Serpentinite-derived low δ^7Li fluids in continental subduction zones: Constraints from the fluid metasomatic rocks (whiteschist) from the Dora-Maira Massif, Western Alps

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ABSTRACT

Whole rock lithium (Li) and Li isotopic compositions of coesite-bearing whiteschists and their country rock metagranites from the Dora-Maira Massif in the Western Alps were investigated to understand their behavior during fluid-rock interaction in mantle depths of continental subduction zones. The whiteschists reveal relatively low δ^7Li values (-6.4‰ to $+2.4$‰, with an average value of -2.1‰) in comparison to the country rock metagranites (δ^7Li $= -1.2$‰ to $+3.6$‰, with an average value of $+1.4$‰). The δ^7Li values of whiteschists do not show any correlations with major elements (e.g. Mg, Fe), Li, or isotopes (i.e., δ^{26}Mg and δ^{18}O values) and cannot be explained by kinetic fractionation. Hence, the low δ^7Li values of whiteschists result from interactions with metasomatic fluids containing isotopically light Li that occurred in deep portions of a continental subduction zone. Fluid-rock interaction modeling suggests that the metasomatic fluids contain low δ^7Li values (down to -4‰) and moderate Li concentrations (50 to 150 ppm), which were probably derived from the dehydration of serpentinites in the subduction channel. The presence of such low δ^7Li fluids in deep subduction zones could cause Li isotopic heterogeneity in the earth's interior.

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1. Introduction

Fluids in subduction zones are critical for mass and energy transfer within the earth's interior (e.g. Bebout, 2014; Xiao et al., 2015; Zheng et al., 2016). Tracing the origin, composition and evolution of deep fluids, and studying the process of fluid-rock interaction contributes to a better understanding of crust-mantle systems (Yardley and Bodnar, 2014). Lithium (Li) isotopes as potential tracers of deep fluids have been extensively studied (e.g. Halama et al., 2008; Penniston-Dorland et al., 2017; Tomascak et al., 2016; Xiao et al., 2011; Zack et al., 2003). Lithium is a moderately incompatible fluid mobile element with two stable isotopes ^{6}Li

($\sim$7.5%) and ^{7}Li ($\sim$92.5%). The large relative mass difference ($\sim$17%) between ^{6}Li and ^{7}Li can lead to significant isotopic fractionation. Extremely light Li isotopic compositions have been found in high pressure (HP) metamorphic rocks (δ^7Li down to -21.9‰) (Marschall et al., 2007b; Xiao et al., 2011; Zack et al., 2003). Modeling studies suggest that metamorphic dehydration alone cannot produce such large Li isotopic fractionation, and thus other mechanisms are required to account for low δ^7Li rocks (Marschall et al., 2007b). Kinetic processes, for instance chemical diffusion, were considered as primary causes to produce low δ^7Li values with elevated Li contents in HP metamorphic rocks (Marschall et al., 2007b; Penniston-Dorland et al., 2012; Pogge von Strandmann et al., 2011; Teng et al., 2006). Alternatively, extremely low δ^7Li values were also found in mantle rocks and minerals (e.g., olivine), which are difficult to be explained by chemical diffusion in some cases, but rather indicate the presence of low δ^7Li melts/fluids in the mantle (Su et al., 2012; Tang et al., 2014b). Fluids derived from sediments are thought to exhibit relatively high Li contents with

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low δ^7Li, and can lower δ^7Li of rocks via fluid-rock interactions (Agostini et al., 2006; Penniston-Dorland et al., 2010; Tang et al., 2014a). However, Simons et al. (2010) modeled various types of sediment dehydration processes and found that none of them can produce sufficiently low δ^7Li fluid to account for the low δ^7Li ($<-5‰$) metamorphic rocks. Thus, the source and process to form low δ^7Li fluids in deep subduction zones is still ambiguous, and detailed Li isotopic studies on fluid-rock interactions are needed.

Whiteschists and other Mg-rich rocks are widespread in the continental units of the Alps (Ferrando, 2012). These Mg-rich rocks in the Western Alps and Eastern Alps show similar chemical characteristics (high SiO_2 and MgO contents), despite different metamorphic P-T conditions and timing (e.g. Deméy et al., 1997; Ferrando, 2012; Ferrando et al., 2009; Gebauer et al., 1997; Schertl and Schreyer, 2008). Previous studies suggested that metagranites are the protoliths of the Mg-rich rocks in both Western Alps and Eastern Alps, which have experienced metasomatism by fluid-assisted exchange of elements within subducted continental crust (e.g. Chen et al., 2016, 2017; Ferrando, 2012), representing excellent targets to study the general characteristics of metasomatic fluids and fluid-rock interaction in continental subduction zones.

The coesite-bearing whiteschists from Dora-Maira Massif in the Western Alps have experienced ultrahigh-pressure (UHP) metamorphism (e.g. Chopin, 1984; Schertl et al., 1991). Some studies suggested a sedimentary protolith for whiteschist in general (e.g. Chopin, 1984; Franz et al., 2013), which, however, not always can explain the key features of the whiteschists, e.g., their relatively low $\delta^{18}O$ values, zircon O isotopic compositions and heavy Mg isotopic compositions (Chen et al., 2016). Thus increasing evidence points to a metasomatic origin of granitic precursor (e.g. Chen et al., 2016; Ferrando, 2012; Schertl and Schreyer, 2008). However, the source of the metasomatic fluid as well as the age and the time span of the metasomatizing event are still under debate (Chen et al., 2016, 2017; Compagnoni and Hirajima, 2001; Ferrando, 2012; Ferrando et al., 2009; Gauthiez-Putallaz et al., 2016; Sharp et al., 1993). Gauthiez-Putallaz et al. (2016) suggested that the granite protolith has experienced strong alteration by a seawater-hydrothermal fluid during the Permian extension. However, this process would generally decrease the Mg contents and increase the $\delta^{18}O$ values of the rocks. This is inconsistent with the high Mg contents of the whiteschist, and the much lower $\delta^{18}O$ values of the metamorphic zircon domains compared to those of the relict magmatic zircons in the whiteschist (Chen et al., 2016). Recently, Chen et al. (2016) used Mg-O isotopes to demonstrate that the metasomatic fluid should derive from dehydration of serpentinites at the slab-mantle interface in a continental subduction channel.

In this contribution, we present a study of whole rock Li isotopes for whiteschists and their country rock metagranites from the Dora-Maira Massif, Western Alps combined with some samples near the eastern end of the Eastern Alps in Austria. The Mg-rich rocks from the two localities represent ideal examples to compare the influence of metasomatic and metamorphic processes on Li isotopes at different P-T conditions, and provide an additional constraint on the source of low δ^7Li fluids for the formation of whiteschists in particular, and a better understanding of the behavior of Li isotopes in subduction zone related fluids in general.

2. Geological setting and samples

The Brossasco-Isasca Unit (BIU) is a high pressure (HP) to ultrahigh pressure (UHP) tectonic unit that is exposed in the southern Dora-Maira Massif, Penninic domain of the Western Alps (Castelli et al., 2007; Chopin, 1984; Compagnoni and Hirajima, 2001) (Fig. 1). The BIU is composed of Variscan amphibolite-facies metamorphic basement and Triassic cover, and the Variscan basement was intruded by Permian granitoids (Compagnoni et al., 2012). These rocks have experienced HP and UHP eclogite-facies metamorphism during the Alpine orogeny in the Late Eocene to Early Oligocene (e.g. Gebauer et al., 1997; Rubatto and Hermann, 2001; Tilton et al., 1991). The peak UHP metamorphism was at ~730 °C and >3.5 GPa, followed by a later pervasive greenschist facies recrystallization (Castelli et al., 2007; Compagnoni et al., 2012; Schertl et al., 1991). 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 (Compagnoni et al., 1995; Gebauer et al., 1997). Field evidence demonstrates continuous transitions between orthogneiss and metagranite which, although being subducted to depths of >100 km, preserved its igneous granitic structure.

The whiteschist outcrops in the BIU monometamorphic complex provide excellent samples of continental crust that experienced UHP metamorphism, possibly even up to the diamond stability field (Chopin, 1984; Hermann, 2003). These whiteschists, mainly composed of quartz/coesite, pyrope, kyanite, phengite and talc, occur as lenses in thickness of a few to tens of meters within orthogneiss. They are characterized by high concentrations of SiO_2 and MgO and are strongly depleted in Fe, Ca and Na. Their protoliths are suggested to be Permian granites, based on the similar whole rock trace element patterns and the similar relict magmatic zircons of whiteschist and orthogneiss (metagranite) (Chen et al., 2016, 2017; Ferrando, 2012; Gebauer et al., 1997; Grevel et al., 2009; Schertl and Schreyer, 2008).

In the present study, we investigated the same suite of samples as reported by Schertl and Schreyer (2008), Grevel et al. (2009) and Chen et al. (2016), with a special focus on the whiteschists and their country rock metagranites. The studied samples are from four localities (No. 1, 3, 5 and 6) of the monometamorphic complex at the Dora-Maira Massif described by Schertl and Schreyer (2008) and Chen et al. (2016) (Table 1 and Fig. 1). The samples contain fine-grained whiteschists, retrogressed whiteschists and their country rock metagranites. The fine-grained whiteschist samples mainly include pyrope, quartz/coesite, kyanite, phengite, talc and jadeite, while in the retrogressed samples, pyrope has been replaced by talc and chlorite (Schertl and Schreyer, 2008). Further samples of whiteschist-like rocks (leucophyllites) as well as their country rock orthogneiss (localities No. 14 and 15, Table 1) were analyzed that come from the eastern end of the Eastern Alps in Austria described by Schertl and Schreyer (2008). These whiteschist-like samples from the Eastern Alps are identical to those from Western Alps in major element chemistry and also occur along shear zones in orthogneiss, but experienced much lower peak P-T conditions of 1.3 GPa, 560 °C (Deméy et al., 1997; Schertl and Schreyer, 2008). They contain a HP mineral assemblage of Mg-chlorite + quartz instead of a pyrope + coesite UHP assemblage in the Western Alps. Since the leucophyllites from the Eastern Alps do not contain the critical assemblage kyanite + talc (which is the high P-T alternative of the chlorite + quartz assemblage; Schreyer, 1973), they were formed at a low P-T preliminary stage of a "real whiteschist" and should not be called "whiteschists". However, all of them have similar protoliths of metagranites and experienced the similar type of metasomatism (Deméy et al., 1997; Schertl and Schreyer, 2008). The sample names are identical to those reported by Schertl and Schreyer (2008) and Chen et al. (2016).

3. Analytical methods

Separation of Li for isotopic composition analysis was achieved by an organic solvent free two-step liquid chromatography procedure described by Sun et al. (2016) and Liu et al. (2019), in a clean lab at the CAS Laboratory of Crust-Mantle Materials and Environments in the University of Science and Technology of China (USTC), Hefei. All separations yielded high Li (>99.8% recovery) and low Na/Li ratio
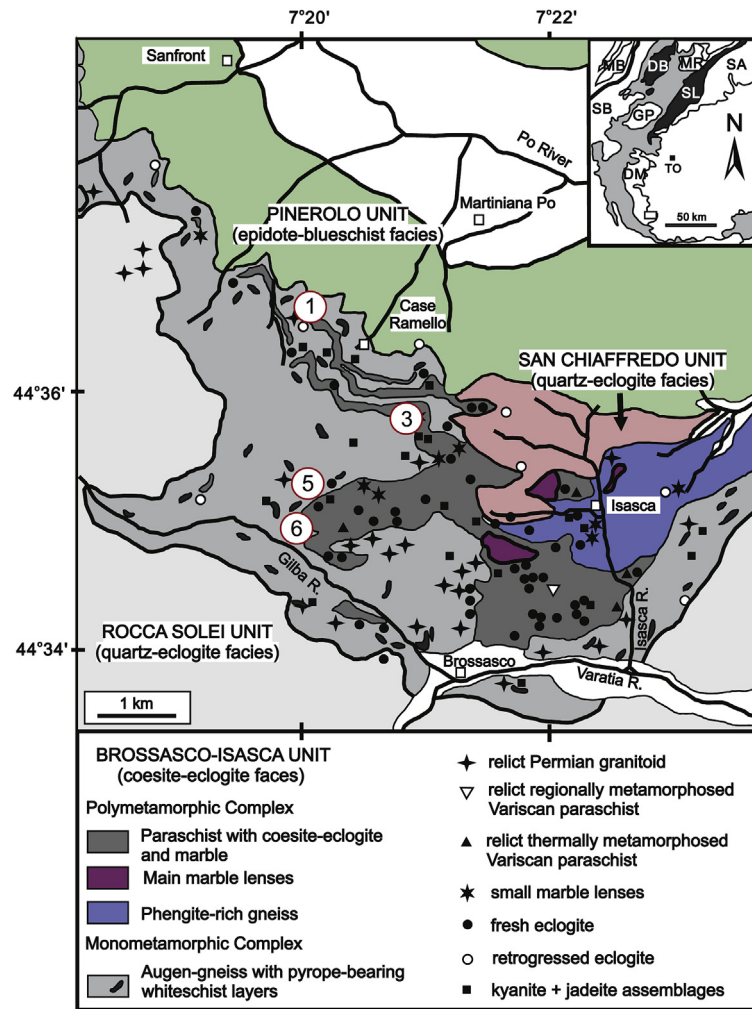
Fig. 1. Geological sketch map of the central portion of the coesite-bearing "Brossasco-Isasca Unit" (BIU) and relationships with adjacent units (modified after Chen et al., 2016). The sample locations labeled are after Schertl and Schreyer (2008). The numbers show the location of studied samples. The inset shows the location of the BIU within a simplified tectonic sketch-map of the Western Alps. Abbreviations: MB, Mont Blanc-Aiguilles Rouges of the Helvetic-Dauphinois Domain; SB, Grand St. Bernard Zone of the external Penninic Domain; MR, Internal Crystalline Massifs of the Penninic Domain: Monte Rosa; GP, Gran Paradiso; DM, Dora-Maira; SZ, Sesia-Lanzo Zone; DB, Dent Blanche nappe of the Austroalpine Domain; SA, Southern Alps; TO: Town of Torino.

(<0.5). The final concentration of Li in the solutions utilized for MC-ICP-MS analyses was about 50–100 ppb to ensure the best precision and accuracy. The total procedural blank was less than ~0.03 ng of Li, compared with the ~500–2000 ng Li used for analysis; the blank correction is not significant at the uncertainty levels achieved.

The Li isotopic compositions were measured using a Thermo Fisher Scientific Neptune Plus MC-ICP-MS following the method of Gou et al. (2017) at the State Key Laboratory of Loess and Quaternary Geology, Xi'an. The sample-standard bracketing method was used with 50–100 ppb L-SVEC standard (Flesch Jr et al., 1973). The long term external precision is better than ±0.3‰ (Gou et al., 2017). For international rock standards, repeated analysis yielded $4.3 \pm 0.3‰$ (2SD, n = 5) for BHVO-2 and $6.8 \pm 0.7‰$ (2SD, n = 5) for AGV-2, which are within the uncertainty of previously published results (Gou et al., 2017; Liu et al., 2019; Magna et al., 2004; Sun et al., 2016).

4. Results

Whole-rock Li and Li isotopic compositions of whiteschists and their country rock metagranites are listed in Table 1. The fine-grained whiteschists show relatively low Li concentrations (9.35–24.9 ppm, mean = 14.9 ppm) and low δ^7Li values (−6.4‰ to +2.4‰, mean = −2.1‰) (Table 1 and Fig. 2). In contrast, the country rocks show various Li concentrations (7.24–47.7 ppm, mean = 22.2 ppm) and high δ^7Li values (−1.2‰ to +3.6‰, mean = +1.4‰). Two retrogressed whiteschist samples have high concentrations of Li (45.1 and 75.1 ppm, respectively) but similar δ^7Li values (−0.3‰ and −1.0‰, respectively). No correlations between δ^7Li values and MgO, FeO^T and Na$_2$O + CaO as well as $\delta^{26}Mg$ and $\delta^{18}O$ values are observed.

5. Discussion

5.1. Low δ^7Li values in the whiteschists
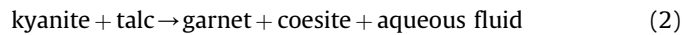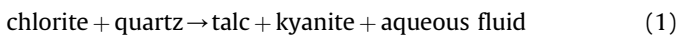
There are three prominent features in Li concentration and Li isotopic composition of whiteschists: (1) a large variation of δ^7Li values with similar concentrations of Li; (2) low δ^7Li values down to −6.4‰; (3) lower δ^7Li values than those of country rock metagranites for most samples. Fractionation of Li isotopes may occur during prograde dehydration, metamorphism and metasomatism during the formation of whiteschist, as well as by later retrogression. In the following, we will discuss the influence of the different processes on Li concentration and Li isotopic compositions of the rocks.

In the current study, no significant difference in Li concentration between whiteschists from Western Alps and whiteschist-like rocks

Table 1
Whole-rock Li concentration and Li isotope data for whiteschist and the country rock from Alps.

Sample No.	Locality	No.	Rock type	Li	δ^7Li (‰)	2sd (‰)
Dora-Maira Massif, Western Alps, Italy						
13AP57	Case Ramello	1	Fine-grained whiteschist	13.1	−2.7	0.3
13AP58	Case Ramello	1	Fine-grained whiteschist	15.3	2.1	0.3
13AP60	Case Ramello	1	Fine-grained whiteschist	10.9	−3.9	0.3
13AP62	Case Ramello	1	Fine-grained whiteschist	19.0	−6.4	0.3
13AP63	Case Ramello	1	Fine-grained whiteschist	13.2	−4.2	0.3
17,672	Case Ramello	1	Fine-grained whiteschist	10.9	0.0	0.3
17482b	Case Ramello	1	Retrogressed whiteschist	75.1	−0.3	0.3
17,469	Case Ramello	1	Biotite gneiss	7.24	2.5	0.3
17,688	Case Ramello	1	Biotite-phengite gneiss	47.7	−0.1	0.3
20,128	Cliff wall E Rocca Dritta	3	Undeformed metagranite	16.1	1.9	0.3
20,151	Tapina	5	Fine-grained whiteschist	11.1	−5.4	0.3
19,314	Tapina	5	Fine-grained whiteschist	9.35	−2.8	0.3
20,156	Tapina	5	Fine-grained whiteschist	14.4	−4.4	0.3
19,317	Tapina	5	Retrogressed whiteschist	45.1	−1.0	0.3
20,178	Tapina	5	Granitic gneiss	39.5	−1.2	0.3
17,641	Masueria	6	Fine-grained whiteschist	21.3	2.4	0.3
21,512	Masueria	6	Biotite-phengite gneiss	14.3	0.8	0.3
Eastern Alps, Austria						
14,606	Miesenbachtal	14	Leucophyllite	24.9	−0.7	0.3
14,605	Miesenbachtal	14	orthogneiss	20.3	2.5	0.3
14,783	Rabenwald	15	Leucophyllite	14.5	−0.9	0.3
14,796	Rabenwald	15	Leucophyllite ("Kornstein")	19.2	−1.0	0.3
14,785	Rabenwald	15	Orthogneiss	10.1	3.6	0.3
International rock standard						
BHVO-2 (n = 5)					4.3	0.3
AGV-2 (n = 5)					6.8	0.7

from Eastern Alps was observed. They yield the same composition of major elements, despite their different metamorphic P-T conditions. Both rocks are suggested to have experienced similar processes during the earlier stages of metamorphism or metasomatism (e.g. Ferrando, 2012; Schertl and Schreyer, 2008), and most of them show lower δ^7Li values than their country rocks (Fig. 2). However, some UHP whiteschists samples from Western Alps generally exhibit lower δ^7Li values than the analogous rocks from Eastern Alps. The HP-UHP prograde dehydration process may decrease δ^7Li values. Step-wise dehydration model calculation reported by Marschall et al. (2007a) was used to explore the effect of such a dehydration process (Table 2). The mineral proportion change and dehydration process (losing ~5.8 wt% H_2O) are from Gauthiez-Putallaz et al. (2016), including two dehydration reactions:

$$chlorite + quartz \rightarrow talc + kyanite + aqueous\ fluid \qquad (1)$$

$$kyanite + talc \rightarrow garnet + coesite + aqueous\ fluid \qquad (2)$$

Mineral-fluid partition coefficients for Li are from Marschall et al. (2007a) and fractionation factors for Li are assumed to be equal to the mica-fluid fractionation coefficient ($\Delta^7Li_{mica-fluid} = -4.52 \times (1000/T) + 4.74$, Wunder et al., 2007). Starting materials are set as average in the whiteschist-like rocks from the Eastern Alps (Li = 19.9 ppm, $\delta^7Li = -0.9$‰). The result documents that dehydration processes could only decrease δ^7Li values by ~1‰ (Table 2). This is consistent with previous studies which reported limited Li isotopic fractionations (<3‰) during prograde metamorphic dehydration (Liu et al., 2019; Marschall et al., 2007b; Qiu et al., 2011; Teng et al., 2007). Thus, dehydration processes cannot explain the very low δ^7Li (down to −6.4‰) of whiteschists in the Dora-Maira Massif.

The retrogressed whiteschist samples exhibit higher Li concentrations than samples that lack minerals produced by
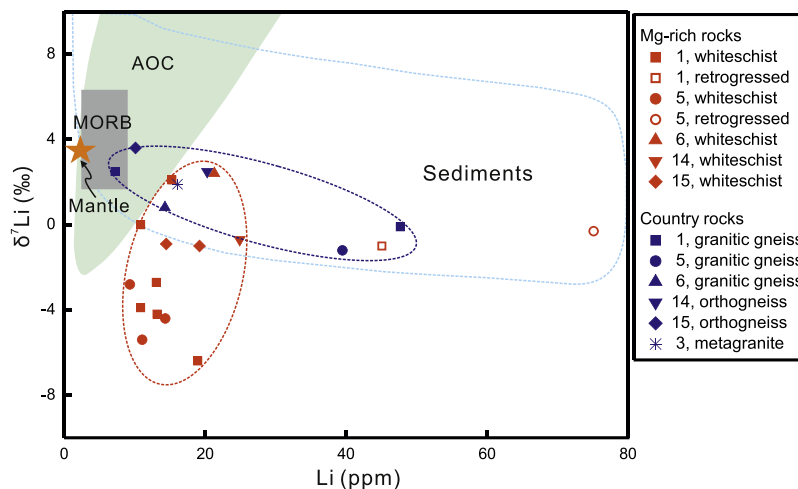

Fig. 2. Lithium concentration vs. δ^7Li values for the whiteschists and their country rock metagranites. Data from mantle (Magna et al., 2008), fresh MORB (Tomascak et al., 2008), altered oceanic crust (AOC, Chan et al., 2002) and oceanic sediments (Bouman et al., 2004; Chan et al., 2006) are also shown for comparison. The locality numbers are from Schertl and Schreyer (2008) and Chen et al. (2016).

Table 2
Parameters and results of Li concentration and Li isotopic composition of dehydration process for whiteschist from Alps.

T (°C)	Mineral proportions (Vol%)						$D_{Li}^{Rock/Fluid}$	F	α	Li_{WR} (ppm)	$δ^7Li_{WR}$ (‰)
	Grt	Ms	Tc	Chl	Qtz	Ky					
500	0	30	3	17	49	1	0.060			19.90	−0.90
500	0	30	6	15	48	1	0.056	0.004	1.0011	18.61	−0.97
550	0	30	10	10	48	2	0.045	0.008	1.0008	15.68	−1.10
600	2	30	16	1	47	4	0.024	0.034	1.0004	3.82	−1.72
650	18	30	0	0	49	3	0.017	0.012	1.0002	1.88	−1.83
$D_{Li}^{Mineral/Fluid}$	0.0048	0.0528	0.0333	0.256	0.000176	nd					

Note: $D_{Li}^{Mineral/Fluid}$ from Marschall et al. (2007a); $Δ^7Li_{rock-fluid} = −4.52*(1000/T)+4.74$ from Wunder et al. (2007)

retrogression. Chlorite and talc are identified as secondary minerals in retrogressed samples and may be responsible for the increase in Li contents. The $δ^7Li$ values of retrogressed samples are around −1−0‰. Although we cannot fully predict the change of Li isotopic compositions during retrogression, it seems that subsequent retrogression cannot explain the low Li isotopic values of whiteschists.

Chemical diffusion can potentially produce large kinetic Li isotopic fractionation in natural samples (Magna et al., 2008; Marschall et al., 2007a; Parkinson et al., 2007; Penniston-Dorland et al., 2012, 2017; Richter et al., 2003; Teng et al., 2006; Tomascak et al., 2016). Isotopic fractionation driven by chemical diffusion will result in the same trend for different isotopic systems as light isotopes will diffuse faster than heavy ones (Penniston-Dorland et al., 2017; Pogge von Strandmann et al., 2011; Richter et al., 2003; Tomascak et al., 2016). For example, Pogge von Strandmann et al. (2011) reported a positive correlation between $δ^7Li$ and $δ^{26}Mg$ in xenolithic peridotites as evidence for kinetic fractionation. However in whiteschists, there are very weak negative or no correlations between $δ^7Li$ and $δ^{26}Mg$ (or $δ^{18}O$) (Fig. 3a, b). We propose, therefore, that the light Li isotopic compositions of whiteschists are unlikely to be explained by kinetic processes like chemical diffusion.

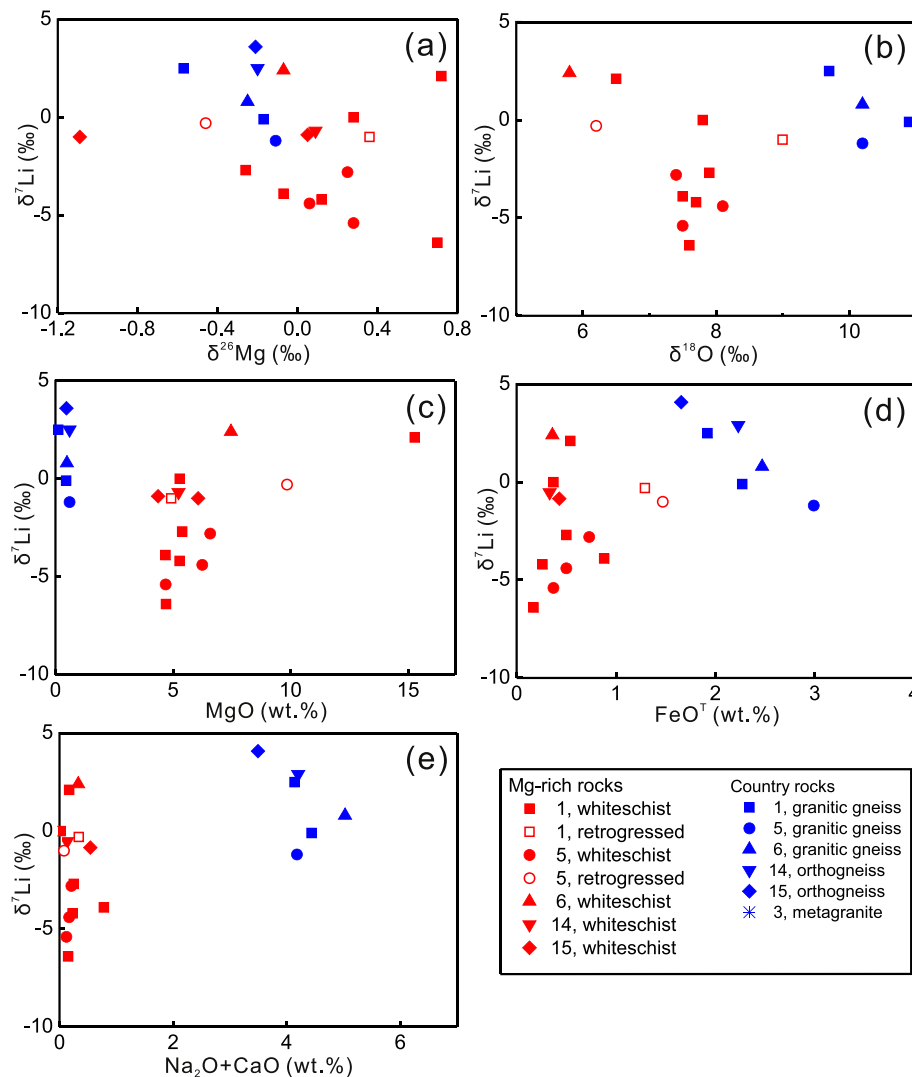Since previous studies have proven the metasomatic origin of

Fig. 3. Correlations between whole-rock $δ^7Li$ values and $δ^{26}Mg$ values (a), $δ^{18}O$ values (b), MgO contents (c), FeO^T contents (d) and $Na_2O + CaO$ contents (e) for whiteschist and country rocks from Western Alps. The whole-rock major elements and Mg-O isotope data are after Schertl and Schreyer (2008) and Chen et al. (2016).

whiteschist (Chen et al., 2016; Gauthiez-Putallaz et al., 2016; Schertl and Schreyer, 2008), fluid-rock interaction during metasomatism is the most plausible cause for low δ^7Li values of whiteschist. The fluid-rock interactions cause ion exchange through progressive precipitation of Mg-bearing minerals and dissolution of Na, Ca, Fe-bearing minerals (Chen et al., 2016; Ferrando, 2012), thus the bulk rock analyses of whiteschists exhibit significantly lower FeO_T, $Na_2O + CaO$, but higher MgO contents than those of the metagranites (Fig. 3c–e). The δ^7Li values of whiteschists are also lower than those of metagranites, which suggests that the low δ^7Li values were produced by fluid metasomatism, and that the variation in δ^7Li values may be primarily controlled by fluid-rock interaction.

5.2. The source of metasomatic fluids during whiteschist formation

A few studies have focused on the characteristics of potential sources of metasomatic fluids which are the prerequisite for the formation of the studied whiteschists, including: (1) dehydration of serpentinites (Barnes et al., 2004; Chen et al., 2016; Ferrando, 2012); (2) seawater-related hydrothermal fluids (Gauthiez-Putallaz et al., 2016; Manatschal et al., 2000); (3) dehydration of sediments (Gebauer et al., 1997; Selverstone et al., 1991). A metasedimentary protolith of the whiteschists from the Dora-Maira Massif (e.g., Chopin, 1984; Gebauer et al., 1997) is incongruent and sediment-derived fluids cannot explain the relatively low $\delta^{18}O$ values of the whiteschist and the much lower $\delta^{18}O$ values of metamorphic zircon domains compared to those of relict magmatic zircon domains in the whiteschist (Chen et al., 2016; Sharp et al., 1993). It is also not possible to explain the whole-rock and zircon O isotopic compositions, as well as the extremely heavy Mg isotope compositions of the whiteschists (Chen et al., 2016), as a consequence of seawater-related hydrothermal fluids metasomatism (Gauthiez-Putallaz et al., 2016). Nevertheless, we have modeled these processes in terms of Li isotopes.

In order to evaluate the effect of metasomatic fluids from different sources, a Rayleigh fractionation method reported by Magenheim et al. (1995) was used to explore the effect of distillation fractionation. In this model, mass balance is applied to each infinitesimal reaction step. The relationship between the initial and final concentration of the two isotopes ^6Li and ^7Li with the rock/water ratio (r/w) in a closed system is described by the following two equations:

$$r/w = -K^{-1} \times ln\left(\frac{^6Li_r^0 - K \times ^6Li_{sol}^{alt}}{^6Li_r^0 - K \times ^6Li_{sol}^0}\right) \qquad (3)$$

$$r/w = -(\alpha K)^{-1} \times ln\left(\frac{^7Li_r^0 - \alpha K \times ^7Li_{sol}^{alt}}{^7Li_r^0 - \alpha K \times ^7Li_{sol}^0}\right) \qquad (4)$$

where $^6Li_r^0$, $^7Li_r^0$ and $^6Li_r^{alt}$, $^7Li_r^{alt}$ are the concentrations of the two isotopes in the initial rock and the final altered rock, respectively; $^6Li_{sol}^0$, $^7Li_{sol}^0$ and $^6Li_{sol}^{alt}$, $^7Li_{sol}^{alt}$ are the concentrations of the two isotopes in the starting solution and the final alteration-affected solution, respectively; K is the distribution coefficient of ^6Li between the altered rock and the alteration-affected fluid ($K = \frac{^6Li_r^{alt}}{^6Li_{sol}^{alt}}$), α is the isotopic fractionation factor ($\alpha = \frac{^7Li_r^{alt}/^6Li_r^{alt}}{^7Li_{sol}^{alt}/^6Li_{sol}^{alt}}$). In the present study, K is assumed to be equal to granite-fluid partition coefficient of Li (K = 0.125) combining plagioclase/granite and plagioclase/fluid partition coefficients (Bea et al., 1994; Caciagli et al., 2011). The isotopic fractionation factor α is assumed to be equal to the mica-fluid fractionation coefficient ($\Delta^7Li_{mica-fluid} = -4.52 \times (1000/T) + 4.74$, Wunder et al., 2007), considering phengite to represent

Table 3
Composition of initial fluids used for Rayleigh fractionation modeling of water-rock interaction.

	T (°C)	Li$_{Fluid}$ (ppm)	δ^7Li $_{Fluid}$ (‰)
AOC Dehydration	400	9.9	6.25
	500	8.56	4.25
	600	8.91	3.25
GLOSS Dehydration	400	231	5.6
	500	228	2.68
	600	218	0.65
Hydrothermal fluid	180	10.1	6.8
	250	6	4.4

Data source: AOC and GLOSS dehydration from Simons et al. (2010); Hydrothermal fluid from Millot et al. (2010).

the main reservoir of Li in whiteschists. The country rock metagranite is set as the initial rock (mean Li = 22.2 ppm and mean $\delta^7Li = +1.4‰$). The input compositions of initial fluids from altered oceanic curst (AOC), average global subducted sediment (GLOSS) and hydrothermal fluids at various temperatures are listed in Table 3.

The Li concentrations and δ^7Li values calculated for metasomatic products with different fluid sources following Magenheim's model are reported in Fig. 4. Seawater is excluded due to the significant high δ^7Li value ($\delta^7Li = +31‰$) that is distinctly different from that of whiteschists. The results show that fluid derived from AOC can significantly lower the Li concentrations of metasomatic phases but δ^7Li values change within 2‰ (Fig. 4a). Fluid derived from GLOSS has high Li concentrations (>200 ppm) and metasomatism by such fluid would result in an enrichment of Li (Fig. 4b). But the δ^7Li values will only slightly decrease (<1.5‰) at high temperatures (600 °C) due to the relative low δ^7Li value (0.65‰) of GLOSS-derived fluids at this condition, and do also not fit the measured amounts of Li and Li isotopes of whiteschists.

Metasomatism by hydrothermal fluid can lower the Li concentrations, and the δ^7Li values can decrease by 3–4‰ at low water/rock ratios (Fig. 4b). This scenario would fit for the whiteschist-like rocks from Eastern Alps and some whiteschist samples from Western Alps. However, other samples from Western Alps show lower δ^7Li which cannot be explained by hydrothermal fluid metasomatism. In addition, this process cannot explain the whole-rock and zircon O isotopic compositions of the whiteschists (Chen et al., 2016).

We propose that a fluid with even lower δ^7Li and moderate Li concentrations is needed to explain the low δ^7Li values of the whiteschists. In this model, a fluid with moderate amounts of Li (50–150 ppm) and low isotopic compositions ($\delta^7Li = -4–0‰$) would best fit the metasomatic fluid source (Fig. 4c), which is difficult to be produced by subducting oceanic crust, submarine sediments, sea water influx or any combination of processes. These considerations are consistent with previous results, documenting that the fluids which derive from sediments and AOC cannot explain the low $\delta^{18}O$ values of metamorphic zircon domains, the high MgO contents and the extremely high $\delta^{26}Mg$ values up to +0.7‰ in the whiteschists (Chen et al., 2016).

In view of the above arguments, we suggest that the metasomatic fluid is derived from dehydration of serpentinites. Such a fluid source would be in agreement with the high Mg and Cl content, heavy Mg and D isotopes, but light O isotopes of the whiteschists (Chen et al., 2016; Ferrando et al., 2009; Sharp et al., 1993). Serpentinites can carry some Li with a low δ^7Li value into subduction zones, which can be released in deep portions of a subduction channel (Deschamps et al., 2011; Wunder et al., 2010).

In subducted serpentinites at relatively shallow depths of <20 km, low-T serpentine polymorphs (lizardite and chrysotile) will convert to high-T serpentine phase (antigorite), which will be stable even at much greater depths (Deschamps et al., 2013; Ulmer and Trommsdorff, 1995; Wunder et al., 2010). Natural rock samples
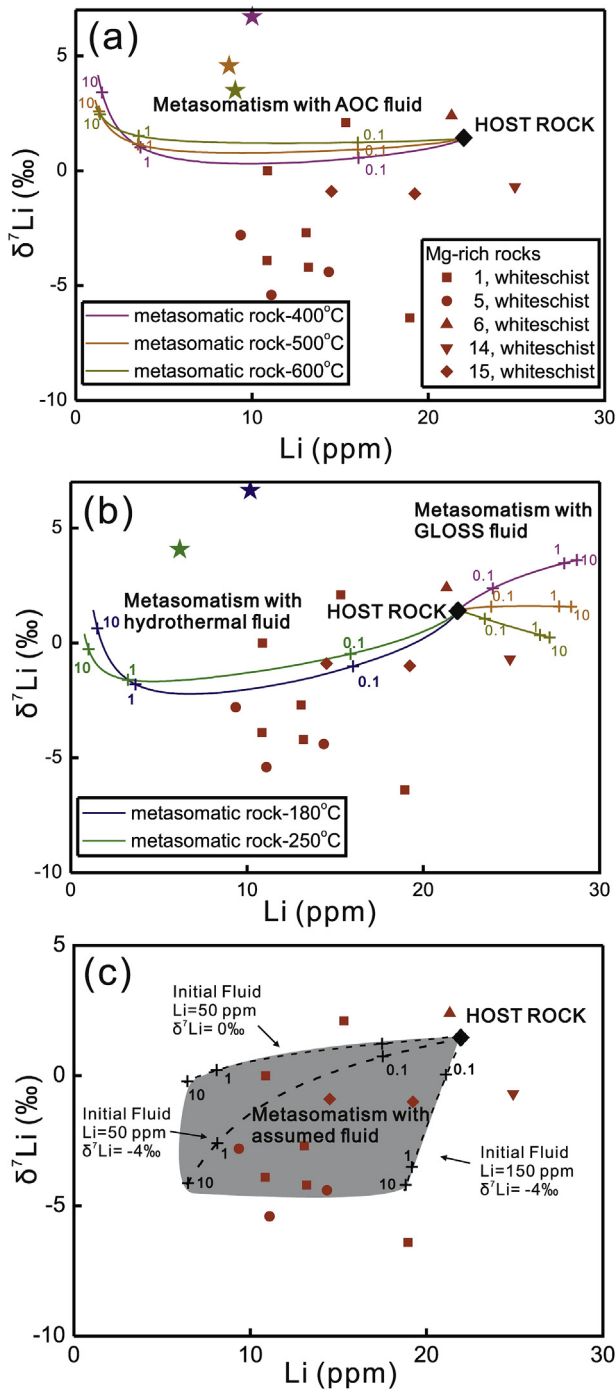
transition can liberate a limited quantity of a Li-bearing fluid, the residual Li will be carried into deep portions of subduction zones where it is released by dehydration of antigorite (Deschamps et al., 2013).

Values of δ^7Li of whole-rock serpentinites vary widely from −19‰ to +28‰ (Benton et al., 2004; Decitre et al., 2002, 2004; Vils et al., 2009, 2011). Experimental studies show that chrysotile reveals an inverse Li isotopic fractionation compared to lizardite and antigorite with fluid (Wunder et al., 2010). Lithium is sixfold coordinated in serpentine (Li[6]), while in chrysotile tubes, some Li is combined with the confined geometry of the Li-water clusters within the tubes (Li[Ch], Wunder et al., 2010). Two distinguishing Li incorporation mechanisms (Li[Ch] and Li[6]) between chrysotile and fluid have been suggested to explain the variation of Li isotopic compositions of serpentines. The dehydration of chrysotile tubes containing heavy Li isotopic compositions (Li[Ch]) will probably occur prior to complete dehydration at low temperatures, which may correspond to metasomatic fluid sources for the whiteschist-like rocks from Eastern Alps at relatively low pressure conditions. And Li with lower δ^7Li compositions will be incorporated into antigorite which is carried to greater depths (Fig. 5a), then subsequent breakdown of antigorite can produce low δ^7Li fluids, which in the case of the Dora-Maira Massif account for the metasomatic fluids sources producing the whiteschists (Fig. 5b). Modeling results indicate that low δ^7Li values down to −4‰ are

Fig. 4. Lithium concentrations vs. δ^7Li values for metasomatic phases produced by metasomatism with fluids derived from altered oceanic crust (AOC) (a), average global subducted sedimentary (GLOSS) and hydrothermal fluid (b), the assumed fluids with Li of 50–150 ppm and δ^7Li of −4–0‰ at 600 °C (c), following Magenheim's model (Magenheim et al., 1995). Red spots refer to measured whiteschist samples of the current study, colored-star spots refer to the compositions of metasomatic fluids. Numbers indicate water/rock ratios of interaction. Grey area represents metasomatic phases by assumed fluids ([Li] = 50–150 ppm; δ^7Li = −4–0‰) at 600 °C. The average Li concentrations and δ^7Li values of the country rock metagranites were used for the host rock compositions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
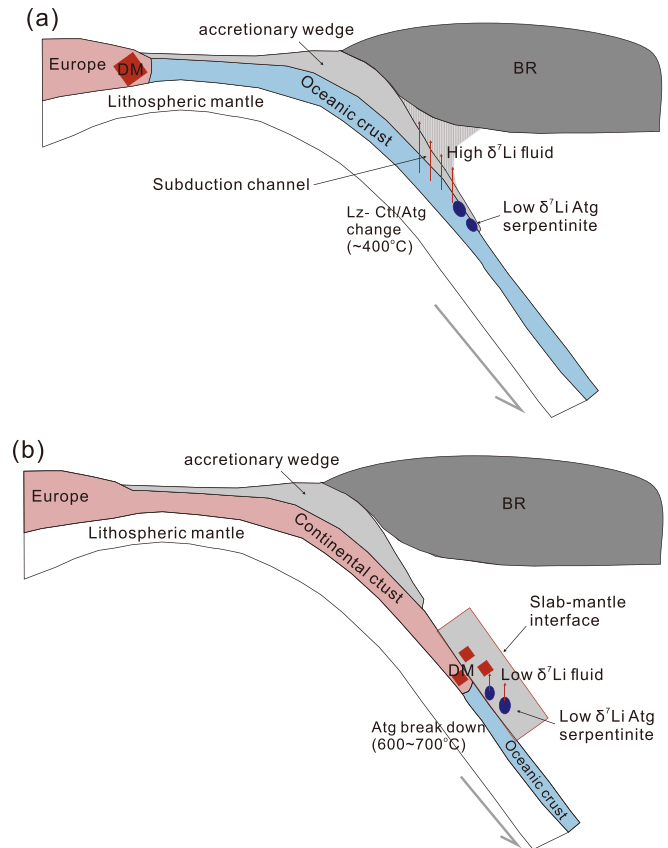

Fig. 5. Schematic diagram showing the metasomatic process for formation of low δ^7Li whiteschist at Dora-Maira Massif in the Western Alps modified after Chen et al. (2016). The Valais oceanic slab was subducted beneath the Briançonnais (BR) terrane (a), stepwise dehydration of lizardite (Lz) and chrysotile (Ctl) produced high δ^7Li fluid, leading to the residual light Li isotope component to become incorporated into antigorite (Atg) (Wunder et al., 2010). And a subduction channel was formed at the slab-mantle interface. Continental supracrustal rocks were dragged downward by the subducting oceanic slab (b). Within the subduction channel, the Dora-Maria metagranite (DM) was metasomatized by fluids derived from the breakdown of low δ^7Li antigorite, resulting in whiteschist with light Li isotopes.

and experimental studies of serpentinites have demonstrated that Li can be enriched in serpentinites (0.1–30 ppm) and that serpentine minerals can host various amounts of Li (0.1–156 ppm) (Deschamps et al., 2010, 2012; Kodolányi et al., 2012; Lafay et al., 2013; Vils et al., 2009, 2011). While the lizardite-to-antigorite

required for the serpentinite-derived fluids, and interaction with such fluids can decrease δ^7Li values up to 6−7‰ for metasomatic phases (Fig. 4c).

Our results agree well with the genetic model of whiteschist formation proposed by Chen et al. (2016). In this model, dehydration of talc-rich serpentinites would provide high $\delta^{26}Mg$, low δ^7Li fluids which account for the metasomatism of supracrustal rocks in the continental subduction channel (Fig. 5b). Break down of antigorite requires relatively high temperatures of 600−700 °C (Deschamps et al., 2013), that can be met at subarc depths in the subduction channel being consistent with the prediction by Chen et al. (2016). An origin of fluids from serpentinite is also in agreement with recent geophysical tomography studies by Solarino et al. (2018) who identified a serpentinized peridotite mantle body below the Dora-Maira UHP continental crust. While the fluids from dehydration of antigorite will carry light Li isotopic compositions, the fluids may also dissolve various Li-rich components like mica in the metagranites, resulting in heterogeneous Li isotopes in the metasomatic rocks. Thus, the whiteschist can record Li signals which originate from deep fluids in the subduction zone.

5.3. Implications of light Li isotopic fluids in deep subduction zones

High pressure metamorphic rocks with light Li isotopic compositions (e.g., eclogite) were found in different subduction zones settings (Halama et al., 2011; Liu et al., 2019; Marschall et al., 2007b; Penniston-Dorland et al., 2010, 2012; Simons et al., 2010; Xiao et al., 2011; Zack et al., 2003). Abnormally low δ^7Li values, lower than those of the depleted mantle (+3~ + 4‰; Marschall et al., 2017) were also found in mantle-derived igneous rocks (Agostini et al., 2006; Tang et al., 2014b; Tomascak et al., 2000). Some rocks that contain low δ^7Li signatures are interpreted to be the result of a metasomatism with sediment-derived fluids (Marschall et al., 2007b; Penniston-Dorland et al., 2010, 2012; Simons et al., 2010). Such an explanation however fails to account for the very low δ^7Li values, because no reasonable sedimentary sources exist to generate such isotopically light fluid (Penniston-Dorland et al., 2017; Tomascak et al., 2016). For this reason, the present study of whiteschists provides insight into the origin of low δ^7Li fluids in deep subduction zones. Serpentinites are suggested to be indicative of carrying light Li isotopic compositions to mantle depths causing Li isotopic heterogeneity.

6. Concluding remarks

The Dora-Maria whiteschists are characterized by variable but relatively low δ^7Li values compared to their country rock metagranites. Modeling calculation, combined with previous petrological and geochemical studies, indicates that metasomatic fluids with low δ^7Li (down to −4‰) are necessary for the formation of whiteschists. Such fluids probably derive from the breakdown of antigorite in serpentinite in the continental subduction channel. By studying UHP-metamorphic whiteschists and their enclosing country rock metagranites, it was possible to demonstrate the presence of low δ^7Li sources in deep subduction zones. Such deeply subducted metasomatic rocks potentially contribute to the understanding of the Li-isotope balance in subduction zones and the Li isotopic heterogeneity observed in the earth's interior.

Acknowledgements

References

Agostini, S., Tonarini, S., Ryan, J.G., Innocenti, F., 2006. Drying and dying of a subducted slab: Li and B isotopes in Western Anatolia Cenozoic Volcanism. Geochim. Cosmochim. Acta 70, A4.

Barnes, J.D., Selverstone, J., Sharp, Z.D., 2004. Interactions between serpentinite devolatilization, metasomatism and strike-slip strain localization during deep-crustal shearing in the Eastern Alps. J. Metamorph. Geol. 22, 283−300.

Bea, F., Pereira, M.D., Stroh, A., 1994. Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation-ICP-MS study). Chem. Geol. 117, 291−312.

Bebout, G.E., 2014. Chemical and isotopic cycling in subduction zones. Treatise Geochem. 4, 703−747.

Benton, L.D., Ryan, J.G., Savov, I.P., 2004. Lithium abundance and isotope systematics of forearc serpentinites, Conical Seamount, Mariana forearc: Insights into the mechanics of slab-mantle exchange during subduction. Geochem. Geophys. Geosyst. 5 (8).

Bouman, C., Elliott, T., Vroon, P.Z., 2004. Lithium inputs to subduction zones. Chem. Geol. 212, 59−79.

Caciagli, N., Brenan, J.M., McDonough, W.F., Phinney, D., 2011. Mineral−fluid partitioning of lithium and implications for slab−mantle interaction. Chem. Geol. 280, 384−398.

Castelli, D., Rolfo, F., Groppo, C., Compagnoni, R., 2007. Impure marbles from the UHP Brossasco-Isasca Unit (Dora-Maira Massif, western Alps): evidence for Alpine equilibration in the diamond stability field and evaluation of the X(CO2) fluid evolution. J. Metamorph. Geol. 25, 587−603.

Chan, L.H., Alt, J.C., Teagle, D.A.H., 2002. Lithium and lithium isotope profiles through the upper oceanic crust: a study of seawater−basalt exchange at ODP Sites 504B and 896A. Earth Planet. Sci. Lett. 201, 187−201.

Chan, L.H., Leeman, W.P., Plank, T., 2006. Lithium isotopic composition of marine sediments. Geochem. Geophys. Geosyst. 7, Q06005.

Chen, Y.X., Schertl, H.P., Zheng, Y.F., Huang, F., Zhou, K., Gong, Y.Z., 2016. Mg−O isotopes trace the origin of Mg-rich fluids in the deeply subducted continental crust of Western Alps. Earth Planet. Sci. Lett. 456, 157−167.

Chen, Y.X., Zhou, K., Zheng, Y.F., Schertl, H.P., 2017. Zircon geochemical constraints on the protolith nature and metasomatic process of the Mg-rich whiteschist from the Western Alps. Chem. Geol. 467, 177−195.

Chopin, C., 1984. Coesite and pure pyrope in high-grade blueschists of the Western Alps: a first record and some consequences. Contrib. Mineral. Petrol. 86, 107−118.

Compagnoni, R., Hirajima, T., 2001. Superzoned garnets in the coesite-bearing Brossasco-Isasca Unit, Dora-Maira massif, Western Alps, and the origin of the whiteschists. Lithos 57, 219−236.

Compagnoni, R., Hirajima, T., Chopin, C., 1995. Ultra-high-pressure metamorphic rocks in the western Alps. In: Coleman, R.G., Wang, X. (Eds.), Ultrahigh Pressure Metamorphism. Cambridge University Press, UK, pp. 206−243 (Chap. 207).

Compagnoni, R., Rolfo, F., Groppo, C., Hirajima, T., Turello, R., 2012. Geological map of the ultra-high pressure Brossasco-Isasca unit (Western Alps, Italy). J. Maps 8, 465−472.

Decitre, S., Deloule, E., Reisberg, L., James, R., Agrinier, P., Mével, C., 2002. Behavior of Li and its isotopes during serpentinization of oceanic peridotites. Geochem. Geophys. Geosyst. 3, 1−20.

Decitre, S., Buatier, M., James, R., 2004. Li and Li isotopic composition of hydrothermally altered sediments at Middle Valley, Juan De Fuca. Chem. Geol. 211, 363−373.

Demény, A., Sharp, Z.D., Pfeifer, H.R., 1997. Mg-metasomatism and formation conditions of Mg-chlorite-muscovite-quartzphyllites (leucophyllites) of the Eastern Alps (W. Hungary) and their relations to Alpine whiteschists. Contrib. Mineral. Petrol. 128, 247−260.

Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., Hattori, K., 2010. In situ characterization of serpentinites from forearc mantle wedges: timing of serpentinization and behavior of fluid-mobile elements in subduction zones. Chem. Geol. 269, 262−277.

Deschamps, F., Guillot, S., Godard, M., Andreani, M., Hattori, K., 2011. Serpentinites act as sponges for fluid-mobile elements in abyssal and subduction zone environments. Terra Nova 23, 171−178.

Deschamps, F., Godard, M., Guillot, S., Chauvel, C., Andreani, M., Hattori, K., Wunder, B., France, L., 2012. Behavior of fluid-mobile elements in serpentines from abyssal to subduction environments: examples from Cuba and Dominican Republic. Chem. Geol. 312−313, 93−117.

Deschamps, F., Godard, M., Guillot, S., Hattori, K., 2013. Geochemistry of subduction zone serpentinites: a review. Lithos 178, 96−127.

Ferrando, S., 2012. Mg-metasomatism of metagranitoids from the Alps: genesis and possible tectonic scenarios. Terra Nova 24, 423−436.

Ferrando, S., Frezzotti, M.L., Petrelli, M., Compagnoni, R., 2009. Metasomatism of continental crust during subduction: the UHP whiteschists from the Southern Dora-Maira Massif (Italian Western Alps). J. Metamorph. Geol. 27, 739−756.

Flesch Jr., G.D., A., A.R., Svec, H.J., 1973. A secondary isotopic standard for $^6Li/$ ^7Li

determinations. Int. J. Mass Spectrom. Ion Phys. 12, 265−272.

Franz, L., Romer, R.L., de Capitani, C., 2013. Protoliths and phase petrology of whiteschists. Contrib. Mineral. Petrol. 166, 255−274.

Gauthiez-Putallaz, L., Rubatto, D., Hermann, J., 2016. Dating prograde fluid pulses during subduction by in situ U−Pb and oxygen isotope analysis. Contrib. Mineral. Petrol. 171, 15.

Gebauer, D., Schertl, H.P., Brix, M., Schreyer, W., 1997. 35 Ma old ultrahigh-pressure metamorphism and evidence for very rapid exhumation in the Dora Maira Massif, Western Alps. Lithos 41, 5−24.

Gou, L.F., Jin, Z.D., Deng, L., Sun, H., Hui-Min, Y.U., Zhang, F., 2017. Efficient purification for Li and high-precision and accuracy determination of Li isotopic compositions by MC-ICP-MS. Geochimica 46, 528−537 (in Chinese).

Grevel, C., Schreyer, W., Grevel, K.D., Schertl, H.P., AP, W., 2009. REE distribution, mobilization and fractionation in the coesite-bearing 'pyrope quartzite' and related rocks of the Dora-Maira Massif, Western Alps. Eur. J. Mineral. 21, 1213−1224.

Halama, R., McDonough, W.F., Rudnick, R.L., Bell, K., 2008. Tracking the lithium isotopic evolution of the mantle using carbonatites. Earth Planet. Sci. Lett. 265, 726−742.

Halama, R., John, T., Herms, P., Hauff, F., Schenk, V., 2011. A stable (Li, O) and radiogenic (Sr, Nd) isotope perspective on metasomatic processes in a subducting slab. Chem. Geol. 281, 151−166.

Hermann, J., 2003. Experimental evidence for diamond-facies metamorphism in the Dora-Maira massif. Lithos 70, 163−182.

Kodolányi, J., Pettke, T., Spandler, C., Kamber, B.S., Gméling, K., 2012. Geochemistry of ocean floor and fore-arc serpentinites: constraints on the ultramafic input to subduction zones. J. Petrol. 53, 235−270.

Lafay, R., Deschamps, F., Schwartz, S., Guillot, S., Godard, M., Debret, B., Nicollet, C., 2013. High-pressure serpentinites, a trap-and-release system controlled by metamorphic conditions: example from the Piedmont zone of the western Alps. Chem. Geol. 343, 38−54.

Liu, H., Sun, H., Xiao, Y., Wang, Y., Zeng, L., Li, W., Guo, H., Yu, H., Pack, A., 2019. Lithium isotope systematics of the Sumdo Eclogite, Tibet: tracing fluid/rock interaction of subducted low-T altered oceanic crust. Geochim. Cosmochim. Acta 246, 385−405.

Magenheim, A.J., Spivack, A.J., Alt, J.C., Bayhurst, G., Chan, L.H., Zuleger, E., Gieskes, J.M., 1995. Borehole fluid chemistry in Hole 504B, Leg 137: formation water or in-situ reaction? In: Erzinger, J., Becker, K., HJB, Dick, Stokking, L.B. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, 137. Ocean Drilling Program, College Station, TX, pp. 141−152.

Magna, T., Wiechert, U.H., Halliday, A.N., 2004. Low-blank isotope ratio measurement of small samples of lithium using multiple-collector ICPMS. Int. J. Mass Spectrom. 239, 67−76.

Magna, T., Ionov, D.A., Oberli, F., Wiechert, U., 2008. Links between mantle metasomatism and lithium isotopes: evidence from glass-bearing and cryptically metasomatized xenoliths from Mongolia. Earth Planet. Sci. Lett. 276, 214−222.

Manatschal, G., Marquer, D., Fruh-Green, G.L., 2000. Channelized fluid flow and mass transfer along a rift-related detachment fault (Eastern Alps, southeast Switzerland). Geol. Soc. Am. Bull. 112, 21−33.

Marschall, H.R., Altherr, R., Rüpke, L., 2007. Squeezing out the slab — modelling the release of Li, Be and B during progressive high-pressure metamorphism. Chem. Geol. 239, 323−335.

Marschall, H.R., Pogge von Strandmann, P.A.E., Seitz, H.-M., Elliott, T., Niu, Y., 2007. The lithium isotopic composition of orogenic eclogites and deep subducted slabs. Earth Planet. Sci. Lett. 262, 563−580.

Marschall, H.R., Wanless, V.D., Shimizu, N., Pogge von Strandmann, P.A.E., Elliott, T., Monteleone, B.D., 2017. The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle. Geochim. Cosmochim. Acta 207, 102−138.

Millot, R., Scaillet, B., Sanjuan, B., 2010. Lithium isotopes in island arc geothermal systems: Guadeloupe, Martinique (French West Indies) and experimental approach. Geochim. Cosmochim. Acta 74, 1852−1871.

Parkinson, I., Hammond, S., James, R., Rogers, N., 2007. High-temperature lithium isotope fractionation: insights from lithium isotope diffusion in magmatic systems. Earth Planet. Sci. Lett. 257, 609−621.

Penniston-Dorland, S.C., Sorensen, S.S., Ash, R.D., Khadke, S.V., 2010. Lithium isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA. Earth Planet. Sci. Lett. 292, 181−190.

Penniston-Dorland, S.C., Bebout, G.E., Pogge von Strandmann, P.A.E., Elliott, T., Sorensen, S.S., 2012. Lithium and its isotopes as tracers of subduction zone fluids and metasomatic processes: evidence from the Catalina Schist, California, USA. Geochim. Cosmochim. Acta 77, 530−545.

Penniston-Dorland, S., Liu, X.-M., Rudnick, R.L., 2017. Lithium isotope geochemistry. Rev. Mineral. Geochem. 82, 165−217.

Pogge von Strandmann, P.A.E., Elliott, T., Marschall, H.R., Coath, C., Lai, Y.-J., Jeffcoate, A.B., Ionov, D.A., 2011. Variations of Li and Mg isotope ratios in bulk chondrites and mantle xenoliths. Geochim. Cosmochim. Acta 75, 5247−5268.

Qiu, L., Rudnick, R.L., McDonough, W.F., Bea, F., 2011. The behavior of lithium in amphibolite- to granulite-facies rocks of the Ivrea−Verbano Zone, NW Italy. Chem. Geol. 289, 76−85.

Richter, F.M., Davis, A.M., DePaolo, D.J., Watson, E.B., 2003. Isotope fractionation by chemical diffusion between molten basalt and rhyolite. Geochim. Cosmochim.

Acta 67, 3905−3923.

Rubatto, D., Hermann, J., 2001. Exhumation as fast as subduction? Geology 29, 3−6.

Schertl, H.-P., Schreyer, W., 2008. Geochemistry of coesite-bearing "pyrope quartzite" and related rocks from the Dora-Maira Massif, Western Alps. Eur. J. Mineral. 20, 791−809.

Schertl, H.P., Schreyer, W., Chopin, C., 1991. The pyrope-coesite rocks and their country rocks at Parigi, Dora Maira Massif, Western Alps: detailed petrography, mineral chemistry and PT-path. Contrib. Mineral. Petrol. 108, 1−21.

Schreyer, W., 1973. Whiteschist: a high-pressure rock and its geologic significance. J. Geol. 81, 735−739.

Selverstone, J., Morteani, G., Staude, J.M., 1991. Fluid channelling during ductile shearing: transformation of granodiorite into aluminous schist in the Tauern Window, Eastern Alps. J. Metamorph. Geol. 9, 419−431.

Sharp, Z.D., Essene, E.J., Hunziker, J.C., 1993. Stable isotope geochemistry and phase equilibria of coesite-bearing whiteschists, Dora Maira Massif, western Alps. Contrib. Mineral. Petrol. 114, 1−12.

Simons, K.K., Harlow, G.E., Brueckner, H.K., Goldstein, S.L., Sorensen, S.S., Hemming, N.G., Langmuir, C.H., 2010. Lithium isotopes in Guatemalan and Franciscan HP−LT rocks: Insights into the role of sediment-derived fluids during subduction. Geochim. Cosmochim. Acta 74, 3621−3641.

Solarino, S., Malusà, M.G., Eva, E., Guillot, S., Paul, A., Schwartz, S., Zhao, L., Aubert, C., Dumont, T., Pondrelli, S., Salimbeni, S., Wang, Q., Xu, X., Zheng, T., Zhu, R., 2018. Mantle wedge exhumation beneath the Dora-Maira (U)HP dome unravelled by local earthquake tomography (Western Alps). Lithos 296-299, 623−636.

Su, B.X., Zhang, H.F., Deloule, E., Sakyi, P.A., Xiao, Y., Tang, Y.J., Hu, Y., Ying, J.F., Liu, P.P., 2012. Extremely high and low δ^7Li signatures in the lithospheric mantle. Chem. Geol. 292−293, 149−157.

Sun, H., Gao, Y., Xiao, Y., Gu, H.-O., Casey, J.F., 2016. Lithium isotope fractionation during incongruent melting: Constraints from post-collisional leucogranite and residual enclaves from Bengbu Uplift, China. Chem. Geol. 439, 71−82.

Tang, M., Rudnick, R.L., Chauvel, C., 2014. Sedimentary input to the source of Lesser Antilles lavas: a Li perspective. Geochim. Cosmochim. Acta 144, 43−58.

Tang, Y.J., Zhang, H.F., Deloule, E., Su, B.X., Ying, J.F., Santosh, M., Xiao, Y., 2014. Abnormal lithium isotope composition of the ancient lithospheric mantle beneath the North China Craton. Sci. Rep. 4, 4274.

Teng, F.Z., McDonough, W.F., Rudnick, R.L., Walker, R.J., 2006. Diffusion-driven extreme lithium isotopic fractionation in country rocks of the Tin Mountain pegmatite. Earth Planet. Sci. Lett. 243, 701−710.

Teng, F.Z., McDonough, W., Rudnick, R., Wing, B., 2007. Limited lithium isotopic fractionation during progressive metamorphic dehydration in metapelites: a case study from the Onawa contact aureole, Maine. Chem. Geol. 239, 1−12.

Tilton, G.R., Schreyer, W., Schertl, H.P., 1991. Pb−Sr−Nd isotopic behavior of deeply subducted crustal rocks from the Dora Maira Massif, Western Alps, Italy-II: what is the age of the ultrahigh-pressure metamorphism? Contrib. Mineral. Petrol. 108, 22−33.

Tomascak, P.B., Ryan, J.G., Defant, M.J., 2000. Lithium isotope evidence for light element decoupling in the Panama subarc mantle. Geology 28, 507−510.

Tomascak, P.B., Langmuir, C.H., le Roux, P.J., Shirey, S.B., 2008. Lithium isotopes in global mid-ocean ridge basalts. Geochim. Cosmochim. Acta 72, 1626−1637.

Tomascak, P.B., Magna, T., Dohmen, R., 2016. Advances in Lithium Isotope Geochemistry. Springer, Heidelberg.

Ulmer, P., Trommsdorff, V., 1995. Serpentine Stability to Mantle Depths and Subduction-Related Magmatism. Science 268, 858−861.

Vils, F., Tonarini, S., Kalt, A., Seitz, H.-M., 2009. Boron, lithium and strontium isotopes as tracers of seawater−serpentinite interaction at Mid-Atlantic ridge, ODP Leg 209. Earth Planet. Sci. Lett. 286, 414−425.

Vils, F., Müntener, O., Kalt, A., Ludwig, T., 2011. Implications of the serpentine phase transition on the behaviour of beryllium and lithium−boron of subducted ultramafic rocks. Geochim. Cosmochim. Acta 75, 1249−1271.

Wunder, B., Meixner, A., Romer, R.L., Feenstra, A., Schettler, G., Heinrich, W., 2007. Lithium isotope fractionation between Li-bearing staurolite, Li-mica and aqueous fluids: an experimental study. Chem. Geol. 238, 277−290.

Wunder, B., Deschamps, F., Watenphul, A., Guillot, S., Meixner, A., Romer, R.L., Wirth, R., 2010. The effect of chrysotile nanotubes on the serpentine-fluid Li-isotopic fractionation. Contrib. Mineral. Petrol. 159, 781−790.

Xiao, Y.L., Hoefs, J., Hou, Z., Simon, K., Zhang, Z., 2011. Fluid/rock interaction and mass transfer in continental subduction zones: constraints from trace elements and isotopes (Li, B, O, Sr, Nd, Pb) in UHP rocks from the Chinese Continental Scientific Drilling Program, Sulu, East China. Contrib. Mineral. Petrol. 162, 797−819.

Xiao, Y.L., Sun, H., Gu, H.O., Huang, J., Li, W., Liu, L., 2015. Fluid/melt in continental deep subduction zones: Compositions and related geochemical fractionations. Sci. China Earth Sci. 58, 1457−1476.

Yardley, B.W.D., Bodnar, R.J., 2014. Fluids in the continental crust. Geochem. Perspect. 3, 1−127.

Zack, T., Tomascak, P.B., Rudnick, R.L., Dalpé, C., McDonough, W.F., 2003. Extremely light Li in orogenic eclogites: the role of isotope fractionation during dehydration in subducted oceanic crust. Earth Planet. Sci. Lett. 208, 279−290.

Zheng, Y.F., Chen, R.X., Xu, Z., Zhang, S.B., 2016. The transport of water in subduction zones. Sci. China Earth Sci. 59, 651−682.