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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 Mgrich 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  $\sim$ 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  $\delta^{18}$ O values of 5.8–6.8‰, whereas the relict magmatic domains have high  $\delta^{18}$ O values of  $\sim 10\%$ . Such high  $\delta^{18}$ O values are also characteristic of the metagranite, indicating that the whiteschist protolith underwent metasomatism by metamorphic fluids with low  $\delta^{18}$ O value of  $\sim 2-4\%$ . The whiteschist mostly has wholerock  $\delta^{26}$ Mg values of -0.07 to 0.72%, considerably higher than country-rock  $\delta^{26}$ 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.

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## 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<sup>2+</sup> 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.

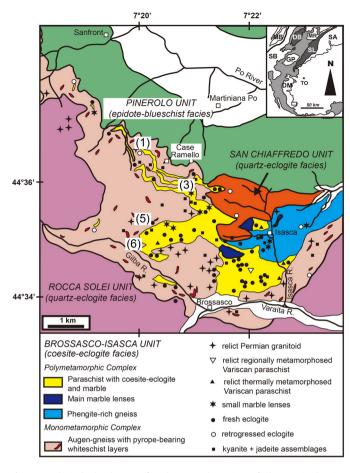
Magnesium isotopes can potentially provide unique constraints on the source of Mg-rich fluids under subduction-zone conditions. Such isotopes are remarkably homogeneous for oceanic mantle peridotites and basaltic rocks from them, and do not show significant fractionation during mantle melting, magma 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 wholerock 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) eclogitefacies 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-almandinephengite 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 meta-morphism. 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 X. 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 jadeitekyanite 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

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