case of the metabasites of the Ile de Groix, hydrothermal alteration appears to have had only a minor effect on Ge concentrations and $\delta^{74}\text{Ge}$ values. As the rocks were totally metamorphosed under blueschist to eclogite facies conditions, the nature and composition of the secondary alteration products cannot be estimated. For this reason, the similar Ge abundances and $\delta^{74}\text{Ge}$ values of the metabasites compared to ocean floor basalts can be related either to low quartz and iron hydroxides precipitation during hydrothermal alteration, or to a reset of the Ge abundances and $\delta^{74}\text{Ge}$ values during the advanced stages of hydrothermal alteration or during subsequent HP–LT metamorphism.

During the early stages of subduction, pelitic sediments start to dehydrate at shallow depth but retain heterogeneous Ge and Ga compositions (Fig. 10). With increasing P–T conditions up to peak eclogite facies conditions, metabasites dehydrate progressively. Our

results indicate that the two main lithologies of the subducted crust (metabasites + pelitic sediments) have conserved Ge contents and $\delta^{74}\text{Ge}$ values similar to average fresh MORB and continental crust, respectively (Figs. 3b, 9 and 10).

Fluids released during dehydration processes flow up along the subduction channel (slab-wedge interface) and are responsible for the rehydration of the rocks and retrograde metamorphism in the greenschist facies during exhumation. Fluid channelisation may be responsible for significant fluid transfer from the subducting crust to the overlying mantle wedge, already at depth of c. 60 km (John et al., 2008). Greenschist formed under restricted fluid-rock interactions (garnet-bearing greenschists) have Ge contents and $\delta^{74}\text{Ge}$ values similar to high-pressure metabasites and average fresh MORB, even if the $\delta^{74}\text{Ge}$ may decrease slightly (by c. 0.1‰). Only greenschists with evidences of intensive fluid-rock interactions (albite- and calcite-bearing greenschists) formed during the advanced stages of retrogression have higher $\delta^{74}\text{Ge}$ values.

Stability of garnet and epidote, which are the main hosts for Ge (Figs. 5, 6 and 7; Table 4), is thought to control Ge fractionation during subduction-related metamorphism of the basic rocks. Garnet-bearing metabasites display a narrow range in $\delta^{74}\text{Ge}$, even if slight variations are observed between the metamorphic facies (Fig. 9). Albite- and calcite-bearing greenschist are free of garnet and have a smaller proportion of epidote (<10% epidote) compared to blueschists, eclogites and other greenschists (17–33% epidote). Their higher $\delta^{74}\text{Ge}$ values underline the importance of garnet in controlling Ge fractionation: release of Ge during garnet destabilisation induces Ge isotope fractionation through fluid-newly formed minerals (epidote, chlorite) isotopic exchange at low temperature (<400°C). Besides, the garnet-free blueschist GR 12b has lower $\delta^{74}\text{Ge}$ and higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ values. The high proportion of Fe^{3+} -rich epidote ($\text{XFe}^{3+} \sim 0.31$ in Ep I and II; El Korh et al., 2009), which

started to grow during the prograde lawsonite destabilisation, highlights the role of epidote in Ge fractionation as well.

Our data highlight the relationships between Ge isotopic fractionation and Fe redox state, which may reflect variations in redox conditions or an effect of $\text{Fe}^{2+}/\text{Fe}^{3+}$ partitioning in metamorphic minerals (glaucophane, omphacite, epidote, garnet) during devolatilisation and rehydration reactions related to subduction-zone metamorphism. The light-Ge isotopes are enriched in the blueschist with a higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ value, i.e. in equilibrium with a reducing fluid. The heavy-Ge isotopes are preferentially incorporated in the garnet-free blueschist with a low $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, i.e. in equilibrium with an oxidising fluid. While the high $\delta^{74}\text{Ge}$ values of albite- and calcite-bearing greenschists may have two possible origins: 1) a higher degree of hydrothermal alteration or, more probably, 2) an effect of intensive fluid-rock interactions during retrogression, our data clearly demonstrate that fluid-rock interactions can enhance Ge isotope fractionation of c. 0.3–0.5‰ at a temperature <400–450°C.

Based on Urey model or Bigeleisen-Mayer equations, Li et al. (2009) have calculated fractionation factors between silicate minerals (quartz, albite, K-feldspar and olivine) and $\text{Ge}(\text{OH})_4$, the dominant Ge species in seawater. Fractionation factor for $\text{Ge}(\text{OH})_4$ –quartz, albite and K-feldspar ($\Delta_{\text{min-Ge}(\text{OH})_4} > 0$), and $\text{Ge}(\text{OH})_4$ –olivine ($\Delta_{\text{min-Ge}(\text{OH})_4} < 0$) are opposite, and would give significant Ge isotopic fractionation in minerals at low temperature. With increasing temperature, the fractionation factor between minerals and $\text{Ge}(\text{OH})_4$ decrease and tend toward zero at 450°C for quartz, albite and K-feldspar, while it remains around -0.5‰ for olivine. Those small fractionation factors explain why variations in Ge isotopic fractionation between metabasites are relatively restricted (<0.3‰) during fluid-rock interactions related to subduction-zone metamorphism at a temperature of equilibrium >450°C.

8. Implications for the Ge isotopic composition of the mantle wedge

The subducted oceanic basic crust is recycled into the mantle with a MORB-like Ga and Ge contents and Ge isotopic composition. As the studied metabasites have higher Ge and Ga contents than ultrabasic mantle rocks (Ge: 0.49–1.6 ppm, Ga: 0.7–10 ppm; Fig. 3 and references therein), partial melting of the deeply subducted basic rocks would produce Ge and Ga enrichment in the fore-arc mantle wedge through melt-induced metasomatism.

The relative small variation of $\delta^{74}\text{Ge}$ values between metabasites ($+0.21 \pm 0.02$ to $+0.98 \pm 0.13\text{‰}$) and mantle rocks (serpentinites: $+0.61 \pm 0.16\text{‰}$; unaltered peridotites and dunites: $+0.46 \pm 0.21\text{‰}$ to $+0.50 \pm 0.04\text{‰}$, respectively; Luais, 2012) implies that the subducted oceanic crust at intermediate temperature (450–600°C) cannot trigger important Ge isotopic heterogeneities in the mantle. However, Ge fractionation during intensive fluid-rock interactions related to retrogression suggests that migration of heavy-Ge fluids along the crust-mantle wedge interface may be responsible for a localised increase of the $\delta^{74}\text{Ge}$ value of the fore-arc mantle wedge along the subduction channel. In parallel, recycling of subducted sediments with variable Ge contents and $\delta^{74}\text{Ge}$ values may be source of mantle heterogeneities through fluid-induced metasomatism or sediment melting contribution at deeper levels. Ge isotopic studies of island arc magmatism could bring information on the possible extent of Ge isotopic variations in the mantle wedge and would help to quantify the fluid fraction infiltrating the mantle wedge and subducted sediments.

7. Conclusions

During subduction and exhumation processes, large amounts of fluids released by devolatilisation reactions are migrating in the subduction zone and are responsible for various fluid-rock interactions. In the specific case of the well-characterised Ile de Groix HP–LT metamorphic rocks, the two lithologies of the subducting crust (oceanic crust + pelitic

sediments) display Ge and Ga concentrations and $\delta^{74}\text{Ge}$ values similar to average MORB and continental felsic rocks. Our study shows that Ge and Ga were weakly mobile during subduction. Ge abundances did not vary significantly during prograde and retrograde metamorphism of metabasites. Although Ga remained relatively immobile during prograde HP–LT metamorphism, a part of Ga may have been released from the rocks during retrogression. Therefore, variations in Ge and Ga abundances between the various metamorphic facies are relatively small, because of the large stability field of Ge- and Ga-hosting minerals (epidote, garnet, titanite, amphiboles and omphacite) under varying P–T conditions.

The small variation of Ge abundances (1.2–2.1 ppm) and $\delta^{74}\text{Ge}$ values (+0.38 to +0.98‰) in blueschists, eclogite and greenschist facies metabasites are restricted by garnet/epidote stability during SZM. For this reason, dehydration reactions in HP metabasites (blueschists and eclogites) cannot be subduction-related sources of important Ge elemental and isotopic heterogeneities in the mantle through fluid-induced mantle metasomatism. However, rehydration reactions during retrograde metamorphism may have a local effect on the fore-arc mantle wedge: fluid migration along the crust-mantle wedge may trigger a heavy-Ge signature of the subduction channel. Besides, the large range of Ge concentrations (2.0–3.0 ppm) and $\delta^{74}\text{Ge}$ values (+0.38 to +0.70‰) in the micaschists suggests that recycling of subducted sediments may generate mantle Ge elemental and isotopic heterogeneities.

This study points to a relationship between Ge isotopic fractionation and Fe redox state during devolatilisation and rehydration reactions related to subduction-zone metamorphism. Enrichment in the Ge heavy isotopes during intensive rehydration is enhanced by: 1) the newly formed minerals controlling the $\text{Fe}^{3+}/\Sigma\text{Fe}$ whole rock ratio (epidote, chlorite, barroisite/actinolite and magnetite); 2) the mineral/fluid isotopic exchange;

and 3) the migration of oxidising fluids, resulting from Fe reduction in the residual bulk metamorphic assemblage during retrograde metamorphic reactions.

Acknowledgments

Thanks to Chantal Peiffert for technical assistance in the LA-ICPMS laboratory, and to Delphine Yeghicheyan (SARM, CRPG-CNRS, Nancy) for her contribution to whole rock trace element analyses. We thank Jeffrey Ryan and Andreas Stracke for their comments on an earlier version of the manuscript. This work benefited from constructive reviews of Sonja Aulbach and anonymous reviewers. Klaus Metzger is acknowledged for the editorial handling of our manuscript. The research was supported by project P300P2_147749 of the Swiss National Science Foundation, and benefited from a funding from the Observatoire de la Terre et de l'Environnement en Lorraine (OTELLO-CNRS). This work has also been supported by the French National Research Agency through the national program "Investissements d'avenir" (ANR-10-LABX-21-LABEX RESSOURCES21). This is a CRPG contribution n°XXX.

Appendix A

A.1. Suppression of argide interferences on Ge during MC-ICPMS analyses using the Neptune Plus at medium resolution mode

Isobaric interferences resulting from the formation of argides, Fe and Ni oxides (Luais, 2007, 2012) occur on all masses of Ge. A careful determination of isobaric interferences is required for accurate measurement of Ge ratios. Molecular isobaric interferences are generally heavier than Ge isotopes and revealed on peak spectra at medium or high resolution using the Neptune Plus (CRPG). The Figure A1 represents a wide spectrum resulting from the

combination of ^{70}Ge peak (69.92425 a.m.u.) and molecular interferences $^{40}\text{Ar}^{14}\text{N}^{16}\text{O}$ (69.96037 a.m.u.) and, to a lesser extent, $^{54}\text{Fe}^{16}\text{O}$ (69.93453 a.m.u.). On the peak centre position (69.93), the ^{70}Ge peak is overlapped by interferences, while it is free from interferences on the left part of the spectrum. Consequently, after having centred all Faraday cups, the analytical mass position was shifted to the left side of the spectrum (on mass 69.89 for ^{70}Ge).

A.2. Mass fractionation monitoring and correction

The effects of the instrumental mass bias on the measured Ge isotope ratios can be monitored using a linear regression of the $\text{Ln}(^{72}\text{Ge}/^{70}\text{Ge})_{\text{meas}}$ and $\text{Ln}(^{74}\text{Ge}/^{70}\text{Ge})_{\text{meas}}$ values for individual measurements (Figure A2). The slopes for the Aldrich, JMC, NIST 3120a and BIR-1 standards (Luais, 2012) for each session, as well as for all sessions, agree with the theoretical slope of 0.5068 predicted for the fractionation line, and yield excellent correlation coefficients (Fig. A2; Table B3). This indicates a long-lasting stability of the instrument during measurement, as well as a good reproducibility of the analytical conditions between each session (see also Luais, 2012).

In the $\text{Ln}(^{72}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ vs. $\text{Ln}(^{74}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ diagram (Fig. A3a), individual Ge isotope measurements for the samples of the Ile de Groix yield a regression line with a slope of 0.5045 ± 0.0032 (1σ), similar within uncertainty to the slope of the kinetic theoretical mass fractionation line (0.5068). In the $\delta^{72}\text{Ge}_{\text{NIST3120a}}$ vs. $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ diagram (Fig. A3b), all data plot within uncertainty on the slope of the equilibrium theoretical mass fractionation line (0.5137) defined by equation $\delta^{72}\text{Ge}_{\text{NIST3120a}} = (1/m^{72}\text{Ge} - 1/m^{70}\text{Ge}) / (1/m^{74}\text{Ge} - 1/m^{70}\text{Ge}) \times \delta^{74}\text{Ge}_{\text{NIST3120a}} \approx 0.5137 \times \delta^{74}\text{Ge}_{\text{NIST3120a}}$.

880 **Electronic Appendix B:** Supplementary data

881 Table B1. Detailed Ge and Ga composition of the metamorphic minerals

882 Table B2. Mineral/mineral partition coefficients calculated for Ge and Ga

883 Table B3. Regression line parameters for the $\text{Ln}({}^{72}\text{Ge}/{}^{70}\text{Ge})$ – $\text{Ln}({}^{74}\text{Ge}/{}^{70}\text{Ge})$ system for the Ge
884 standards (Luais, 2012), during sessions of February 2014 to September 2014

885 Figure B1. Ge and Ga variations vs. $\delta^{18}\text{O}$ (a, b), Rb (c, d) and Y (g, h). Compositions in $\delta^{18}\text{O}$,

886 Rb and Y are from El Korh et al. (2009, 2011, 2013).

887

888 **References**

- 889 Audren, C., Triboulet, C., Chauris, L., Lefort, J. P., Vignerresse, J. L., Audrain, J.,
 890 Thiéblemont, D., Goyallon, J., Jégouzo, P., Guennoc, P., Augris, C., Carn, A., 1993.
 891 Notice explicative de la feuille Ile de Groix à 1/25000, carte géologique (BRGM, Orléans).
- 892 Angiboust, S., Pettke, T., De Hoog, J.C.M., Caron, B., Oncken O., 2014. Channelized fluid
 893 flow and eclogite-facies metasomatism along the subduction shear zone. *J. Petrol.* 55, 883–
 894 916.
- 895 Bailey, J.C., 2001. Distribution of germanium in rocks and minerals of the Ilímaussaq
 896 alkaline complex, South Greenland. *Geol. Greenland Surv. Bull.* 190, 55–64.
- 897 Bailey, J.C., Gwozdz, R., Rose-Hansen, J., Sørensen, H., 2001. Geochemical overview of the
 898 Ilímaussaq alkaline complex, South Greenland. *Geol. Greenland Surv. Bull.* 190, 55–64.
- 899 Ballèvre, M., Pitra, P., Bohn, M., 2003. Lawsonite growth in the epidote blueschists from the
 900 Ile de Groix (Armorican massif, France): a potential geobarometer. *J. Metamorph. Geol.*
 901 21, 723–735.
- 902 Barrientos, X., Selverstone, J., 1993. Infiltration vs. thermal overprinting of epidote
 903 blueschists, Ile de Groix, France. *Geology* 21, 69–72.
- 904 Belissant, R., Boiron, M.-C., Luais, B., Catelineau, M., 2014. LA-ICP-MS analyses of minor
 905 and trace elements and bulk Ge isotopes in zoned Ge-rich sphalerites from the Noailhac –
 906 Saint-Salvy deposit (France): Insights into incorporation mechanisms and ore deposition
 907 processes. *Geochim. Cosmochim. Acta* 126, 518–540.
- 908 Bernard-Griffiths, J., Carpenter, M.S.N., Peucat, J.J., Jahn, B.M., 1986. Geochemical and
 909 isotopic characteristics of blueschist facies rocks from the Ile de Groix, Armorican Massif
 910 (northwest France). *Lithos* 19, 235–253.
- 911 Bernstein, L.R., 1985. Germanium geochemistry and mineralogy. *Geochim. Cosmochim.*
 912 *Acta* 49, 2409–2422.

913 Bezos, A., Humler, E., 2005. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of MORB glasses and their implications for
 914 mantle melting. *Geochim. Cosmochim. Acta* 69, 711–725.

915 Bigeleisen, J., Mayer, M.G., 1947. Calculation of equilibrium constants for isotopic exchange
 916 reactions. *J. Chem. Phys.* 15, 261–267.

917 Boekhout, F., Spikings, R., Sempere, T., Chiaradia, M., Ulianov, A., Schaltegger, U., 2012.
 918 Mesozoic arc magmatism along the southern Peruvian margin during Gondwana breakup
 919 and dispersal. *Lithos* 146–147, 48–64.

920 Bosse, V., Ballèvre, M., Vidal, O., 2002. Ductile thrusting recorded by the garnet isograd
 921 from blueschist-facies metapelites of the Ile de Groix, Armorican Massif, France. *J. Petrol.*
 922 43, 485–510.

923 Bosse, V., Féraud, G., Ballèvre, M., Peucat, J.J., Corsini, M., 2005. Rb–Sr and $^{40}\text{Ar}/^{39}\text{Ar}$
 924 ages in blueschists from the Ile de Groix (Armorican Massif, France): implications for
 925 closure mechanisms in isotopic systems. *Chem. Geol.* 220, 21–45.

926 Brandon, A.D., Draper, D.S., 1996. Constraints on the origin of the oxidation state of mantle
 927 overlying subduction zones: an example from Simcoe, Washington, USA. *Geochim.*
 928 *Cosmochim. Acta* 60, 1739–1749.

929 Brandon, A.D., Draper, D.S., 1998. Reply to the comment by B. R. Frost and C. Ballhaus on
 930 ‘Constraints on the origin of the oxidation state of mantle overlying subduction zones: an
 931 example from Simcoe, Washington, USA’. *Geochim. Cosmochim. Acta* 62, 333–335.

932 Burton, J.D., Culkin, J.D., Riley, J.P., 1959. The abundance of gallium and germanium in
 933 terrestrial materials. *Geochim. Cosmochim. Acta* 16, 151–180.

934 Carpenter, M.S.N., 1976. Petrogenetic study of the glaucophane schists and associated rocks
 935 from the Ile de Groix, Brittany, France. Unpublished PhD Thesis, Oxford University, 271
 936 pp.

- 937 Carignan, J., Hild, P., Mevelle, G., Morel, J., Yeghicheyan, D., 2001. Routine analyses of
938 trace elements in geological samples using flow injection and low pressure on-line liquid
939 chromatography coupled to ICP-MS: A study of geochemical reference materials BR, DR-
940 N, UB-N, AN-G and GH. *Geostandard Newslett.* 25, 187–198.
- 941 Cartwright, I., Barnicoat, A.C., 1999. Stable isotope geochemistry of alpine ophiolites: a
942 window to ocean floor hydrothermal alteration and constraints on fluid–rock interaction
943 during high-pressure metamorphism. *Int. J. Earth Sci.* 88, 219–235.
- 944 Christie, D.M., Carmichael, I.S.E., Langmuir, C.H., 1986. Oxidation states of mid-ocean
945 ridge basalt glasses. *Earth Planet. Sci. Lett.* 79, 397–411.
- 946 Cottrell, E., Kelley, K.A., 2011. The oxidation state of Fe in MORB glasses and the oxygen
947 fugacity of the upper mantle. *Earth Planet. Sci. Lett.* 305, 270–282.
- 948 Cogné, J., Jeannette, D., Ruhland, M., 1966. L'Ile de Groix: étude structurale d'une série
949 métamorphique à glaucophane en Bretagne méridionale. *Bull. Serv. Carte Géol. Alsace-
950 Lorraine* 19, 41–95.
- 951 Djro, S.C., Triboulet, C., Audren, C., 1989. Les chemins pression-température- temps-
952 déformation-espace (P–T–t–d–e) dans les micaschistes associés aux schistes bleus de l'île
953 de Groix, Bretagne Méridionale, France. *Schweiz. Mineral. Petrogr. Mitt.* 69, 73–90.
- 954 Davidson, J.P., 1997. Deciphering crust and mantle signatures in subduction zone
955 magmatism. *Amer. Geophys. Un., Geophys. Monogr.* 96, 251–262.
- 956 De Argollo, R., Schilling, J., 1978a. Ge/Si and Ga/Al variations along the Reykjanes Ridge
957 and Iceland. *Nature* 276, 24–28.
- 958 De Argollo, R., Schilling, J., 1978b. Ge–Si and Ga–Al fractionation in Hawaiian volcanic
959 rocks. *Geochim. Cosmochim. Acta* 42, 623–630.

960 El Korh, A., Schmidt, S.Th., Ballèvre, M., Ulianov, A., Bruguier, O., 2012. Discovery of an
 961 albite gneiss from the Ile de Groix (Armorican Massif, France): geochemistry and LA-ICP-
 962 MS U–Pb geochronology of its Ordovician protolith. *Int. J. Earth Sci.* 101, 1169–1190.

963 El Korh, A., Schmidt, S.Th., Ulianov, A., Potel, S., 2009. Trace element partitioning in HP–
 964 LT metamorphic assemblages during subduction-related metamorphism, Ile de Groix,
 965 France: a detailed LA-ICPMS study. *J. Petrol.* 50, 1107–1148.

966 El Korh, A., Schmidt, S.Th., Vennemann, T., Ballèvre, M., 2013. Trace element and isotopic
 967 fingerprints in HP–LT metamorphic rocks as a result of fluid-rock interactions (Ile de
 968 Groix, France). *Gondwana Res.* 23, 880–900.

969 El Korh, A., Schmidt, S.Th., Vennemann, T., Ulianov, A., 2011. Trace element and O-isotope
 970 composition of polyphase metamorphic veins of the Ile de Groix (Armorican Massif,
 971 France): implication for fluid flow during HP subduction and exhumation processes, in:
 972 Dobrzhinetskaya, W. Faryad, S. Wallis and S. Cuthbert S. (Eds.), *Ultrahigh Pressure*
 973 *Metamorphism: 25 years after discovery of coesite and diamond*. Elsevier, Amsterdam,
 974 Netherlands. pp. 243–291.

975 Escoube, R., Rouxel, O., Edwards, K., Glazer, B., Donard, O.F.X., 2015. Coupled Ge/Si and
 976 Ge isotope ratios as geochemical tracers of seafloor hydrothermal systems: Case studies at
 977 Loihi Seamount and East Pacific Rise 9°500N. *Geochim. Cosmochim. Acta* 167, 93–112.

978 Escoube, R., Rouxel, O., Luais, B., Ponzevera, E., Donard, O.F.X., 2012. Intercomparison
 979 study of germanium isotope composition of geological and reference materials.
 980 *Geostandards Geoanal. Res.* 36, 149–159.

981 Evans, K.A., 2012. The redox budget of subduction zones. *Earth Sci. Rev.* 113, 11–32.

982 Evans, M.J., Derry, L.A., 2002. Quartz control of high germanium/silicon ratios in
 983 geothermal waters. *Geology* 30, 1019–1022.

984 Frost, B.R., Ballhaus, C., 1998. Comment on ‘Constraints on the origin of the oxidation state

985 of mantle overlying subduction zones: an example from Simcoe, Washington, USA'.
 986 *Geochim. Cosmochim. Acta* 62, 329–331.
 987 Galvez, M.E., Beyssac, O., Martinez, I., Benzerara, K., Chaduteau, C., Malvoisin, B.,
 988 Malavieille, J., 2013. Graphite formation by carbonate reduction during subduction. *Nature*
 989 *Geosci.* 6, 473–477.
 990 Gao, S., Luo, T.-C., Zhang, B.-R., Zhang, H.-F., Han, Y.-W., Hu, Y.-K., Zhao, Z.-D., 1998.
 991 Chemical composition of the continental crust as revealed by studies in east China.
 992 *Geochim. Cosmochim. Acta* 62, 1959–1975.
 993 Govindaraju, K., 1994. 1994 Compilation of working values and sample description for 383
 994 geostandards. *Geostandards Newslett.* 18, 1–158.
 995 Groppo, C., Castelli, D., 2010. Prograde P–T evolution of a lawsonite eclogite from the
 996 Monviso metaophiolite (Western Alps): dehydration and redox reactions during subduction
 997 of oceanic FeTi-oxide gabbro. *J. Petrol.* 51, 2489–2514.
 998 Halicz, L., 1990. Germanium contents of selected international geostandards by hydride
 999 generation ICP-AES. *Geostandards Newslett.* 14, 459–460.
 1000 Harris, P.G., 1954. The distribution of germanium among coexisting phases of partly glassy
 1001 rocks. *Geochim. Cosmochim. Acta* 5, 185–195.
 1002 Hertoogen, J., Janssen, M.J., Palme, H., 1980. Trace elements in ocean ridge basalt glasses:
 1003 implications for fractionations during mantle evolution and petrogenesis. *Geochim.*
 1004 *Cosmochim. Acta* 44, 2125–2143.
 1005 Hirata, T., 1997. Isotopic variations of germanium in iron and stony meteorites. *Geochim.*
 1006 *Cosmochim. Acta* 61, 4439–4448.
 1007 Höll, R., Kling, M., Schroll, E., 2007. Metallogenesis of germanium—A review. *Ore Geol.*
 1008 *Rev.* 30, 145–180.

1009 Hörmann, P.K., 1963. Zur Geochemie des Germaniums. *Geochim. Cosmochim. Acta* 27,
1010 861–876.

1011 Humphris, S., Thompson, G., 1978. Hydrothermal alteration of basalts by seawater. *Geochim.*
1012 *Cosmochim. Acta* 42, 107–125.

1013 Imai, N., Terashima, S., Itoh, S., Ando, A., 1995. 1994 compilation values for GSJ reference
1014 samples, “Igneous rock series”. *Geochem. J.* 29, 91–95.

1015 Jenner, F.E., O’Neill, H.St.C., 2012. Analysis of 60 elements in 616 ocean floor basaltic
1016 glasses, *Geochem. Geophys. Geosyst.* 13, Q02005, doi:10.1029/2011GC004009.

1017 John, T., Klemm, R., Gao, J., Garbe-Schönberg, C.D., 2008. Trace-element mobilization in
1018 slabs due to non steady-state fluid–rock interaction: constraints from an eclogite-facies
1019 transport vein in blueschist (Tianshan, China). *Lithos* 103, 1–24.

1020 Kretz, R., 1983. Symbols for rock-forming minerals. *Am. Miner.* 68, 277–279.

1021 Kurtz, A.C., Derry, L.A., Chadwick, O.A., 2002. Germanium-silicon fractionation in the
1022 weathering environment. *Geochim. Cosmochim. Acta* 66, 1525–1537.

1023 Lee, C. T. A., Luffi, P., Chin, E. J., Bouchet, R., Dasgupta, R., Morton, D. M., Le Roux, V.,
1024 Yin, Q.-Z., Jin, D., 2012. Copper systematics in arc magmas and implications for crust-
1025 mantle differentiation. *Science* 336, 64–68.

1026 Li, X. F., Liu, Y., 2010. First-principles study of Ge isotope fractionation during adsorption
1027 onto Fe(III)-oxyhydroxides surfaces. *Chem. Geol.* 278, 15–22.

1028 Li, X., Zhao, H., Tang, M., Liu, Y., 2009. Theoretical prediction for several important
1029 equilibrium Ge isotope fractionation factors and geological implications. *Earth Planet. Sci.*
1030 *Lett.* 287, 1–11.

1031 Liu, M.H., Fleet, M.E., 2001. Partitioning of siderophile elements (W, Mo, As, Ag, Ge, Ga,
1032 and Sn) and Si in the Fe-S system and their fractionation in iron meteorites. *Geochim.*
1033 *Cosmochim. Acta* 65, 671–682.

1034 Longerich, H.P., Jackson, S.E., Günther, D., 1996. Laser ablation inductively coupled plasma
 1035 mass spectrometric transient signal data acquisition and analyte concentration calculation.
 1036 J. Anal. Atom. Spectrom. 11, 899–904.

1037 Luais, B., 2007. Isotopic fractionation of germanium in iron meteorites: significance for
 1038 nebular condensation, core formation and impact processes. Earth Planet. Sci. Lett. 262,
 1039 21–36, Erratum: Earth Planet. Sci. Lett. 273, 400 (2008).

1040 Luais, B., 2012. Germanium chemistry and MC-ICPMS isotopic measurements of Fe–Ni, Zn
 1041 alloys and silicate matrices: Insights into deep Earth processes. Chem. Geol. 334, 295–311.

1042 Machlan, L.A., Gramlich, J.W., Powell, L.J., Lambert, G.M., 1986. Absolute isotope
 1043 abundance ratio and atomic weight of a reference sample of gallium. J. Res. Nat. Bur.
 1044 Stand. 91, 323–331.

1045 Makishima, A., Nakamura, E., 2009. Determination of Ge, As, Se and Te in Silicate Samples
 1046 Using Isotope Dilution-Internal Standardisation Octopole Reaction Cell ICP-QMS by
 1047 Normal Sample Nebulisation. Geostandards Geoanal. Res. 33, 369–384.

1048 Malaspina, N., Poli, S., Fumagalli, P., 2009. The oxidation state of metasomatized mantle
 1049 wedge: insights from C–O–H-bearing garnet peridotite. J. Petrol. 50, 1533–1552.

1050 Malaspina, N., Scambelluri, M., Poli, S., van Roermund, H.L.M., Langenhorst, F., 2010. The
 1051 oxidation state of mantle wedge majoritic garnet websterites metasomatised by C-bearing
 1052 subduction fluids. Earth Planet. Sci. Lett. 298, 417–426.

1053 Malvin, D.J., Drake, M.J., 1987. Experimental determination of crystal/melt partitioning of
 1054 Ga and Ge in the system forsterite-anorthite-diopside. Geochim. Cosmochim. Acta 51,
 1055 2117–2128.

1056 Manning, C.E., 2004. The chemistry of subduction-zone fluids. Earth Planet. Sci. Lett. 223,
 1057 1–16.

1058 Martin, L.A.J., Wood, B.J., Turner, S., Rushmer, T., 2011. Experimental measurements of
 1059 trace element partitioning between lawsonite, zoisite and fluid and their implication for the
 1060 composition of arc magmas. *J. Petrol.* 52, 1049–1075.

1061 McDonough, W.F., 2003. Compositional model for the Earth's core, in: Carlson, R.W. (Ed.),
 1062 The Mantle and Core, *Treatise on Geochemistry*, vol. 2 (Holland, H.D., Turekian, K.K.,
 1063 Eds.), Elsevier-Pergamon, Oxford, pp. 547–568.

1064 McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. *Chem. Geol.* 120, 223–
 1065 253.

1066 Mišković, A., Schaltegger, U., 2009. Crustal growth along a non-collisional cratonic margin:
 1067 A Lu–Hf isotopic survey of the Eastern Cordilleran granitoids of Peru. *Earth Planet. Sci.*
 1068 *Lett.* 279, 303–315.

1069 Mortlock, R.A., Froelich, P.N., 1986. Hydrothermal Germanium over the southern East
 1070 Pacific Rise. *Science* 231, 43–45.

1071 Mortlock, R.A., Froelich, P.N., 1987. Continental weathering of germanium: Ge/Si in the
 1072 global discharge. *Geochim. Cosmochim. Acta* 51, 2075–2082.

1073 Mortlock, R.A., Froelich, P.N., 1996. Determination of germanium by isotope-hydride
 1074 generation inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 332, 277–
 1075 284.

1076 Mortlock, R.A., Froelich, P.N., Feely, K.A., Massot, G.J., Butterfield, D.A., Lupton, J.F.,
 1077 1993. Silica and germanium in Pacific Ocean: hydrothermal vents and plumes. *Earth*
 1078 *Planet. Sci. Lett.* 119, 365–378.

1079 Parkinson, I.J., Arculus, R.J., 1999. The redox state of subduction zones: insights from arc
 1080 peridotites. *Chem. Geol.* 160, 409–423.

1081 Philippon, M., Brun, J.-P., Gueydan, F., 2009. Kinematic records of subduction and exhu-
 1082 mation in the Ile de Groix blueschists (Hercynian belt; Western France). *J. Struct. Geol.*

1083 31, 1308–1321.

1084 Plank, T., Langmuir, C.H., 1988. An evaluation of the global variations in the chemistry of
 1085 arc basalts. *Earth Planet. Sci. Lett.* 90, 349–370.

1086 Plank, T., Langmuir, C.H., 1993. Tracing trace elements from sediment input to volcanic
 1087 output at subduction zones. *Nature* 362, 739–742.

1088 Pokrovski, G.S., Schott, J., 1998. Thermodynamic properties of aqueous Ge(IV) hydroxide
 1089 complexes from 25 to 350°C: implications for the behavior of germanium and the Ge/Si
 1090 ratio in hydrothermal fluids. *Geochim. Cosmochim. Acta* 62, 1631–1642.

1091 Pokrovsky, O.S., Pokrovski, G.S., Schott, J., Galy, A., 2006. Experimental study of
 1092 germanium adsorption on goethite and germanium coprecipitation with iron hydroxide: X-
 1093 ray absorption fine structure and macroscopic characterization. *Geochim. Cosmochim.*
 1094 *Acta* 70, 3325–3341.

1095 Pokrovsky, O.S., Galy, A., Schott, J., Pokrovski, G.S., Mantoura, S., 2014. Germanium
 1096 isotope fractionation during Ge adsorption on goethite and its coprecipitation with Fe
 1097 oxy(hydr)oxides. *Geochim. Cosmochim. Acta* 131, 138–149.

1098 Qi, H.-W., Rouxel, O., Hu, R.-Z., Bi, X.-W., Wen, H.-J., 2011. Germanium isotopic
 1099 systematics in Ge-rich coal from the Lincang Ge deposit, Yunnan, Southwestern China.
 1100 *Chem. Geol.* 286, 252–265.

1101 Quinquis, H., 1980. Schistes bleus et déformation progressive: l'exemple de l'île de Groix.
 1102 Thèse de 3ème cycle, Université de Rennes, 145 pp.

1103 Quinquis, H., Choukroune, P., 1981. Les schistes bleus de l'île de Groix dans la chaîne
 1104 hercynienne: implications cinématiques. *Bulletin de la Société Géologique de France*
 1105 XXIII (7), 409–418.

1106 Rouxel, O., Galy, A., Elderfield, H., 2006. Germanium isotopic variations in igneous rocks
 1107 and marine sediments. *Geochim. Cosmochim. Acta* 70, 3387–3400.

- 1108 Rouxel, O.J., Luais, B., 2017. Germanium Isotope Geochemistry. *Rev. Mineral. Geochem.*
1109 82, 56 p.
- 1110 Rowe, M.C., Kent, A.J.R., Nielsen, R.L., 2009. Subduction influence on oxygen fugacity and
1111 trace and volatile elements in basalts across the Cascade Volcanic Arc. *J. Petrol.* 50, 61–
1112 91.
- 1113 Rudnick, R.L., Fountain, D.M., 1995. Nature and composition of the continental crust: a
1114 lower crustal perspective. *Rev. Geophys.* 33, 267–309.
- 1115 Rudnick, R.L., Gao, S., 2003. Composition of the continental crust, in: Rudnick, R.L. (Ed.),
1116 The Crust, *Treatise on Geochemistry*, vol. 3 (Holland, H.D., Turekian, K.K., Eds.),
1117 Elsevier-Pergamon, Oxford, pp. 1–64.
- 1118 Rüpke, L.H., Morgan, J.P., Hort, M., Connolly, J.A.D., 2004. Serpentine and the subduction
1119 zone water cycle. *Earth Planet. Sci. Lett.* 223, 17–34.
- 1120 Schauble, E.A., 2004. Applying stable isotope fractionation theory to new systems, in:
1121 Johnson, C.M., Beard, B.L., Albarède, F. (Eds.), *Geochemistry of Non-Traditional Stable*
1122 *Isotopes*, *Rev. Mineral. Geochem.* 55, Mineralogical Society of America, Washington DC,
1123 pp. 65–111.
- 1124 Schmidt, M.W., Poli, S., 1998. Experimentally based water budgets for dehydrating slabs and
1125 consequences for arc magma generation. *Earth Planet. Sci. Lett.* 163, 361–379.
- 1126 Schmitt, W., Palme, H., Wanke, H., 1989. Experimental determination of metal/silicate
1127 partition coefficients for P, Co, Ni, Cu, Ga, Ge, Mo, and W and some implications for the
1128 early evolution of the Earth. *Geochim. Cosmochim. Acta* 53, 173–186.
- 1129 Schramm, B., Devey, C.W., Gillis, K.M., Lackschewitz, K., 2005. Quantitative assessment of
1130 chemical and mineralogical changes due to progressive low-temperature alteration of East
1131 Pacific Rise basalts from 0 to 9 Ma. *Chem. Geol.* 218, 281–313.

1132 Schulz, B., Triboulet, C., Audren, C., Pfeifer, H.R., Gilg, A., 2001. Two-stage prograde and
 1133 retrograde Variscan metamorphism of glaucophane-eclogites, blueschists and greenschists
 1134 from the Ile de Groix (Brittany, France). *International Journal of Earth Sciences* 90, 871–
 1135 889.

1136 Siebert, C., Ross, A., McManus, J., 2006. Germanium isotope measurements of high-
 1137 temperature geothermal fluids using double-spike hydride generation MC-ICP-MS.
 1138 *Geochim. Cosmochim. Acta* 70, 3986–3995; Erratum (2011) . *Geochim. Cosmochim. Acta*
 1139 75, 6267–6269.

1140 Siebert, C., Ross, A., McManus, J., 2011. Erratum to “Germanium isotope measurements of
 1141 high-temperature geothermal fluids using double-spike hydride generation MC-ICP-MS.
 1142 *Geochim. Cosmochim. Acta* 70, 3986–3995”. *Geochim. Cosmochim. Acta* 75, 6267–6269.

1143 Sorensen, S.S., Grossman, J.N., 1989. Enrichment of trace elements in garnet amphibolites
 1144 from a paleo-subduction zone: Catalina Schist, southern California. *Geochim. Cosmochim.*
 1145 *Acta* 53, 3155–3177.

1146 Spandler, C.J., Hermann, J., Arculus, R.J., Mavrogenes, J.A., 2004. Geochemical
 1147 heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-
 1148 pressure basic rocks from New Caledonia. *Chem. Geol.* 206, 21–42.

1149 Spandler, C., Hermann, J., 2006. High-pressure veins in eclogite from New Caledonia and
 1150 their significance for fluid migration in subduction zones. *Lithos* 89, 135–153.

1151 Stoll, B., Jochum, K.P., Herwig, K., Amini, M., Flanz, M., Kreuzburg, B., Kuzmin, D.,
 1152 Willbold, M., Enzweiler, J., 2008. An Automated Iridium-Strip Heater for LA-ICPMS
 1153 Bulk Analysis of Geological Samples. *Geostandards Geoanal. Res.* 32, 5–26.

1154 Taylor, S.R., 1964. Abundance of chemical elements in the continental crust—a new table.
 1155 *Geochim. Cosmochim. Acta* 28, 1273–1285.

1156 Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust.

1157 Rev. Geophys. 33, 241–265.

1158 Triboulet, C., 1974. Les glaucophanites et roches associées de l’Ile de Groix (Morbihan,
 1159 France): étude minéralogique et pétrogénétique. Contrib. Min. Petrol. 45, 65–90.

1160 Urey, H.C., 1947. The thermodynamic properties of isotopic substances. J. Chem. Soc.
 1161 London 1, 562–581.

1162 Wasson, J.T., Baedeker, P.A., 1970. Ga, Ge, In, Ir and Au in lunar, terrestrial and meteoritic
 1163 basalts. Proceedings of the Apollo 11 Lunar Science Conference, Geochim. Cosmochim.
 1164 Acta, Suppl. 1, 1741–1750.

1165 Wedepohl, H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta
 1166 59, 1217–1239.

1167 Wickman, F., 1943. Some aspects of the geochemistry of igneous rocks and of differentiation
 1168 by crystallization. Geol. Foeren. Stockh. Foeh. 65, 371-396.

1169 Wood, S.A., Samson, I.M., 2006. The aqueous geochemistry of gallium, germanium, indium
 1170 and scandium. Ore Geol. Rev. 28, 57–102.

1171

1172

List of figures

Figure 1. Geological map of the Ile de Groix. (after Audren et al., 1993; Bosse et al., 2002; El Korh et al., 2013). * The beach “Plage des Grands Sables” has moved with the oceanic currents. The ductile thrust divides the island into the Upper and Lower Units (Bosse et al., 2002). The large-scale metamorphic zonation of the Ile de Groix results from superimposed effects of variable dehydration states due to the distinct peak P–T conditions in the two parts of the island (Bosse et al., 2002; Ballèvre et al., 2003) and variable hydrothermal alteration intensities (El Korh et al., 2013) during low-T seafloor hydrothermal alteration and early subduction metasomatism. The schematic P–T path is from El Korh et al. (2009). The grey field represents the maximum peak P–T conditions calculated for eclogite GR 29.

Figure 2. Photomicrographs of the studied metabasites in plane-polarised light; scale bars: 0.25 mm. (a) Lozenge-shaped pseudomorph after lawsonite (dashed line) in blueschist GR 25a. It is surrounded by a schistous matrix composed of ep (epidote), gln (glaucophane), and ttn (titanite), which has replaced rutile. (b) Eclogite GR 29; grt (garnet), omph (omphacite), gln (glaucophane), ep (epidote), phe (phengite), rt (rutile). Omphacite is rimmed by ab (albite) + barr (barroisite) symplectites, resulting from a partial retrogression of the rock. (c) Retrograde greenschist GR 23a; chl (chlorite), mt (magnetite). Garnet is partially replaced by chlorite, actinolite and retrograde epidote.

Figure 3. Comparison of the Ge (a) and Ga (b) concentrations of the studied metabasites and micaschists with a representative set of magmatic rocks compiled from the literature (Harris, 1954; Burton et al., 1959; Hörmann, 1963; Taylor, 1964; Wasson and Baedeker, 1970; De Argollo and Schilling, 1978a, 1978b; Hertoogen et al., 1980; Bernstein, 1985; Mortlock and Froelich, 1986, 1987, 1996; Halicz, 1990; Govindaraju, 1994; Imai et al., 1995; Rudnick and

Fountain, 1995; Taylor and McLennan, 1995; Wedepohl, 1995; Gao et al., 1998; Bailey, 2001; Bailey et al., 2001; Kurtz et al., 2002; Rudnick and Gao, 2003; Rouxel et al., 2006; Stoll et al., 2008; Makishima et al., 2009; Mišković and Schaltegger, 2009; Arevalló et al., 2011; Boekhout et al., 2011; Jenner and O'Neill, 2012; Angiboust et al., 2014). Grey bars correspond to the range of values. The fine black line represents the 2σ standard errors. The hydrothermally altered metabasites of the Ile de Groix, corresponding to former MORB-type basalts, have Ge and Ga abundances of 1.2–2.1 ppm and 17–22 ppm, respectively, that are within the range of tholeiitic basalts (Ge: 1.1–1.9 ppm; Ga: 14–23 ppm). The micaschists, deriving from pelitic sediments, have Ge and Ga contents of 2.0–3.0 and 23–29 ppm, respectively, within the range of schists (Ge: 0.9–2.9 ppm; Ga: 12–37 ppm) and granites (Ge: 0.5–3.5 ppm; Ga: 9.5–59 ppm).

Figure 4. Ga vs. Ge abundances in metabasites and micaschists. Ge abundances do not vary between metabasites of different facies. Ga abundances in blueschists (GR 02, 11b, and 25a) and eclogites (GR 21, 24a and 29) are generally higher than in greenschists (GR 06a, 23, 25b, GROA 43 and 52). Blueschists, which underwent a partial retrogression in the greenschist facies (GR 12b and GROA 56) have Ga contents similar to those of greenschists. Micaschists have higher Ga and Ge contents than metabasites.

Figure 5. Ga/Al and Ge/Si distribution in the various minerals of metabasites. Ga and Ge were normalised to Al and Si, because of their respective affinity.

Figure 6. Ga and Ge budgets for blueschist GR 02 (a), eclogite GR 29 (b) and greenschist GR 25b. Calculation employed the relative proportion of minerals in thin section and their mean Ge and Ga composition, as well as the whole rock Ge and Ga composition. The following

mineral modal percentages were used: (a) grt [16], ep [32], gln [32], phe [6], ttn [3], barr [4; n. a.], ap [2–3; n. a.], qtz [2–3; n. a.], rt [1–2; n. a.]; (b) grt [16], ep [17], gln [33], omph [21], phe [4], rt [4], qtz [3], ap [2]; (c) grt [16], ep [30], gln [12], act/barr [12], chl [15], ab [7], ttn [1–2], rt [1–2], qtz [1–2], ap [1–2], phe [1], Fe ox (mt) [1]. n. a.: not analysed during this study. The Ga abundances for phengite in eclogite GR 29 are from El Korh et al (2009). The distribution of Ga is relatively well constrained, while Ge is slightly overestimated in minerals compared to the whole rock. This poorer budgeting results from compositional heterogeneities in mineral phases and/or to non-analysed accessory minerals.

Figure 7. Partition coefficients for Ge (a) and Ga (b) calculated for the main minerals (epidote, garnet, glaucophane, omphacite) of metabasites. Epidote plays a significant role in the Ga budget, while Ga content in garnet strongly depends on the co-existing mineral phases (omphacite, glaucophane). Ge is mostly partitioned between epidote and garnet, while glaucophane and omphacite play a minor role in the Ge budget. 2σ standard errors are large for $D_{\text{EpII/Gln}}$ and $D_{\text{EpII/Grt}}$, due to large variations in Ge abundances in Ep II.

Figure 8. Ga/Al vs. Ge/Si variations in garnet (a-c) and epidote (d-f). Black arrows represent the variations between the various generations of minerals during the prograde metamorphic path.

Figure 9. (a) $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ vs. Ge/Si diagram for the rocks from the Ile de Groix (Tables 3 and 5). (b) $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ vs. Ge/Fe diagram. Garnet-bearing blueschists, eclogites and garnet-bearing greenschists have $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ ratios within uncertainty to the mean value for silicate mantle and basic crust [$\delta^{74}\text{Ge}_{\text{NIST3120a}}$ of $+0.52 \pm 0.15\text{‰}$ (2σ SD); Luais, 2012], represented by the grey line and field in ordinate. The width of the grey field along the abscissa represents the range of Ge/Si and Ge/Fe ratios for tholeiitic ocean floor basalts

(including both fresh and low-T hydrothermally altered basalts). (c) $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ diagram. The $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ is dependant on the $\text{Fe}^{3+}/\Sigma\text{Fe}_t$ ratio in metabasites. A low $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ was recorded by the grt-free blueschist with an oxidising signature. On the other hand, greenschist facies rocks with high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios show heavy-Ge enrichments.

Figure 10. Variations of the mean $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ in the subduction zone. Thicknesses of oceanic and continental crust are not in scale. 2σ standard deviations in parentheses are given as decimals. The number of samples is given in the last position. The data for granites and diorites, oceanic basalts (MORB + OIB), upper mantle and serpentinites (in italic) are from Luais (2012) and Escoube et al., (2012). The data for the deep-sea clay are from Rouxel et al. (2006) ($+1.33 \pm 0.18\text{‰}$ relative to the Aristar standard) and were renormalised to the NIST 3120a using the $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ value for the Aristar standard from Escoube et al. (2012). *Hydrothermal alteration of ocean floor basalts may result in variable Ge enrichment and $\delta^{74}\text{Ge}$ values (Escoube et al., 2015; this study). Grey arrows indicate displacements of the oceanic crust during subduction and exhumation. Three main stages of dehydration are recognised (Rüpke et al., 2004): (A) Dehydration of sediments at the onset of subduction processes at shallow depths (<20 km). Sediments can release water until depths of 100 km; (B) Progressive dehydration of hydrothermally altered oceanic crust between 20 and 200 km; and (C) Deserpentinisation of upper mantle between 120 and 200 km. The basic oceanic crust releases large amounts of fluids at the transition from blueschist to eclogite facies (60–150 km, according to the thermal regime of the subduction zone). Fluids generated by the dehydration of blueschists and underlying serpentinites are channelised (John et al., 2008) and mainly interact with fluid channel boundaries (high-permeability pathways). Fluids flow up along the subduction channel (upper slab-mantle interface) and are responsible for the

rehydration of the rocks and retrograde metamorphism in the greenschist facies during exhumation.

Figure A1. Neptune Plus MC-ICP-MS wide and flat spectrum of ^{70}Ge peak and overlapping interferences measured at medium-resolution ($M/\Delta M = 6000$) in blank HNO_3 0.5N acid (<0.5 ppb Ge), using SEM counting mode. The Ge isotopes are measured on the left side of the peak that is free of any interferences.

Figure A2. $\text{Ln}(^{72}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ vs. $\text{Ln}(^{74}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ diagram (compilation of all analytical sessions) for the Ge standards Aldrich, JMC, NIST3120a and BIR-1 (Luais, 2012). The calculated regression lines for the three standards have slopes ($\pm 1\sigma$) similar to the slope of the kinetic theoretical mass fractionation line (0.5068) obtained using the exponential mass fractionation law [$\text{ts} = \text{Ln}(m^{72}\text{Ge}/m^{70}\text{Ge}) / \text{Ln}(m^{74}\text{Ge}/m^{70}\text{Ge})$], where $m^x\text{Ge}$ refers to the atomic masses of Ge isotopes.

Figure A3. (a) $\text{Ln}(^{72}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ vs. $\text{Ln}(^{74}\text{Ge}/^{70}\text{Ge})_{\text{measured}}$ diagram for the rocks from the Ile de Groix. (b) $\delta^{72}\text{Ge}_{\text{NIST3120a}}$ vs. $\delta^{74}\text{Ge}_{\text{NIST3120a}}$ diagram for the studied samples. Error bars are 95% confidence level external reproducibility, based on replicate analyses, including full procedural replicates for some samples.

1297 **List of Tables**

1298 Table 1. Provenance and mineral assemblage of the studied HP-LT metamorphic rocks from
1299 the Ile de Groix

1300 Table 2. Neptune Plus MC-ICPMS instrumental setup and operating conditions

1301 Table 3. Silica, iron and trace element (Ga, Ge) composition of the studied rocks

1302 Table 4. Ge and Ga composition of the various generations of epidote and garnet in
1303 metabasites

1304 Table 5. Germanium isotopic compositions of Ge standards and studied metabasites

1305
1306

Table 1. Provenance and mineral assemblage of the studied HP-LT metamorphic rocks from the Ile de Groix

1307
1308

Sample	Locality*	UTM coordinates x / y (m)	Facies	Mineralogical assemblage**	Reference***
1309	GR 02	Les Sables Rouges	468550 / 5275006	Blueschist	Grt-gln-ep-barr-phe-qtz-ttn-rt-ap- $\diamond$ lws [1]
1310	GR 04	Beg er Skeul	464994 / 5277375	Blueschist	Grt-gln-ep-barr-phe-qtz-ttn-ap- $\diamond$ lws [2]
1311	GR 11b	Les Saisies	466697 / 5274607	Blueschist	Grt-gln-ep- barrphe-chl-ab-ttn-Fe ox (mt)- $\diamond$ lws [1]
1312	GR 12b	Porh Roëd	466646 / 5274714	Blueschist	Gln-act-ep-phe-chl-ab-ttn-ap-qtz-Fe ox (hm)- $\diamond$ lws [1]
1313	GR 25a	Port Lay	465455 / 5277071	Blueschist	Grt-gln-ep-phe-act-qtz-chl-ttn-Fe ox (mt)- $\diamond$ lws [1]
1314	GROA 56	Lumiaret	467856 / 5274577	Blueschist	Grt-gln-ep-barr-phe-qtz-ttn-chl-ap-Fe ox (hm, mt) [2]
1315	GR 21	Poskedoul	467512 / 5276718	Eclogite	Grt-gln-omph-ep-barr-phe-chl-qtz-Fe ox (hm) [1]
1316	GR 24a	Plage du Rolaz	465785 / 5276945	Eclogite	Grt-gln-ep-omph-barr-phe-chl-qtz-Fe ox (hm, mt) [1]
1317	GR 29	Porh Giguéou	467382 / 5274810	Eclogite	Grt-gln-omph-ep-barr phe-chl-qtz-ap-rt-ttn- $\pm$ $\diamond$ lws [1]
1318	GR 06a	S of Locqueltas	466281 / 5274488	Greenschist	Chl-ep-ab-phe-barr-qtz-Fe ox (mt)-Fe hydrox [2]
1319	GR 23	Côte d'Héno	466150 / 5276845	Greenschist	Grt-ep-chl-ab-barr-phe-act-gln-ttn-rt-Fe ox (mt) - $\diamond$ lws [1]
1320	GR 25b	Port Lay	465455 / 5277071	Greenschist	Grt-ep-chl-gln-barr-act-ab-qtz-ap-ttn-rt-phe-Fe ox (mt) [1]
1321	GROA 43	Biléric	462025 / 5277677	Greenschist	Chl-ab-cc-qtz-phe-ilm-czo-Fe ox (mt) [2]
1322	GROA 52	Gadoëric	464462 / 5274940	Greenschist	Ab-chl-qtz-ep-act-barr-cc-ttn-Fe ox (mt) [3]
1323	GROA 110	W of Porh Morvil	467601 / 5274553	Micaschist (BS)	Cld-grt-phe-qtz-ap-pg-rt-chl-Fe ox (hm)-tur [2]
1324	GR 26b	Port Melin	464578 / 5277376	Micaschist (GS)	Grt-phe-ep-qtz-chl-ab-ttn-ap-Fe ox (mt)-tur [1]
1325	GROA 104	Côte d'Héno	466186 / 5276839	Micaschist (GS)	Grt-phe-pg-gln-chl-qtz-ap-act-rt -ilm [2]

1327
1328

BS: blueschist; GS: greenschist; $\diamond$ lws: pseudomorphs after lawsonite.

* see Figure 1

1329

** The mineral abbreviations are from Kretz (1983)

1330

*** [1] El Korh et al. (2009); [2] El Korh et al. (2013); [3] El Korh et al. (2011)

1331

Table 2. Neptune Plus MC-ICPMS instrumental setup and operating conditions

model	Neptune Plus (ThermoFischer Scientific)
type	multi-collector ICPMS
cool flow (Ar)	15 L/min
auxiliary flow (Ar)	0.8 L/min
sample flow (Ar)	0.95–1.11 L/min
load coil power	1180 W
sampler cone	Ni
skimmer cone	Ni, H geometry
focus lens	-676 to -664 V
shape quadrupole	201 V
focus quadrupole	0.5 V
nebuliser *	cyclonic chamber; Apex HF (Elemental Scientific, USA)
resolution	medium (6000)
scanning mode	static mode
detector counting mode	Faraday cups
cup configuration	Low 3 (68Zn), Low 2 (69Ga), Low 1 (70Ge), Axial (71Ga), High 1 (72Ge), High 2 (73Ge), High 3 (74Ge)
integration cycles	60 (9 min)
washout	200 s in HNO ₃ (0.6 N)
cleaning between samples	8 min in HNO ₃ (0.01 N) 2 min in HNO ₃ (0.01 N)

* The cyclonic nebuliser was employed for the analyses performed during February 2014; the Apex HF nebuliser was employed for the analyses carried out from June to September 2014.

1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390

Table 3. Silica, iron, $\delta^{18}\text{O}$ and trace element [Ga, Ge, Rb, Y, (Ce/Yb)_{PM}] composition of the studied rocks

	SiO ₂	Fe ₂ O ₃ total	FeO	Fe ³⁺ /ΣFe (calculated)	Ga	Ge				Ge/Si *	Ge/Fe *
						Routine analysis		Standard		(x 10 ⁻⁶)	(x10 ⁻⁵)
						fusion 1	fusion 2	addition	Mean		
GR 02	46.61 [1]	13.37 [1]	5.53	0.54	21.6	2.0	1.9	2.0	2.0 (0.2)	8.68	2.02
GR 04	46.44 [2]	9.59 [2]	4.03	0.47	18.9	1.4	–	1.6	1.5 (0.2)	6.72	2.17
GR 11b	47.63 [1]	12.45 [1]	5.12	0.54	22.4	1.8	–	1.8	1.8 (0.1)	7.65	1.96
GR 12b	46.91 [1]	10.34 [1]	3.35	0.64	16.9	1.5	–	1.5	1.5 (0.1)	6.72	2.04
GR 25a	47.56 [1]	12.67 [1]	7.37	0.35	21.3	1.7	1.5	1.5	1.6 (0.2)	6.77	1.70
GROA 56	46.42 [2]	11.29 [2]	4.52	0.56	19.3	1.7	–	1.6	1.6 (0.1)	7.13	1.96
GR 21c	48.75 [1]	12.65 [1]	6.45	0.43	21.8	1.6	–	1.8	1.7 (0.2)	7.20	1.85
GR 24a	49.39 [1]	13.12 [1]	7.71	0.35	21.1	1.6	1.6	1.5	1.5 (0.2)	6.51	1.64
GR 29	49.48 [1]	14.18 [1]	8.73	0.32	21.0	2.1	1.9	1.9	2.0 (0.3)	8.25	1.92
GR 06a	49.50 [2]	10.56 [2]	6.34	0.33	18.4	1.7	1.7	1.5	1.6 (0.2)	6.51	2.04
GR 23c	48.04 [1]	14.30 [1]	6.48	0.50	20.7	1.5	1.6	1.5	1.5 (0.2)	6.54	1.47
GR 25b	48.49 [1]	12.26 [1]	6.69	0.49	19.7	1.9	1.8	1.7	1.8 (0.2)	7.69	2.03
GROA 43	43.22 [2]	11.86 [2]	8.51	0.20	18.9	1.8	–	1.9	1.9 (0.1)	8.01	1.95
GROA 52	44.75 [3]	11.40 [3]	7.90	0.23	16.9	1.3	1.2	1.2	1.2 (0.1)	5.25	1.38
GROA 110	62.95 [2]	7.23 [2]	5.74	0.12	28.7	3.2	2.8	3.1	3.0 (0.3)	9.91	5.76
GR 26b	50.96 [1]	9.49 [1]	5.48	0.36	27.7	2.0	2.0	2.1	2.0 (0.1)	8.11	2.91
GROA 104	69.32 [2]	5.47 [2]	3.47	0.29	22.7	2.1	1.9	2.0	2.0 (0.2)	5.92	5.02

2σ standard errors for mean Ge abundances are given in parentheses.

SiO₂, Fe₂O₃ total and FeO concentrations are given in weight %; Ga and Ge abundances are given in ppm.

*The Ge/Si and Ge/Fe ratios were calculated using SiO₂, Fe₂O₃ and FeO contents that were recalculated for an anhydrous rock composition, in order to cancel out the effects related to the various degrees of hydration (i.e. variations of the LOI content) between the different metamorphic facies.

References in square brackets as in Table 1.

1392 Table 4. Ge and Ga abundances measured using LA-ICPMS in the various generations of epidote and garnet in metabasites
1393

		P–T conditions (El Korh et al., 2009)	Ga (ppm)		Ga/Al (x 10 ⁻⁴)		Ge (ppm)		Ge/Si (x 10 ⁻⁴)	
			Range	Mean	Range	Mean	Range	Mean	Range	Mean
1394										
1395										
1396	<i>Blueschists</i>									
1397	Ep I	1.0-2.0 GPa, < 450°C	20–59	40 (7)	1.82–5.21	3.49 (0.57)	2.0–5.4	3.1 (0.6)	0.12–0.33	0.18 (0.04)
1398	Ep II	1.6-2.3 GPa, 450-500°C	30–64	44 (6)	2.20–5.59	3.68 (0.54)	2.5–10	6.2 (1.1)	0.14–0.59	0.36 (0.07)
1399	Ep III	1.6-2.3 GPa, 500-600°C	35–66	45 (4)	2.55–5.05	3.60 (0.28)	2.6–6.2	3.9 (0.4)	0.14–0.35	0.22 (0.02)
1400	Garnet core	1.6-2.3 GPa, 450-500°C	2.5–4.4	3.5 (0.5)	0.23–0.40	0.33 (0.05)	3.8–5.2	4.6 (0.5)	0.22–0.30	0.27 (0.03)
1401	Garnet rim	1.6-2.3 GPa, 500-600°C	2.8–4.8	3.9 (0.5)	0.26–0.45	0.36 (0.05)	4.1–5.5	4.8 (0.4)	0.24–0.31	0.28 (0.02)
1402										
1403	<i>Eclogites</i>									
1404	Ep I	1.0-2.0 GPa, < 450°C	61–79	73 (3)	4.52–5.70	5.32 (0.18)	2.5–4.5	3.5 (0.4)	0.14–0.26	0.20 (0.02)
1405	Ep II	1.6-2.3 GPa, 450-500°C	68–79	74 (4)	4.89–5.80	5.35 (0.35)	3.1–5.6	4.3 (0.8)	0.18–0.41	0.26 (0.08)
1406	Ep III	1.6-2.3 GPa, 500-600°C	72–112	86 (6)	5.20–8.00	6.18 (0.44)	3.0–6.0	4.2 (0.5)	0.17–0.35	0.24 (0.03)
1407	Garnet core	1.6-2.3 GPa, 450-500°C	5.3–8.6	6.9 (0.7)	0.46–0.78	0.62 (0.07)	5.0–7.2	5.9 (0.4)	0.28–0.42	0.34 (0.03)
1408	Garnet rim	1.6-2.3 GPa, 500-600°C	5.3–7.6	6.3 (0.5)	0.47–0.67	0.55 (0.04)	5.8–8.3	6.8 (0.5)	0.33–0.49	0.40 (0.03)
1409										
1410	<i>Greenschists</i>									
1411	Ep I	1.0-2.0 GPa, < 450°C	48–58	52 (4)	3.43–4.49	4.11 (0.37)	3.2–7.5	4.6 (1.5)	0.18–0.43	0.27 (0.08)
1412	Ep II	1.6-2.3 GPa, 450-500°C	50–55	52 (3)	4.14–4.52	8.66 (0.21)	8.2–13	11.3 (3.1)	0.47–0.75	0.65 (0.18)
1413	Ep III	1.6-2.3 GPa, 500-600°C	54–66	60 (4)	4.16–4.63	9.00 (0.15)	3.2–6.4	4.1 (1.0)	0.18–0.37	0.24 (0.06)
1414	Ep IV	< 1.6 GPa, < 500°C	47–64	55 (4)	3.43–5.32	8.52 (0.39)	3.1–6.0	3.8 (0.7)	0.18–0.35	0.22 (0.04)
1415	Garnet core	1.6-2.3 GPa, 450-500°C	3.5–5.0	4.1 (0.6)	0.31–0.47	0.75 (0.07)	3.7–4.6	4.0 (0.4)	0.21–0.27	0.23 (0.03)
1416	Garnet rim	1.6-2.3 GPa, 500-600°C	3.1–4.6	4.0 (0.4)	0.27–0.41	0.73 (0.04)	3.3–5.3	4.4 (0.6)	0.19–0.31	0.26 (0.03)
1417										

1417
1418 2 σ standard errors for mean abundances are given in parentheses
1419
1420
1421

1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464

Table 5. Germanium isotopic compositions of Ge standards and studied metabasites

Sample		n	$\delta^{72}\text{Ge}$ (‰)		$\delta^{73}\text{Ge}$ (‰)		$\delta^{74}\text{Ge}$ (‰)	
			Mean	$\pm 2\sigma^*$	Mean	$\pm 2\sigma^*$	Mean	$\pm 2\sigma^*$
Aldrich	Ge standard	83	-1.01	0.03	-1.53	0.06	-1.97	0.03
Reference**								
[1]			-1.05	0.15	-1.58	0.27	-2.04	0.23
[2]			-1.03	0.12	-1.54	0.17	-2.01	0.23
JMC	Ge standard	82	-0.16	0.02	-0.21	0.04	-0.30	0.02
Reference**								
[2]			-0.16	0.07	-0.23	0.12	-0.29	0.10
BIR-1 basalt (Iceland)	USGS standard	4	0.27	0.12	0.50	0.36	0.52	0.25
Reference**								
[1]			0.24	0.04	0.47	0.06	0.57	0.04
[2]			—	—	—	—	0.62	0.13
GR 02	Blueschist	4	0.30	0.25	—	—	0.52	0.13
GR 11b	Blueschist	5	0.46	0.11	0.45	0.07	0.65	0.12
GR 12b	Blueschist	3	0.17	0.03	0.21	0.56	0.21	0.02
GR 25a	Blueschist	2	0.50	0.10	0.38	0.37	0.63	0.12
GR 21b	Eclogite	3	—	—	0.65	0.12	0.48	0.15
GR 24a	Eclogite	4	0.44	0.06	0.46	0.27	0.55	0.13
GR 29	Eclogite	4	0.24	0.08	0.30	0.09	0.42	0.07
GR 06a	Greenschist	4	0.37	0.01	0.38	0.50	0.40	0.13
GR 23	Greenschist	4	0.37	0.19	0.25	0.50	0.49	0.07
GR 25b	Greenschist	4	—	—	0.33	0.04	0.38	0.03
GROA 43	Ab-/cc-greenschist	3	0.58	0.17	0.87	0.20	0.88	0.20
GROA 52	Ab-/cc-greenschist	5	0.74	0.01	0.73	0.13	0.98	0.13
GROA 110	Micaschist (BS)	4	0.13	0.21	0.15	0.26	0.29	0.08
GR 26b	Micaschist (GS)	3	—	—	0.31	—	0.38	0.24
GROA 104	Micaschist (GS)	2	0.44	0.27	—	—	0.70	0.04

* 2σ uncertainties for the reference values of Aldrich and JMC standards given as 2σ standard deviations; 2σ uncertainties for the measured Aldrich and JMC standards, for BIR-1 and for the samples from the Ile de Groix at 95% confidence level according to the Student's t-distribution

** Reference values are from [1] Luais (2012); and [2] Escoubé et al. (2012)

n = number of replicates; $\delta^x\text{Ge}$ values (‰) refer to NIST3120a Ge standard normalisation
Overestimated $\delta^{72}\text{Ge}$ and $\delta^{73}\text{Ge}$ are not given in the table. They may result from irresolvable interferences of ^{72}Ge (71.9221 a.m.u.) with $^{56}\text{Fe}^{16}\text{O}$ (71.9299 a.m.u.) on mass 72, and of ^{73}Ge (72.9234 a.m.u.) with $^{57}\text{Fe}^{16}\text{O}$ (72.9303 a.m.u.) on mass 73. Interference on mass 74 is resolvable at a medium mass resolution: (^{74}Ge : 73.9212 a.m.u.; $^{58}\text{Fe}^{16}\text{O}$: 73.9327 a.m.u)

High-pressure facies

Retrograde facies

Blueschists

Eclogites

Greenschists

◆ Grt-bearing blueschists	▲ Grt-bearing greenschists
◆ Grt-free blueschists	▲ Ab/Cc-bearing greenschists
● Eclogites	✱ Micaschists