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Mg–O isotopes trace the origin of Mg-rich fluids in the deeply subducted continental crust of Western Alps

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ABSTRACT

Fluids are important for mass transfer at the slab–mantle interface in subduction zones. However, it is usually difficult to trace fluids from specific sources in a subducting slab, especially those derived from dehydration of serpentinite. Coesite-bearing whiteschist at Dora-Maira in the Western Alps is characterized by strong Mg enrichment relative to the country rocks, which requires infiltration of Mg-rich fluids into the supracrustal rock. In order to constrain the origin of such Mg-rich fluids, we have performed an integrated study of whole-rock Mg and O isotopes, zircon U–Pb ages and O isotopes for the whiteschist and related rocks. Zircons in the whiteschist show two groups of U–Pb ages at ∼262 Ma and ∼34 Ma, respectively, for relict and newly grown domains. The Permian U–Pb ages of relict magmatic domains are consistent with the protolith age of host metagranite, suggesting that their common protolith is the Permian granite. The Tertiary U–Pb ages occur in coesite-bearing metamorphic domains, consistent with the known age for ultrahigh-pressure metamorphism. The metamorphic domains have δ^{18}O values of 5.8–6.8‰, whereas the relict magmatic domains have high δ^{18}O values of ∼10‰. Such high δ^{18}O values are also characteristic of the metagranite, indicating that the whiteschist protolith underwent metasomatism by metamorphic fluids with low δ^{18}O value of ∼2–4‰. The whiteschist mostly has whole-rock δ^{26}Mg values of −0.07 to 0.72‰, considerably higher than country-rock δ^{26}Mg values of −0.54 to −0.11‰. Thus, the metamorphic fluids are not only rich in Mg but also heavy in Mg isotopes. They were probably derived from the breakdown of Mg-rich hydrous minerals such as talc and antigorite in serpentinite at the slab–mantle interface in the subduction channel. Therefore, the dehydration of mantle wedge serpentinite during the subduction and exhumation of continental crust can provide the Mg-rich fluids responsible for the metasomatism of crustal rocks at subarc depths.

1. Introduction

Fluids are important for mass transfer in subduction zones. Arc volcanics are commonly characterized by enrichment of large ion lithophile elements (LILE) and light rare earth elements (LREE) relative to the high field strength elements (HFSE) and heavy rare earth elements (HREE). This geochemical feature is generally attributed to slab-derived fluids, which transfer the characteristic signature from subducting slabs to arc volcanics via metasomatism of the mantle wedge (Manning, 2004; Bebout, 2007). However, it is usually tricky to trace fluids from different sources, especially those from dehydration of serpentinite (Tonarini et al., 2011; Scambelluri et al., 2014, 2015).

Coesite-bearing whiteschist at Dora-Maira in the Western Alps is characterized by enrichment in Mg but depletion in Na, Ca, Fe^{2+} and LILE relative to the host metagranite (e.g., Schertl and Schreyer, 2008; Ferrando et al., 2009; Ferrando, 2012). This provides an excellent target to study the fluid–rock interaction in a typical continental subduction zone. Although intensive studies have been devoted to the whiteschist since the first discovery of coesite in it (Chopin, 1984), its petrogenesis is still a matter of hot debate. The controversy mainly focuses on the timing and mechanism of Mg enrichment (e.g., Schertl and Schreyer, 2008; Ferrando et al., 2009; Ferrando, 2012). Early studies suggested a protolith of evaporitic sediment for the whiteschist (Schreyer, 1977; Chopin, 1984), which is favored by the recent phase diagram modeling of Franz et al. (2013). However, observations increasingly

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point to a metasomatic origin. But the opinions on the timing and the sources of metasomatic fluids are still controversial (Sharp et al., 1993; Compagnoni and Hirajima, 2001; Ferrando et al., 2009; Ferrando, 2012; Gauthiez-Putallaz et al., 2016). Based on studies of stable isotopes and fluid inclusions, it is proposed that the fluids originated from the subducting oceanic slab, possibly from serpentinite dehydration during prograde metamorphism of Alpine orogeny (Sharp et al., 1993; Ferrando et al., 2009; Ferrando, 2012). However, Gauthiez-Putallaz et al. (2016) suggest the Mg enrichment by alteration of continental crust in a Permian extensional setting. Pawlig and Baumgartner (2001) envisaged that a similar Mg-rich rock at Monte Rosa in the Western Alps was formed by pre-Alpine argillitic alteration of the metagranite. Resolving the metasomatic timing and the source of metasomatic fluids in whiteschist petrogenesis can shed new light on fluid–rock interaction in subduction zones and its effect on the geochemistry of deeply subducted crustal rocks.

Magnesium isotopes can potentially provide unique constraints on the source of Mg-rich fluids under subduction-zone conditions. Such isotopes are remarkably homogeneous for oceanic mantle peridotites and basaltic rocks from them, and do not show significant fractionation during mantle melting, magma differentiation, and metamorphic dehydration of crustal rocks (Teng et al., 2007, 2010a; Liu et al., 2010; Li et al., 2014a; Wang et al., 2014). However, chemical weathering can induce large Mg isotope fractionations, resulting in Mg-bearing carbonates and silicate weathered residues with very light and heavy Mg isotope compositions, respectively (e.g., Young and Galy, 2004; Teng et al., 2010b). Therefore, Mg isotopes can be an important geochemical tracer of either magmatic sources that contain recycled crustal material (e.g., Huang et al., 2015a), or potentially the variable sources of metamorphic fluids from the dehydration of different hydrous minerals in subduction zones.

In this contribution, we present an integrated study of whole-rock Mg and O isotopes, and zircon U–Pb ages and O isotopes for whiteschist and its host rock from Dora-Maira. The new results, integrated with previous data, shed new light not only on the origin of Mg-rich fluids for whiteschist formation in Western Alps but also on fluid–rock interaction in the continental subduction channel.

2. Geological setting and samples

Dora-Maira (Fig. 1), together with outcrops at Gran Paradiso and Monte Rosa, constitute three Internal Crystalline Massifs within the Penninic Domain in the Western Alps (Chopin, 1984; Compagnoni and Hirajima, 2001; Castelli et al., 2007). It is composed of Variscan crystalline basement and Triassic cover, and the former was intruded by Permian granitoids. These rocks experienced high-pressure (HP) and ultrahigh-pressure (UHP) eclogite-facies metamorphism during the Alpine orogeny. During this orogeny, they formed a nappe pile and were juxtaposed to the oceanic lithosphere-derived units of the Piemonte Zone. The Brossasco–Isasca Unit (BIU) in the southern part of Dora-Maira experienced peak UHP metamorphism at $\sim$730 °C and $\sim$4.0 GPa, followed by multi-stage retrograde recrystallizations (e.g., Sharp et al., 1993; Hermann, 2003; Castelli et al., 2007). The BIU is subdivided into a polymetamorphic complex formed by Alpine metamorphic reworking of the Variscan amphibolite-facies basement and a monometamorphic complex consisting of orthogneiss with different extents of deformation (Gebauer et al., 1997). The polymetamorphic complex is mainly composed of kyanite–almandine–phengite paraschist with interlayers of marble and eclogite (Fig. 1).

The monometamorphic complex locally contains whiteschist, which occurs as layers or lenses of several meters to tens of meters in thickness within the granitic gneisses (Fig. 1). Notably, the

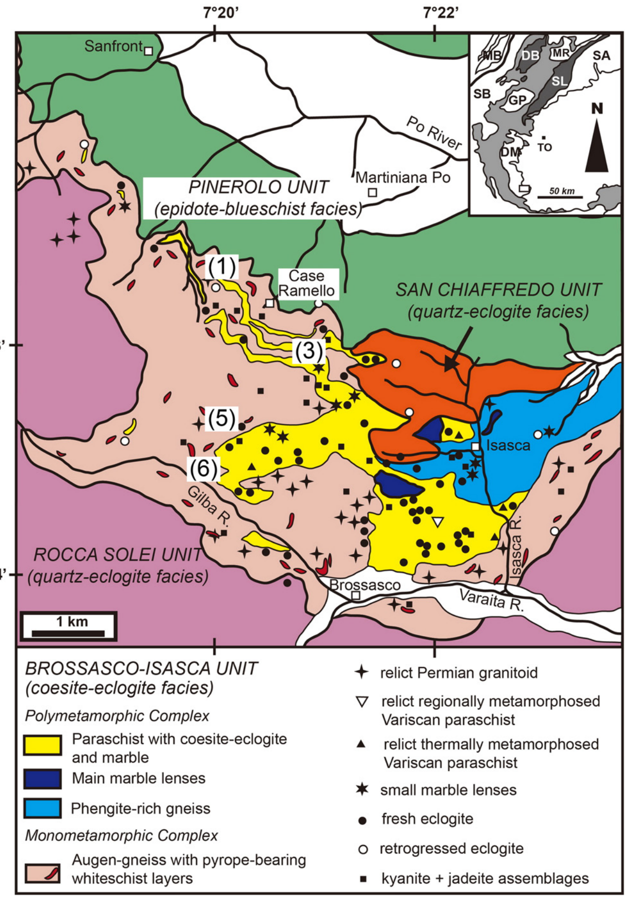

Fig. 1. Geological sketch map for the central portion of the coesite-bearing "Brossasco–Isasca Unit" (BIU) and relationships with other adjacent units (modified after Castelli et al., 2007). The sample locations labeled are after Schertl and Schreyer (2008). Note that the "Pinerolo Unit" is composed of graphite-rich schists and metaclastics of the epidote–blueschist facies; the tectonically lower and upper units, "San Chiaffredo Unit" and "Rocca Solei Unit", respectively, consist of pre-Alpine basement rocks overprinted by the Alpine quartz–eclogite facies metamorphism. The inset shows the location of the BIU within a simplified tectonic sketch-map of Western Alps. Abbreviations in the Internal Crystalline Massifs of the Penninic Domain: MR, Monte Rosa; GP, Gran Paradiso; DM, Dora-Maira; SL, Sesia–Lanzo Zone. Abbreviations elsewhere: DB, Dent Blanche nappe of the Austroalpine Domain; MB, Mont Blanc–Aiguilles Rouges of the Helvetic–Dauphinois Domain; SB, Grand St. Bernard Zone of the external Penninic Domain; SA, Southern Alps; TO, Torino Town.

term "whiteschist" was introduced by Schreyer (1977); such a rock has also been named pyrope quartzite in the literature (Schertl and Schreyer, 2008). The contact between whiteschist and orthogneiss can be very sharp in the field (Chopin, 1984). However, such a contact can also be transitional, marked by a few decimeters to several meters of phengite-rich rocks (Schertl and Schreyer, 2008). Inside the whiteschist blocks, there are phengite schist and jadeite–kyanite quartzite layers (Schertl and Schreyer, 2008). The common main minerals of whiteschist include quartz/coesite, pyrope, kyanite, phengite and talc. The size of pyrope crystals is highly variable, from several millimeters to more than 20 cm (e.g., Chopin, 1984; Ferrando et al., 2009). Rare superzoned garnet of centimeter size was discovered in the whiteschist, showing an almandine core and a pyrope rim (Compagnoni and Hirajima, 2001).

The present study focuses on the whiteschist and its country rock from four outcrops in the monometamorphic complex at Dora-Maira (Fig. 1), corresponding to localities 1, 3, 5 and 6 in Schertl and Schreyer (2008). We collected five additional samples (with prefix 13AP in Table A1). Taken together, the studied samples contain fine-grained whiteschists, pyrope megablasts, and

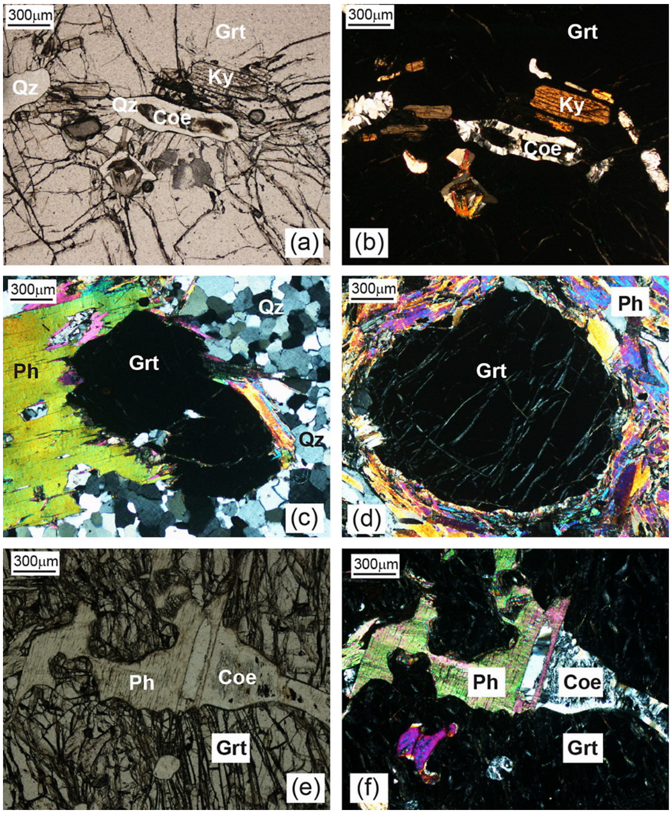

Fig. 2. Microphotographs of whiteschists from Dora-Maira in the Western Alps. Panels (a–b) Coesite inclusions in garnet of sample 13AP57. Parts of the coesite grains have been retrogressed to palisade quartz; (c) typical mineral assemblage in 13AP57, composed of pyrope garnet, phengite and quartz. Note the slight retrogression imprint along the garnet margins; (d) pyrope garnet in contact with phengite and quartz (13AP58). The garnet margins also show slight retrogression; (e–f) coesite inclusions in garnet of sample 13AP58. Parts of the coesite grains have been retrogressed to palisade quartz. Note the coesite is in contact with phengite. Panels (a) and (e) are taken under plane-polarized light (PPL), whereas the other panels are under cross-polarized light. Mineral abbreviations: Grt, garnet; Ky, kyanite; Qz, quartz; Coe, coesite; Ph, phengite.

their country rocks (metagranite and granitic gneiss). For convenience, the country rocks are all called metagranite in the following, if not otherwise specified. The five whiteschist samples 13AP57 to 13AP63 show the same petrographic features as those studied previously from this outcrop (Chopin, 1984; Schertl and Schreyer, 2008). Abundant coesite inclusions occur in small pyrope grains, and the coesite is always surrounded by palisade quartz (Fig. 2). The pyrope grains show multi-stage coronas on their margins (Fig. 2c–d), similar to those found by Hermann (2003), suggesting different degrees of retrogression. In addition, sample 13AP58 is particularly rich in pyrope crystals.

3. Analytical methods

Magnesium isotopes were measured using a Thermo Scientific Neptune Plus MC-ICPMS followed the method of An et al. (2014) at the CAS Laboratory of Crust–Mantle Materials and Environments in University of Science and Technology of China, Hefei. Whole-rock powders were fully digested to obtain ∼20 μg Mg for chemical purification. A mixture of concentrated $HF–HNO_3$ was used for digestion. Mg purification was performed in Savillex microcolumns loaded with 2 ml of Bio-Rad AG50W-X12 resin. For Mg isotope analysis, the sample-standard bracketing (SSB) method was used, with DSM-3 as bracketing standard. The Mg isotope results are reported using the standard δ notation relative to DSM-3. Uncertainties for δ^{25}Mg and δ^{26}Mg of standards and samples are given as two standard deviations (2σ) based on repeated measurements.

The data quality was carefully controlled by repeated analyses of multiple Mg isotope standards (Table A1). The long term external precision is better than ±0.05‰ (An et al., 2014). At the same time, several samples were repeatedly processed through the whole procedure under the same conditions. During the analytical session, the δ^{26}Mg results of CAM-1 (-2.59 ± 0.04‰), SRM980 (-2.80 ± 0.06‰), IGGMg1 (-1.73 ± 0.07‰), BHVO-2 (-0.24 ± 0.04‰), RGM-1 (-0.19 ± 0.06‰; $n = 3$), GSP-2 (0.05 ± 0.03‰) and AGV-2 (-0.14 ± 0.06‰; $n = 2$) are all identical within error with the established values (An et al., 2014). The replicate analysis of three samples (17688, 13AP57 and 13AP58) with MgO contents of 0.45 wt.%, 5.39 wt.% and 15.29 wt.%, respectively, gave identical values within error for each sample (Table A1).

The analytical methods for zircon CL images and mineral inclusions, whole-rock major elements and O isotopes, and zircon O isotopes and U–Pb ages are presented in the Supplementary Information. The whole-rock Mg and O isotope data are listed in supplementary Table A1. Zircon O isotope and U–Pb isotope data are listed in supplementary Tables A2 and A3, respectively.

4. Results

4.1. Whole-rock major elements

Five whiteschist samples yield similar compositions to those reported by Schertl and Schreyer (2008). Four of them show high SiO_2 (72.7–76.4 wt.%), high MgO (4.68–5.66 wt.%), and low Na_2O, CaO and Fe_2O_3. One sample (13AP58) shows much lower SiO_2 (53.7 wt.%), and significantly higher MgO (15.29 wt.%) and Al_2O_3 (22.8 wt.%). This is consistent with its higher pyrope modal content, as observed in thin section (Fig. 2d–f).

4.2. Zircon U–Pb ages and O isotopes

Most zircons in 13AP57 are euhedral to subhedral with a core-rim structure (Fig. 3c–d). The cores usually exhibit oscillatory zoning and are surrounded by multiple overgrowth domains. Coesite inclusions occur along the core-rim boundaries (Fig. 3a–c), and in the rims. The cores show high Th contents of 30–1188 ppm and high Th/U ratios of >0.1 (except analysis #2c). Some core domains show concordant U–Pb ages of 253–270 Ma with a weighted mean of 263 ± 4 Ma ($n = 12$). The rim domains show low Th contents of 2.1–43 ppm and low Th/U ratios of <0.2. Most of these domains ($n = 6$) give concordant ages of 32.5–35.0 Ma with a weighted mean of 34.1 ± 0.8 Ma. One domain (#9r) shows a significantly older concordant age of 40.2 ± 0.6 Ma. The cores exhibit δ^{18}O values of 9.0–11.1‰, whereas the rims show δ^{18}O values of 6.3–7.2‰ (Fig. 5b). Note a few analytical spots are across different rims (Fig. 3d), but they do not show significant O isotope differences.

Most zircons in 13AP58 are anhedral to subhedral, with some showing resorption structure and patchy zoning (Fig. 3g). Only a few grains show a core-rim structure, with an oscillatory zoned core and an unzoned rim. Some unzoned rims or patchy zoned domains contain coesite (Fig. 3g–i), rutile and garnet. The cores have high Th contents of 59–540 ppm and Th/U ratios of >0.1, and three analyses yield concordant U–Pb ages of 256–267 Ma. The remaining domains ($n = 14$) mostly show low Th contents of 8.9–539 ppm and low Th/U ratios of 0.02–0.25. Most of these domains ($n = 13$) show concordant ages of 32.8–34.8 Ma with a weighted mean of 34.0 ± 0.3 Ma. One domain (#7c) gives an older concordant age of 36.5 ± 0.6 Ma. The three relict cores show δ^{18}O values of 7.1–10.0‰, and the overgrown domains exhibit δ^{18}O values of 5.3–6.5‰ (Fig. 5d).

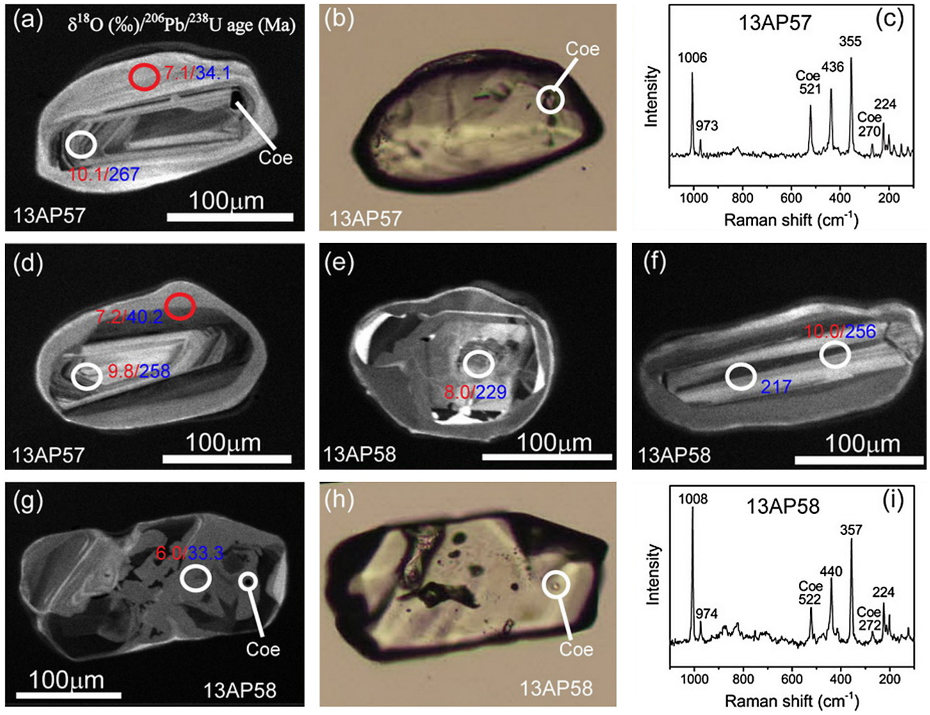

Fig. 3. Zircon cathodoluminescence (CL) images, coesite inclusions and laser Raman spectrograms of coesite. Panels (a–d), 13AP57; (e–i), 13AP58. Note panels (b) and (h) are under PPL for the zircon grains shown in (a) and (g), respectively.

Taking together, the newly grown domains in 13AP57 and 13AP58 have a weighted mean age of 34.1 ± 0.3 Ma (except for two domains of 36.5 Ma and 40.2 Ma), and the core domains have a mean age of 262 ± 3 Ma (Fig. 4b, c).

4.3. Whole-rock Mg and O isotopes

The $\delta^{18}O$ values of whiteschist and metagranite are 5.5–9.0‰ and 7.5–10.2‰, respectively (Table A1). In each outcrop, whiteschist has significantly lower $\delta^{18}O$ values than metagranite by 3–5‰. Across outcrops both whiteschist and metagranite show significant O isotope variations.

On the Mg three-isotope diagram (Fig. 6), all the samples fall on a mass-dependent isotope fractionation line with a slope of 0.520. Except two samples (13AP57 and 17482b), the whiteschists show high $\delta^{26}Mg$ values of −0.07 to 0.72‰, considerably higher than $\delta^{26}Mg$ values of −0.54 to −0.11‰ for the country rocks (Figs. 7 and 8).

Whiteschist mostly has high MgO, low Na_2O + CaO, and high CIA (Fig. 8). In addition, there is no correlation between $\delta^{26}Mg$ values and whole-rock Al_2O_3/MgO ratios. The metagranite shows low MgO, high Na_2O + CaO, and low CIA.

5. Discussion

5.1. The nature of the Dora-Maira whiteschist protolith

Most zircon cores in 13AP57 and 13AP58 show oscillatory zoning and high Th/U ratios of >0.1, indicating that they are relict magmatic domains (Gebauer et al., 1997). The weighted mean U–Pb age of 262 ± 3 Ma is considered to be the protolith age of whiteschist, which is consistent with previous estimates (Gebauer et al., 1997; Gauthiez-Putallaz et al., 2016). Notably, there are no detrital zircons with significantly older U–Pb ages (Fig. 4). In addition, the relict magmatic zircon domains in both whiteschist and metagranite show similar protolith ages of 250–275 Ma, providing compelling evidence for their derivation from the same protolith,

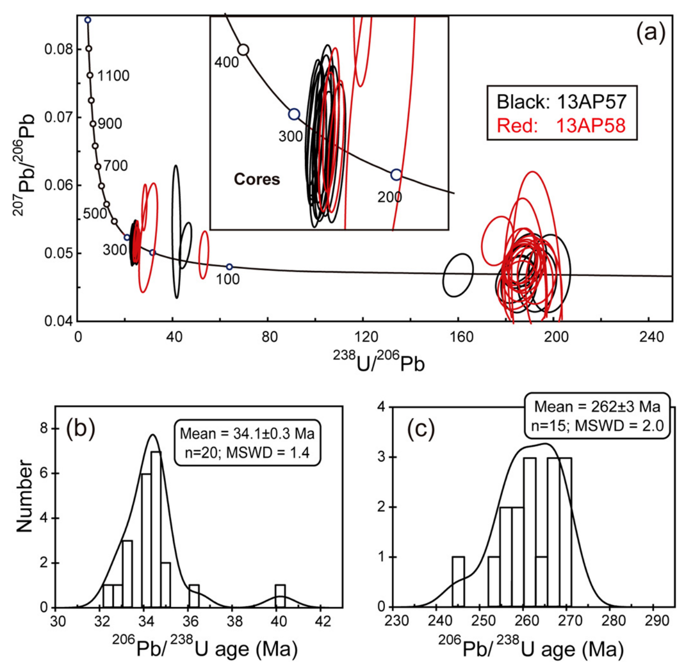

Fig. 4. Zircon U–Pb concordia diagrams (a) and histograms (b–c) for whiteschist from Dora-Maira. In panel (a), black and red circles denote the analyses from 13AP57 and 13AP58, respectively. All the analyses in both samples are included in panels (b) and (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

i.e., a Permian granite (Gebauer et al., 1997; Gauthiez-Putallaz et al., 2016). This interpretation is also supported by the high SiO_2 contents (mostly >70 wt.%) and similar REE patterns between whiteschist and metagranite (Ferrando et al., 2009; Grevel et al., 2009).

The metagranite is mostly peraluminous, and contains phengite and garnet, especially in those that are undeformed and were least

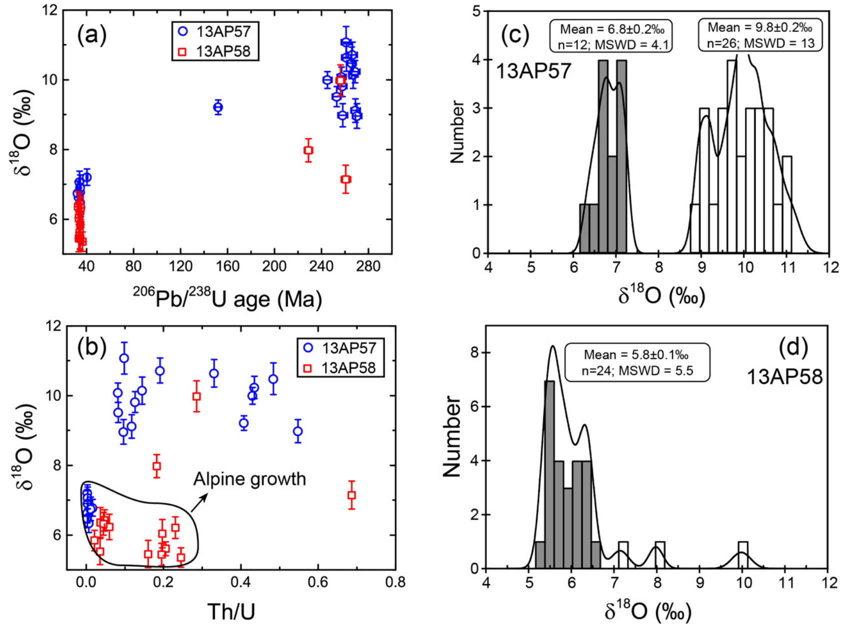

Fig. 5. Zircon O isotope compositions and their relationship to U–Pb ages for whiteschist from Dora-Maira. (a) $\delta^{18}O$ vs. $^{206}Pb/^{238}U$ ages; (b) $\delta^{18}O$ vs. Th/U; (c) and (d) are histograms for zircon $\delta^{18}O$ in 13AP57 and 13AP58, respectively. In panels (c) and (d), the gray bars denote metamorphic domains, and the others are for relict zircon cores.

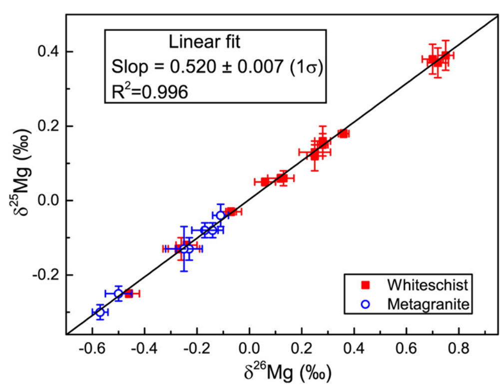

Fig. 6. Diagram of $\delta^{26}Mg$ vs. $\delta^{25}Mg$ for metamorphic rocks from Dora-Maira. Repeated measurements of individual samples are shown as individual points, as they are in Figs. 7 and 8. The solid line represents the fractionation line with a slope of 0.520. Error bars represent 2sd uncertainties. Data are from Table A1.

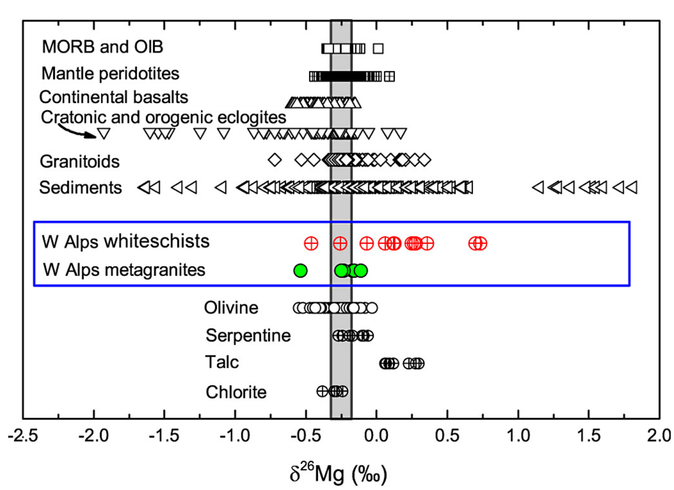

Fig. 7. $\delta^{26}Mg$ values for Dora-Maira samples compared to terrestrial rocks. Note carbonates are not included. See Supplementary Information for data sources and references. The gray shaded area denotes the mantle range after Teng et al. (2010a).

affected by the Alpine metamorphism (Schertl and Schreyer, 2008). Combined with high $\delta^{18}O$ values of 7.5–10.2‰ for whole-rocks and ∼10.0‰ for magmatic zircons, the protolith of both metagranite and whiteschist are probably S-type granite (Schertl and Schreyer, 2008). The Permian zircon domains show a $\delta^{18}O$ variation of ∼2‰, significantly larger than the analytical uncertainty of $\sim\pm 0.4$‰. There is no correlation between their U–Pb ages and O isotopes (Fig. 5a), suggesting that this $\delta^{18}O$ variation is not caused by the Alpine metamorphism, but inherited from the protolith. This interpretation is confirmed by the even larger $\delta^{18}O$ variation of 3.4‰ among metagranite whole-rocks across different outcrops.

The Alpine zircon domains in 13AP57 and 13AP58 show low Th contents and variable Th/U ratios, suggesting that they represent metamorphic growth zones (Gebauer et al., 1997). Some coesites occur along the core-rim boundary (Fig. 3a), similar to the observations by Gebauer et al. (1997) in this area and others in the Dabie–Sulu orogenic belt (Zhang et al., 2009; Gao et al., 2015). These coesites can be transported by fluids into magmatic domains along fractures at UHP conditions. However, coesite inclusions also occur along with rutile and garnet in undoubtedly metamorphic domains (Fig. 3g), demonstrating their growth at UHP conditions. There is no systematic difference in zircon U–Pb ages between metamorphic domains with and without coesite, though prograde zircon growth was identified by Gauthiez-Putallaz et al. (2016). Thus the weighted mean age of 34.1 ± 0.3 Ma is considered as the UHP metamorphic age, consistent with previous estimates (Gebauer et al., 1997; Gauthiez-Putallaz et al., 2016). Notably, the metamorphic zircon and whiteschist whole-rock show low $\delta^{18}O$ values down to 5.3‰ and 5.5‰, respectively, inconsistent with a protolith of evaporitic sediment that typically shows significantly higher $\delta^{18}O$ values of >10‰ (Sharp et al., 1993). In addition, the fluids originating from such a sediment would show a $\delta^{18}O$ value that is too high to explain the low $\delta^{18}O$ values for metamorphic zircons in the whiteschist.

5.2. Zircon O isotope constraints on the origin of metasomatic fluids

The $\delta^{18}O$ values of metamorphic zircon domains in 13AP57 and 13AP58 are markedly lower than those of relict magmatic domains, similar to the observation of Gauthiez-Putallaz et al. (2016). Due to

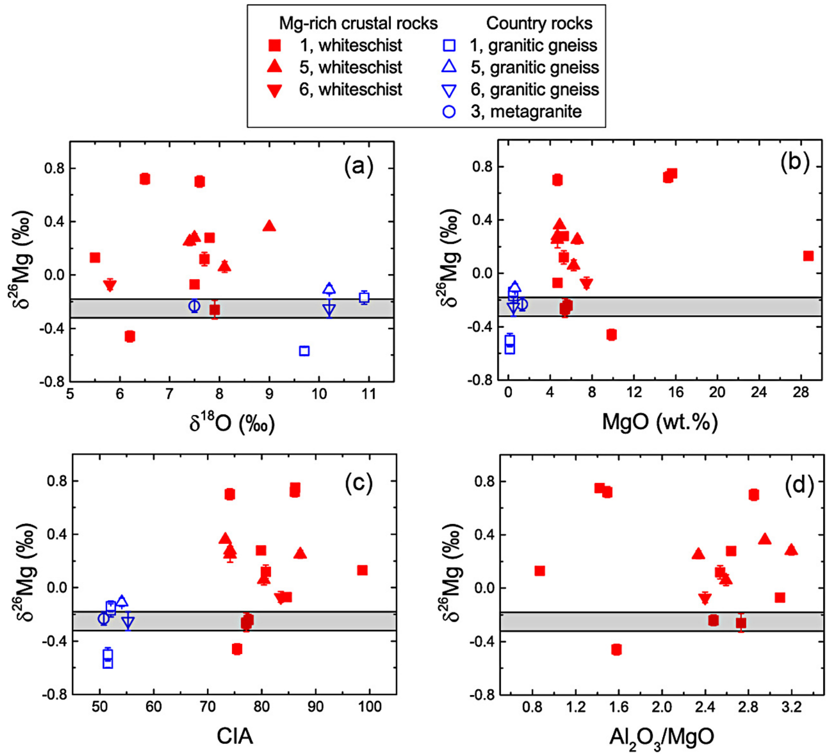

Fig. 8. The correlation between whole-rock δ^{26}Mg values and whole-rock δ^{18}O values (a), MgO contents (b), CIA (c) and Al_2O_3/MgO ratios (d) for whiteschist and country rocks from Dora-Maira. The shaded area represents the mantle δ^{26}Mg values after Teng et al. (2010a). CIA, the chemical weathering index is after Nesbitt and Young (1982), in molecular ratios of $Al_2O_3/(Al_2O_3 + Na_2O + K_2O + CaO)$. Numbers in the legend are the sampling localities as shown in Fig. 1. Note in Fig. 8d, only whiteschists are plotted.

the insignificant O isotope fractionation between zircon and garnet at 600–800 °C (Zheng, 1993a), the zircon δ^{18}O difference between both samples suggests that the whiteschist O isotopes are heterogeneous at ∼1–2‰ level. This is confirmed by the whole-rock δ^{18}O values of whiteschist, which show a difference of ∼2.5‰ across different outcrops.

In a closed system, metamorphic zircon grown at high temperatures (>600 °C) in a metagranite generally shows slightly lower δ^{18}O values than the relict magmatic zircon, as implied by the calculated O isotope fractionation between granite and zircon (Zhao and Zheng, 2003). However, there is a large δ^{18}O decrease of ∼3–5‰ in the metamorphic zircon of whiteschist. The O isotope analyses of mineral separates (Sharp et al., 1993) and whole-rocks (this study) also indicate that the whiteschist shows lower δ^{18}O values by ∼3–5‰ than the metagranite. The much lower δ^{18}O values of the whiteschist compared to the metagranite provide compelling evidence for the infiltration of external fluids with relatively low δ^{18}O values.

Considering the UHP metamorphic temperature of 700–750 °C for the Dora-Maira whiteschist (Sharp et al., 1993; Hermann, 2003), the δ^{18}O value of equilibrated fluids can be calculated by using the zircon-water O isotope fractionation equation of Zheng (1993a). This yields 3.5–4.5‰ for 13AP57 and 2.5–3.8‰ for 13AP58. Based on thermodynamic modeling and microanalysis of garnet and zircon, Gauthiez-Putallaz et al. (2016) suggest that both minerals started to grow at ∼2.2 GPa and 630 °C. This indicates that the fluid infiltration occurred prior to the UHP metamorphism. Petrological and geochemical observations of superzoned garnet and its fluid inclusions provide further constraints on the timing of this metasomatism at the prograde stage (Compagnoni and Hirajima, 2001; Ferrando et al., 2009). If the metasomatism occurred at lower temperatures of 560–590 °C (Ferrando et al., 2009), the fluid equilibrated with zircon should have δ^{18}O value of ∼2.4–4.3‰. Because O isotope exchange between water and rock cannot be completed at low water/rock ratios, the lowest measured δ^{18}O value for the rocks can be considered as the upper limit δ^{18}O value for the fluids (Bindeman et al., 2010). Considering the whole-rock δ^{18}O value of the whiteschist, the fluid δ^{18}O value is possibly lower than ∼4‰. Thus, such fluid probably has δ^{18}O values of ∼2–4‰ in view of all the above data and uncertainties.

Gauthiez-Putallaz et al. (2016) hypothesize that the metagranite may have experienced chemical weathering on the seafloor and formed a kaolinite–chlorite-rich protolith. If so, high δ^{18}O values are expected for these clay minerals, which is inconsistent with the low δ^{18}O values for whiteschist. Furthermore, Mg is a water-soluble element, so that chemical weathering of continental crust will lead to strong Mg depletion in residues (Teng et al., 2010b; Liu et al., 2014). However, the high Mg contents are prominent for whiteschist, in disagreement with the weathering hypothesis. Therefore, the whiteschist is unlikely to have been formed through the chemical weathering of Permian granites.

5.3. Mg isotope constraints on the metasomatic origin of Dora-Maira whiteschist

As summarized in Fig. 7 and references therein, δ^{26}Mg values are variable for mantle peridotites (−0.44 to 0.09‰), continental basalts (−0.60 to −0.15‰) and eclogites (−1.93 to 0.17‰), but they rarely exceed −0.1‰. Granitoids have δ^{26}Mg of −0.72 to 0.34‰, but only a few A-type granites show values above −0.1‰. Sediments show a large range, with both very light and heavy Mg isotopes. For minerals, except some biotites in granites that show high δ^{26}Mg of >0‰ (Shen et al., 2009), talc in serpentinite is the most prominent Mg-rich hydrous mineral with heavy Mg isotopes (Fig. 7). Such Mg isotope data for crustal and mantle reservoirs allow us to link the Dora-Maira whiteschist Mg isotopes to its Mg enrichment mechanism.

5.3.1. Comparison of Mg isotope composition between whiteschist and metagranite

The Dora-Maira metagranite shows low CIA values of 51–55, suggesting a negligible effect of chemical weathering (Nesbitt and Young, 1982). Its δ^{26}Mg values are not correlated with CIA and MgO (Fig. 8). Because of the insignificant Mg isotope fractionation during differentiation of granitic magmas and metamorphic dehydration of crustal rocks, the δ^{26}Mg variation in the metagranite probably reflect its protolith composition. One granitic gneiss (20178) has a slightly higher δ^{26}Mg value of −0.11‰ than normal mantle values, which may imply a protolith that incorporated weathered residues or was influenced by a melting process that preferentially consumed ^{26}Mg-rich minerals (Shen et al., 2009). One gneiss (17469) has a low δ^{26}Mg value of −0.57‰, the lowest value known for unaltered granites (Fig. 7 and references therein). Because Mg-bearing carbonates are the most common materials with low δ^{26}Mg, typically below −0.4‰ (Young and Galy, 2004; Huang et al., 2015b), such a low δ^{26}Mg value possibly suggests incorporation of sedimentary carbonates during partial melting to form its granitic protolith.

The Dora-Maira whiteschist shows variable δ^{26}Mg values of −0.46 to 0.72‰. In order to evaluate the possible effect of heterogeneous mineral distribution on the Mg isotopes, a hand specimen as large as possible was used for making whole-rock powders. In particular, the whole-rock powders for 13AP57 and 13AP58 were each made from two different chips of the rocks. The two sets of each sample show identical major elements and Mg isotopes (Table A1), suggesting that the powders are representative of the bulk rocks. Although some samples (like 13AP58 and 19317) show weak retrogression, they do not show systematic Mg isotope differences compared to the fresh ones. This is consistent with the insignificant Mg mobility at hand specimen scale.

In the whiteschist, pyrope and talc are the major host minerals for Mg, whereas phengite and kyanite are Al-rich minerals (Schertl and Schreyer, 2008). Kyanite is only a minor mineral, and the absence of correlation between δ^{26}Mg and K_2O (not shown) suggests that the Mg isotope variation is not controlled by phengite modal abundances. In addition, petrographic observations show that phengite modal abundances are mostly similar in the whiteschist. In this regard, the whole-rock Al_2O_3/MgO ratios can be used to estimate the relative modal abundances of pyrope and talc. It is reasonable to assume that the Mg content of whiteschist is largely derived from metasomatic fluids due to the low Mg content of metagranite. The absence of a significant correlation between δ^{26}Mg and Al_2O_3/MgO (Fig. 8d) suggests that δ^{26}Mg variation in whiteschist is not caused by different modal proportions of pyrope and talc, but primarily controlled by the heterogeneous metasomatism of their protoliths by Mg-rich fluids. This is consistent with the observation that some samples, like 13AP58 with high pyrope modal contents, still show high δ^{26}Mg values, though garnet preferentially takes up light Mg isotopes (Li et al., 2011). This further indicates that the metasomatic fluids have heterogeneous but mostly heavy Mg isotopes.

5.3.2. The source of metasomatic fluids: dehydration of metasediment vs. serpentinite

The whiteschist shows three prominent features in Mg isotope composition: (1) a large δ^{26}Mg range of 1.2‰; (2) extremely high δ^{26}Mg value up to 0.75‰; (3) mostly higher δ^{26}Mg values than those of metagranite. Diffusion can induce considerable Mg isotope fractionation when there is a significant thermal or compositional gradient (Richter et al., 2008; Huang et al., 2010). However, the whiteschist and metagranite share the same UHP metamorphic evolution during the Alpine orogeny (Gebauer et al., 1997; Gauthiez-Putallaz et al., 2016), so that it is difficult to form a stable and significant thermal gradient between them. In addition, the whiteschist sporadically occurs as lenses or boudins of several meters to tens of meters in thickness within the metagranite. Its δ^{18}O value is significantly lower than that of host rocks (Sharp et al., 1993), but the Mg isotopes show a reversed trend (Fig. 8). Thermal diffusion typically operates at the meter scale, resulting in the same trend of isotope fractionations for different isotope systems (Richter et al., 2008; Huang et al., 2010). In this regard, the spatial occurrence and Mg–O isotope compositions of the whiteschist cannot be explained by thermal diffusion.

Diffusion transport of Mg in fluids can also induce Mg isotope fractionation of up to ∼1‰, as shown at the serpentinite–metapelite interface in the Syros mélange zone (Pogge von Strandmann et al., 2015). If we consider a similar process, for example, the formation of the Dora-Maira whiteschist precursor along a serpentinite–metagranite interface by Mg diffusion from serpentinite-derived fluids into the metagranite, the marked Mg enrichment in the whiteschist suggests that the high δ^{26}Mg values would primarily originate from metasomatic fluids. Whatever conditions chemical diffusion occurs at, it would lead to a positive correlation not only between MgO and δ^{26}Mg but also between Mg and O isotopes (Pogge von Strandmann et al., 2015). However, such correlations are not present in our dataset on the whiteschist. In particular, the chemical diffusion process cannot explain the whiteschist with high MgO content but low δ^{26}Mg value. Consequently, this process cannot explain the Mg isotope composition of whiteschist.

Chemical weathering of crustal rocks increases their CIA values due to the loss of Ca, Na and K by dissolution of feldspars into aqueous solutions (Nesbitt and Young, 1982). It seems that the high CIA of ∼70–100 in whiteschist could be ascribed to the chemical weathering of their protoliths. However, the following observations make this possibility unlikely. (1) Chemically weathered products typically show strong Mg depletion; they also exhibit highly variable Si due to the formation of clay minerals or (Al,Fe)-hydroxides/oxides (Huang et al., 2012; Liu et al., 2014). These expectations are contradictory to the high MgO and SiO_2 contents of whiteschist (Schertl and Schreyer, 2008). (2) The Mg isotopes in whiteschist are heterogeneous, and no significant correlation occurs between δ^{26}Mg and CIA (Fig. 8). (3) The low δ^{18}O values of whole-rocks and metamorphic zircons are not consistent with a chemically weathered protolith, but require metasomatism by fluids with low δ^{18}O values of ∼2–4‰. Gauthiez-Putallaz et al. (2016) hypothesize that the whiteschist has a kaolinite–chlorite-rich protolith due to chemical weathering of metagranite. This hypothesis, however, cannot explain the heterogeneous Mg isotopes, especially the low δ^{26}Mg and δ^{18}O values in the whiteschist, and also the absence of correlation between δ^{26}Mg and CIA.

On the other hand, the following observations argue for the involvement of seawater-derived fluids in whiteschist petrogenesis: (1) there are high δD values of −32 to −27‰ for primary talc and phengite in the whiteschist (Sharp et al., 1993); (2) primary fluid inclusions within prograde kyanite of whiteschist indicate involvement of a Mg, Cl-rich brine (Ferrando et al., 2009). In addition, the superzoned garnet in the whiteschist shows an almandine core and a pyrope rim, consistent with metasomatism by Mg-rich fluids during prograde metamorphism (Compagnoni and Hirajima, 2001). Thus, the protolith of the whiteschist probably underwent metasomatism by fluids that were not only high in δ^{26}Mg and δD and low in δ^{18}O, but also rich in Mg and Cl.

Fluids released from altered oceanic basalt and seafloor sediment in the subduction zone typically show low Mg contents (Manning, 2004). In addition, the metamorphic dehydration of these supracrustal rocks cannot lead to significant Mg isotope change (Li et al., 2014a; Wang et al., 2014; Teng et al., 2016). Thus, such slab-derived fluids cannot account for the high Mg contents and heavy Mg isotopes in the whiteschist.

In view of the above arguments it is possible that the fluids were derived from the dehydration of serpentinite either inside the subducting oceanic lithosphere or at the slab–mantle interface in a subduction channel. The fluids released by serpentinite dehydration can have high Mg contents (Scambelluri et al., 2015), and can also have heavier Mg isotopes than the normal mantle (Teng et al., 2016). In this regard, such fluids can account not only for the geochemical features such as high Mg, high Cl, light O isotopes and heavy D isotopes, but also for the heavy Mg isotopes in the whiteschist.

5.3.3. Metasomatic fluids from serpentinites: the role of antigorite and talc

While chrysotile and lizardite in serpentinite will break down at shallow depths of <20 km, antigorite can be stable at much greater depths depending on the thermal structure of subduction zones (Deschamps et al., 2013). Serpentine is a major carrier of Cl, and the fluids released by antigorite breakdown can contain significant Mg and Cl (Scambelluri et al., 2004, 2015). In addition, serpentinite may acquire variably low $\delta^{18}O$ values of 1.6–5.2‰ by seafloor fluid–rock interaction (Bonifacie et al., 2008). With further subduction, the released fluids may have $\delta^{18}O$ values of ∼3–7‰ at 500–700 °C (Zheng, 1993b), generally consistent with the O isotope composition of metasomatic fluids. Therefore, antigorite breakdown is a potential mechanism for generation of the metasomatic fluids.

Magnesium isotope data for serpentine are still scarce, which show $\delta^{26}Mg$ of −0.27 to −0.06‰ (Beinlich et al., 2014). These values are similar to the coexisting olivine, suggesting insignificant Mg isotope fractionation during serpentinization. If the above Mg isotope data are representative, a huge Mg isotope fractionation, as large as ∼1‰, is required during antigorite breakdown in order to account for the extremely heavy Mg isotopes in whiteschist. This seems unlikely, especially at temperatures >500 °C. Theoretical calculations suggest that Mg isotope fractionations between olivine, clinopyroxene, orthopyroxene and aqueous solution are <0.2‰, even at a low temperature of 300 °C (Schauble, 2011). The Mg isotope fractionation between brucite and aqueous solution is also <0.5‰, even at temperature of <40 °C (Li et al., 2014b). Therefore, it is unlikely that the breakdown of antigorite alone can result in significantly heavier Mg isotopes in the released fluids.

Chlorite in serpentinite shows $\delta^{26}Mg$ values of −0.38 to −0.24‰ (Pogge von Strandmann et al., 2015), which cannot be the primary source for fluids with heavy Mg isotopes. Talc has high $\delta^{26}Mg$ values of 0.06–0.30‰ (Beinlich et al., 2014), consistent with the higher $\delta^{26}Mg$ values of serpentinite that has larger modal talc contents (Pogge von Strandmann et al., 2015). Talc can be a major phase when serpentinite experiences significant carbonation (Kelemen et al., 2011; Beinlich et al., 2014) or metasomatism by Si-rich fluids (King et al., 2003). Talc produced by the former process shows high $\delta^{18}O$ values of 9.9–11.1‰ (Beinlich et al., 2014), whose dehydration will produce fluids with high $\delta^{18}O$ values of >9.0‰ at 500–700 °C (Zheng, 1993b). This is significantly higher than the $\delta^{18}O$ values of metasomatic fluids. However, if talc is produced by metasomatism of Si-rich fluids at the slab–mantle interface, with temperatures >500 °C (King et al., 2003), its dehydration can yield fluids with low $\delta^{18}O$ value of <4‰ based on calculation using the talc-water O isotope fractionation equation of Zheng (1993b). Beinlich et al. (2014) found that $\delta^{26}Mg$ differences between talc and magnesite are 0.73–1.34‰ at 250–290 °C. Assuming both minerals attained Mg isotope equilibrium, and using the theoretical calibration of Mg isotope fractionation between magnesite and aqueous solution (Schauble, 2011), the latter will have $\delta^{26}Mg$ values of 0.42–0.95‰ at such temperatures. If the fluid metasomatism occurred at ∼500–600 °C (Ferrando et al., 2009), the fluids released by talc breakdown would possibly still show high $\delta^{26}Mg$ values that may account for the heavy Mg isotopes in the whiteschist, although quantitive estimates of the fluid $\delta^{26}Mg$ values are not available. In addition, talc is a Mg-rich silicate mineral, so that the fluids released by its breakdown are possibly rich in Mg but poor in Na, K and Ca (Ferrando, 2012). Thus the metasomatism by such fluids can also account for the high Mg and low Na and Ca contents of whiteschist.

6. A possible model for the metasomatic origin of Dora-Maira whiteschist

To explain the high Mg contents in the Dora-Maira whiteschist, metasomatism by high $\delta^{26}Mg$ fluids derived from dehydration of talc-rich serpentinite is the most plausible mechanism, because talc is the only prominent Mg-rich mineral with such heavy Mg isotopes. In this regard, we propose a petrogenetic model whereby the metagranite was metasomatized by Mg-rich fluids released by serpentinite in the continental subduction channel. The deep subduction of continental crust is usually realized by pulling of a previously subducted oceanic slab (Zheng et al., 2015). The Cenozoic subduction of continental crust in the Western Alps is preceded by the Mesozoic subduction of Tethyan oceanic crust along the same subduction channel (Lapen et al., 2007). If the fluids could be derived from serpentinite dehydration inside the subducting slab, they would readily exchange Mg isotopes with the overlying crust to acquire lower $\delta^{26}Mg$ values, which cannot account for the high $\delta^{26}Mg$ values in the whiteschist. Thus, we prefer the dehydration of serpentinite inside the subduction channel.

During subduction of oceanic slab, aqueous solutions would be released from oceanic crust and infiltrate into the overlying mantle wedge (Tonarini et al., 2011; Deschamps et al., 2013), generating serpentinite with antigorite, talc and chlorite at forearc depths (Fig. 9a). With further subduction of the oceanic slab, the continental crust was dragged into the same subduction channel for UHP metamorphism at subarc depths of 80–160 km. Because of the ductile property of serpentinite, it would be scrapped off from the mantle wedge base into the subduction channel (Zheng et al., 2016). On the other hand, the supracrustal rocks would be scrapped off from the descending continental lithosphere into the same subduction channel (von Huene and Scholl, 1991; Scambelluri et al., 2015). These two types of rocks would produce a tectonic mélange and undergo metasomatism by both mantle- and crust-derived fluids at elevated P–T conditions (Bebout, 2007; Zheng, 2012; Zheng et al., 2015).

We suggest that the breakdown of talc in the subduction channel would possibly provide high $\delta^{26}Mg$, low $\delta^{18}O$ fluids for the metasomatism of supracrustal rocks at subarc depths (Fig. 9b, c). Talc stability in serpentinite has been relatively well constrained, and its dehydration requires relatively high temperatures of >600 °C (Scambelluri et al., 2004, 2014). This condition can be met in the subduction channel where the rocks were subducted to subarc depths (Zheng et al., 2016). Geodynamic modeling and petrological thermobarometry suggest heating of the subducting slab surface beneath the mantle wedge (Penniston-Dorland et al., 2015). The addition of fluids from the dehydration of antigorite and chlorite will result in heterogeneous and lighter Mg isotopes in the metasomatic rocks. Locally, the fluids may dissolve Mg-carbonates originated from the subducting sediments, yielding very light Mg isotopes. Thus, the fluids within the subduction channel can acquire distinct Mg isotopes. Such Mg isotope signals can be recorded by the metasomatic rocks in the subduction channel.

In general, our model can account for the Mg–O isotope composition of the Dora-Maira whiteschist. However, in the field such rocks do not at present occur in the direct vicinity of serpentinite or as a tectonic mélange. However, this observation does not pre-

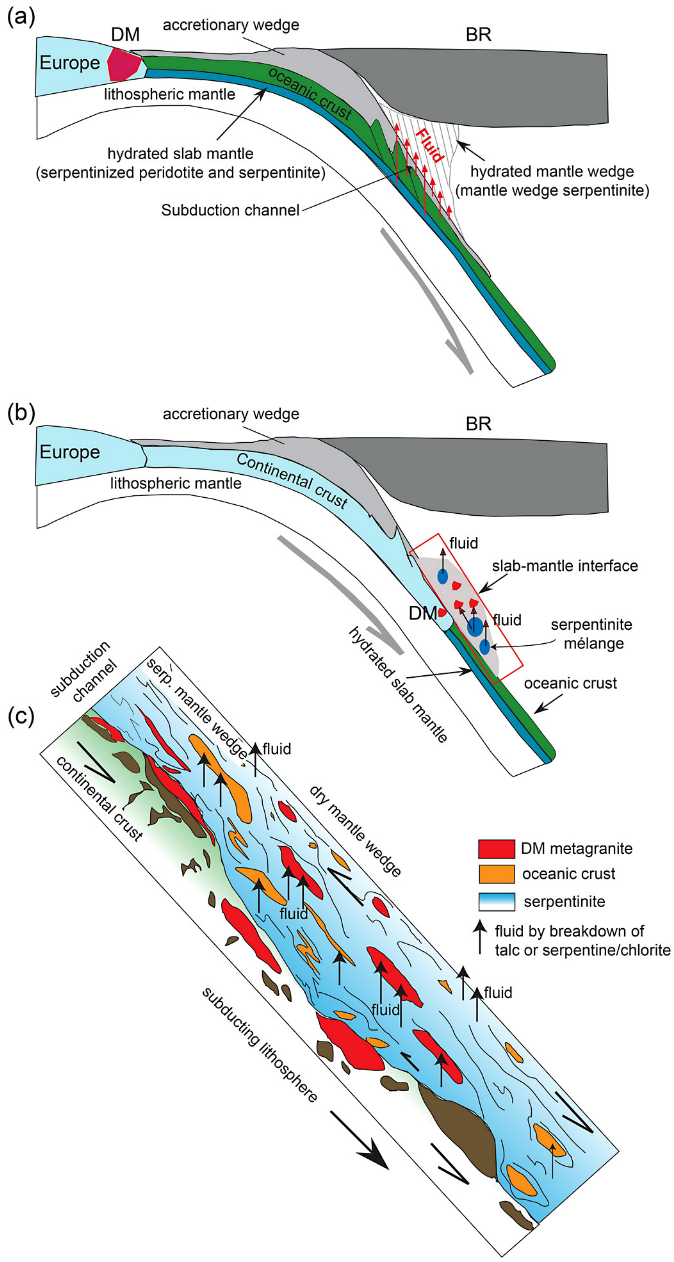

Fig. 9. Schematic diagram showing the metasomatic process for the generation of Mg-rich whiteschist at Dora-Maira in the Western Alps. Based on the tectonic evolution of the Western Alps (Rosenbaum and Lister, 2005), during the period ∼45–40 Ma, the Valais ocean was subducted beneath the Briançonnais (BR) terrane (a). However, it is uncertain whether the Internal Crystalline Masssifs, including Dora-Maira, belonged to the Briançonnais terrane or the European Block at that time. Here it is supposed that they belonged to the European Block, as proposed by Froitzheim (2001). At this stage, the mantle wedge was hydrated by fluids derived from dehydration of the subducting oceanic slab, and a subduction channel was formed at the slab–mantle interface. (b) At ∼40–35 Ma, continental supracrustal rocks were dragged downward by the subducting Valais oceanic slab. Within the subduction channel, the metagranite was metasomatized by fluids derived from the dehydration of serpentinite (c). The breakdown of talc and antigorite/chlorite released Mg-rich fluids with distinct Mg isotopes, resulting in whiteschist with heterogeneous but mostly heavy Mg isotopes. Locally, the fluids dissolve Mg-carbonates derived from the subducting sediments, which may have very light Mg isotopes. Those Mg-rich metasomatic rocks continuously subducted to subarc depths, forming the UHP whiteschists that were then exhumed to the surface. The green and brown colors in panel (c) denote other fluid/melt metasomatic supracrustal rocks. This figure is redrawn after Guillot et al. (2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

clude their contact with serpentinite at sub-arc depths, considering that subduction of oceanic slab is a continuous process lasting tens of million years. As suggested by a recent model of Malusà et al. (2011), the mantle wedge in the Western Alps can coexist with subducted continental rocks during the period of 50–35 Ma. The seismic observations of Zhao et al. (2015) show the presence of the deeply subducted continental slab at ∼70 km at present.

7. Implications for petrogenesis of other Mg-metasomatic rocks in the Alps and the Pyrenees

Crustal rocks with major element composition similar to the Dora-Maira whiteschist also occur in many other localities of the Alps (e.g., Pawlig and Baumgartner, 2001; Demény et al., 1997). Following Ferrando (2012), they were called Mg-metasomatic rocks. Based on their similarities in field, petrological and geochemical features, Ferrando (2012) further proposed that such rocks, while involving different tectonic scenarios, all experienced metasomatism by serpentinite-derived fluids. However, Pawlig and Baumgartner (2001) suggested that the Mg-metasomatic rocks at Monte Rosa were formed through Late Permian argillitic-type alteration of a granitic protolith by late magmatic hydrothermal fluids. The origin of such Mg-metasomatic rocks can be elucidated by examining their Mg–O isotope compositions. Late-stage hydrothermal alteration of granites would not fractionate Mg isotopes (Telus et al., 2012). In this regard, such rocks would keep the protolith Mg isotope composition. On the other hand, if they show high δ^{26}Mg values similar to the Dora-Maira whiteschist but considerably lowered δ^{18}O values relative to the granite protoliths, they were plausibly products of metasomatism by Mg-rich fluids derived from talc-rich serpentinites.

The above arguments may also apply to the origin of the world-class talc-chlorite deposit in the Pyrenees, in Trimouns, France. The metasomatic origin of this deposit is well established, but the metasomatism has long been thought to be caused by late magmatic hydrothermal fluids in the Hercynian (Moine et al., 1989). Recent studies reveal that the metasomatism occurred in the Late Mesozoic (97–112 Ma), possibly related to mantle denudation in a hyperextended margin, and that the metasomatic fluids probably originated from altered peridotite on the seafloor (Boutin et al., 2016, and references therein). Previous studies found that the altered peridotite could acquire slightly higher δ^{26}Mg values than the normal mantle (−0.25 to 0.10‰; Teng et al., 2016). Thus, the rocks metasomatized by fluids derived from dehydration of altered peridotite can have higher δ^{26}Mg values than their protoliths. However, it is unlikely for these rocks to have the extremely heavy Mg isotope compositions as those found in the Dora-Maira whiteschist.

The talc deposit in Trimouns was formed by hydrothermal alteration of carbonates (Moine et al., 1989). Due to the low δ^{26}Mg values of carbonates (e.g., Young and Galy, 2004), the talc-rich samples could acquire very low δ^{26}Mg values. On the other hand, the chlorite deposit is associated with the alteration of basement rocks (Moine et al., 1989), which may acquire significantly higher δ^{26}Mg values than the talc deposit. Thus, a systematic difference in Mg isotopes is expected between the talc and chlorite deposits. In this regard, Mg isotope study can potentially provide new constraints on the origin of such Mg-metasomatic rocks in both the Alps and Pyrenees.

8. Conclusions

A combined study of whole-rock and zircon geochemistry provides new insights into the origin of Dora-Maira whiteschist in Western Alps. Zircon from the whiteschist have two types of genetic domains: (1) relict magmatic domains with U–Pb ages of ∼262 Ma and δ^{18}O values of ∼10‰; (2) UHP metamorphic domains with U–Pb ages of ∼34 Ma and δ^{18}O values of 5.8–6.8‰. The uniform distribution of Permian U–Pb ages between whiteschist and metagranite indicates that they have a common Permian granite protolith. The significantly lower δ^{18}O values in metamorphic zircon domains indicate that the whiteschist protolith underwent metasomatism by fluids with low δ^{18}O values of ∼2–4‰. The δ^{26}Mg values of whiteschist are heterogeneous but mostly in the range of −0.07 to 0.72‰, considerably higher than the metagranite. This requires that the metasomatic fluids are Mg-rich with heterogeneous and primarily heavy Mg isotopes. Such fluids were possibly derived by dehydration of talc and antigorite in serpentinite at the slab–mantle interface in the continental subduction channel. Therefore, coupled Mg–O isotope study can be used to elucidate the timing and process of fluid metasomatism for the origin of Mg-metasomatic rocks in continental collisional orogens.

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Appendix A. Supplementary material

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