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Tracing subduction zone fluid-rock interactions using trace element and Mg-Sr-Nd isotopes

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ABSTRACT

Slab-derived fluids play a key role in mass transfer and elemental/isotopic exchanges in subduction zones. The exhumation of deeply subducted crust is achieved via a subduction channel where fluids from various sources are abundant, and thus the chemical/isotopic compositions of these rocks could have been modified by subduction-zone fluid–rock interactions. Here, we investigate the Mg isotopic systematics of eclogites from southwestern Tianshan, in conjunction with major/trace element and Sr-Nd isotopes, to characterize the source and nature of fluids and to decipher how fluid–rock interactions in subduction channel might influence the Mg isotopic systematics of exhumed eclogites. The eclogites have high LILEs (especially Ba) and Pb, high initial ^{87}Sr/^{86}Sr (up to 0.7117; higher than that of coeval seawater), and varying Ni and Co (mostly lower than those of oceanic basalts), suggesting that these eclogites have interacted with metamorphic fluids mainly released from subducted sediments, with minor contributions from altered oceanic crust or altered abyssal peridotites. The positive correlation between ^{87}Sr/^{86}Sr and Pb* (an index of Pb enrichment; $\text{Pb}^* = 2^*\text{Pb}_N/[\text{Ce}_N + \text{Pr}_N]$), and the decoupling relationships and bidirectional patterns in ^{87}Sr/^{86}Sr-Rb/Sr, Pb*-Rb/Sr and Pb*-Ba/Pb spaces imply the presence of two compositionally different components for the fluids: one enriched in LILEs, and the other enriched in Pb and ^{87}Sr/^{86}Sr. The systematically heavier Mg isotopic compositions ($\delta^{26}\text{Mg} = -0.37$ to $+0.26$) relative to oceanic basalts (-0.25 ± 0.07) and the roughly negative correlation of δ^{26}Mg with MgO for the southwestern Tianshan eclogites, cannot be explained by inheritance of Mg isotopic signatures from ancient seafloor alteration or prograde metamorphism. Instead, the signatures are most likely produced by fluid–rock interactions during the exhumation of eclogites. The high Rb/Sr and Ba/Pb but low Pb* eclogites generally have high bulk-rock δ^{26}Mg values, whereas high Pb* and ^{87}Sr/^{86}Sr eclogites have mantle-like δ^{26}Mg values, suggesting that the two fluid components have diverse influences on the Mg isotopic systematics of these eclogites. The LILE-rich fluid component, possibly derived from mica-group minerals, contains a considerable amount of isotopically heavy Mg that has shifted the δ^{26}Mg of the eclogites towards higher values. By contrast, the ^{87}Sr/^{86}Sr- and Pb-rich fluid component, most likely released from epidote-group minerals in metasediments, has little Mg so as not to modify the Mg isotopic composition of the eclogites. In addition, the influence of talc-derived fluid might be evident in a very few eclogites that have low Rb/Sr and Ba/Pb but slightly heavier Mg isotopic compositions. These findings represent an important step toward a broad understanding of the Mg isotope geochemistry in subduction zones, and contributing to understanding why island arc basalts have averagely heavier Mg isotopic compositions than the normal mantle.

1. Introduction

Subduction channel is a highly reactive interface between subducting oceanic lithosphere and mantle wedge, in which mass transfer as well as elemental and isotopic exchanges actively occur (e.g., Bebout and Penniston-Dorland, 2016). In this region, fluids released from various subducting slab lithologies (e.g., sediments,

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altered oceanic crust, and altered abyssal peridotites) can be mixed and penetrate into exhuming rocks, inducing extensive fluid–rock interactions (John et al., 2008; van der Straaten et al., 2008, 2012; Zack and John, 2007). The fluids, when emanating from the interface into the mantle wedge, can further impart their chemical/isotopic signatures to the juxtaposed mantle rocks and associated arc volcanism.

Trace elements in conjunction with Sr-Nd-O isotopic systematics have been widely used to identify and understand fluid–rock interactions in subduction channels (Glodny et al., 2003; Halama et al., 2011; John et al., 2004, 2012; King et al., 2006). The magnesium (Mg) isotopic systematics might be a useful tracer of subduction-zone fluid–rock interactions, potentially providing insights into the source and nature of fluids. Magnesium is fluid-mobile at low temperatures, which leads to large Mg isotope fractionations as much as 7‰ during Earth's surface processes (Teng, 2017 and references therein). Recent studies also documented high mobility of Mg during subduction-zone metamorphism (Chen et al., 2016; Horodyskyj et al., 2009; Pogge von Strandmann et al., 2015; van der Straaten et al., 2008). Chen et al. (2016) found high δ^{26}Mg values (up to +0.72) for white schists from Western Alps, and linked them to infiltration of Mg-rich fluids derived from dehydration of serpentinites. Recent studies also documented generally heavier Mg isotopic compositions in arc volcanic rocks relative to normal peridotitic sources ($\delta^{26}\text{Mg} = -0.25 \pm 0.07$), which were explained as the addition of heavy Mg isotopes from subducting slabs to the mantle wedge (Li et al., 2017; Teng et al., 2016). A general conclusion derived from these studies is that the subduction-zone fluids might be isotopically heavy in terms of Mg isotopes. Nevertheless, the interpretation of any Mg isotopic variations in subduction-related rocks requires the knowledge of how Mg isotopes behave in subduction channels, and how fluid–rock interactions could affect the Mg isotopic systematics of a rock.

Orogenic eclogites of seafloor protolith may be the best choice to study subduction channel processes. Oceanic crust undergoes seawater alteration prior to subduction and is, therefore, more hydrated relative to the continental crust (Miller et al., 1988). It experiences extensive dehydration together with the sediment veneer during subduction (Gerya et al., 2002). In addition, the exhumation of oceanic crust via the subduction channel proceeds at relatively slower rate (mm/yr; Agard et al., 2009). All of these allow eclogites of seafloor protolith to preserve a record of extensive fluid–rock interactions during exhumation. An increasing number of studies have shown that fluid–rock interactions can readily modify the chemical and isotopic compositions of exhumed eclogites (e.g., Bebout, 2007; Klemd, 2013; Xiao et al., 2012), although how the chemical/isotopic composition shift depends on the nature and abundance of fluids with which the eclogites have interacted.

In this study, we investigate a suite of well-characterized eclogites/blueschists and mica schists from southwestern Tianshan, China. We present the first Mg isotopic data for the orogenic eclogites of seafloor protolith, and in combination with Sr-Nd isotopic and trace elemental data, we explore the influence of subduction-zone fluid–rock interactions on the Mg isotopic systematics of eclogites. Our results show that these eclogites are variably enriched in heavy Mg isotopes, which may result from interactions of the eclogites with both high-MgO and low-MgO fluids released from different hydrous minerals in the subduction channel.

2. Geological settings and samples

The high-pressure to ultrahigh-pressure (HP-UHP) metamorphic belt of Chinese southwestern Tianshan, located along the suture between the Yili and the Tarim blocks, was formed during the northward subduction of the Palaeo-South Tianshan oceanic crust beneath the Yili block (Gao et al., 1999; Windley et al., 1990; Zhang et al., 2002, 2008). The eclogites and retrograded blueschists in southwestern Tianshan occur as interlayers or lenticular bodies in mica schists, representing the relic oceanic crust that experienced subduction and exhumation in response to later continental collision. The protoliths of eclogites and associated blueschists range from MORBs to OIBs as indicated by the geochemical data and their preserved pillow structures in the field (Ai et al., 2006; Gao and Klemd, 2003; Zhang et al., 2002, 2008). The eclogites and their host rocks have experienced peak coesite-bearing eclogite-facies metamorphism at 324 ~ 312 Ma (Zhang et al., 2005; Su et al., 2010; Klemd et al., 2011; Q.-L. Li et al., 2011a; Yang et al., 2013), followed by a slow exhumation rate to amphibolite-facies between 320 Ma and 240 Ma (e.g., Zhang et al., 2013). The peak and retrograde metamorphic temperatures estimated for the southwestern Tianshan eclogites vary from 450 to 630 °C (e.g., Du et al., 2014a, 2014b). The retrograde metamorphic temperatures are slightly higher than the peak-eclogite facies temperatures as a result of thermal relaxation during the exhumation (e.g., Zhang et al., 2013). The presence of abundant millimeter to decimeter-wide and centimeter to meter-long veins in southwestern Tianshan blueschists and eclogites indicates extensive fluid–rock interactions and fluid-mediated mass transport during crustal subduction and exhumation (Beinlich et al., 2010; Gao et al., 2007; Gao and Klemd, 2001; John et al., 2008, 2012; Lü et al., 2012).

The petrology and metamorphic evolution of the studied eclogites and mica schists have been well characterized (Zhang et al., 2003; Ai et al., 2006; Lü et al., 2009; Du et al., 2011, 2014b; Xiao et al., 2012). The eclogites consist mainly of garnet, omphacite, glaucophane, paragonite, epidote, calcite, dolomite and quartz/coesite; the mica schists are mainly composed of garnet, glaucophane, phengite, epidote, paragonite, plagioclase and quartz/coesite. A detail description of the studied eclogites and mica schists including the sample localities has been given in Supplementary Table S1.

3. Analytical methods

3.1. Major and trace elements

Major elements were analyzed at the Hebei Institute of Regional Geology and Mineral Resources, China, by wavelength dispersive X-ray fluorescence spectrometry (Gao et al., 1995). Analytical uncertainties are generally better than 1%. The H_2O^+ and CO_2 were determined by gravimetric methods and potentiometry, respectively. Trace elements were analyzed using an Elan 6100 DRC ICP-MS at the CAS key laboratory of crust-material and environments, University of Science and Technology of China, Hefei. Samples were analyzed with aliquots of USGS standards BHVO-2, BIR-1, AGV-2 and GSP-2. Results for the USGS standards together with the reference values are reported in Supplementary Table S2. Analytical uncertainties are better than 5% for most of the elements.

3.2. Strontium and Nd isotopic analysis

The Sr and Nd were separated from the matrix with cation exchange chromatography with Bio-Rad AG50W-X12 resin using the method described by Chu et al. (2009). The Sr and Nd isotopes were performed using an Isoprobe-T thermal ionization mass spectrometer (TIMS) at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for mass-fractionation using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. During the course of this study, standards of NBS987-Sr and jNdi-Nd yielded a value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 20$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512117 \pm 10$, respectively.

3.3. Magnesium isotopic analysis

Magnesium isotopic ratios were analyzed for bulk rock powders and mineral separates at the University of Washington, Seattle. The separation of Mg was achieved by cation exchange chromatography using Bio-Rad AG50W-X8 resin in 1N HNO3 media (Li et al., 2010; Teng et al., 2007, 2010, 2015; Yang et al., 2009). Two standards, Kilbourne Hole (KH) olivine and seawater, were processed together with samples for each batch of column chemistry. The Mg isotopic ratios were determined using the standard-sample bracketing protocol on a *Nu* plasma MC-ICPMS (Teng and Yang, 2014). The blank Mg signal for ^{24}Mg was <10^{-4} V, which is negligible relative to the sample signals of 3–5 V. The KH olivine and seawater yielded average δ^{26}Mg of -0.25 ± 0.05 and -0.82 ± 0.06, respectively, consistent with previous reported values (Foster et al., 2010; Li et al., 2010; Ling et al., 2011; Teng et al., 2010; Wang et al., 2016)

4. Results

Major and trace elemental compositions of the eclogites and mica schists are summarized in Supplementary Table S3. The eclogites have SiO_2 ranging from 39.82 to 52.47 wt.% and MgO ranging from 3.19 to 9.68 wt.% (Supplementary Table S3), and plot in subalkalic basalt field in Zr/Ti versus Nb/Y diagram (Supplementary Fig. S1; Pearce, 1996). The high contents of H_2O^+ (0.58 to 3.38 wt.%) and CO_2 (0.08 to 8.96 wt.%) are consistent with the presence of water- and/or carbon oxide-bearing minerals such as zoisite/clinozoisite and calcite/dolomite. The eclogites have variably high LILEs (e.g., Ba, Rb, Cs, and K) and Pb, but low Ni and Co concentrations (Supplementary Table S3). The mica schists are felsic with SiO_2 ranging from 59.53 to 76.66 wt.% and MgO ranging from 1.81 to 3.60 wt.% (Supplementary Table S3). They are characterized by variable contents of LILEs, Sr and Pb, which may be controlled by different proportions of mica-group minerals (host of LILEs) and epidote-group minerals (major host of Sr and Pb) in southwestern Tianshan metasediments (e.g., Xiao et al., 2012).

The Sr and Nd isotopic compositions of the eclogites are reported in Table 1. The eclogites have positive age-corrected εNd_{320Ma} value ranging from +2.8 to +10.1 (with one exception of −2.4; Fig. 1). They have extremely high and variable initial Sr isotopic compositions ($^{87}Sr/^{86}Sr_{320Ma}$) varying from 0.7058 to 0.7117 (Fig. 1), a range that is even higher than that of Ordovican to Carboniferous seawater ($^{87}Sr/^{86}Sr = 0.7075–0.7090$; Veizer, 1989). As a result, the eclogites plot rightward far from the field defined by depleted MORB and OIB in εNd(t) - $^{87}Sr/^{86}Sr(t)$ diagram (Fig. 1).

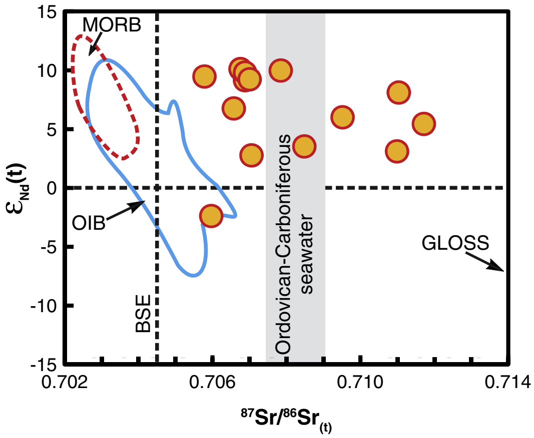

Fig. 1. The Sr and Nd isotopic compositions of the eclogites from southwestern Tianshan. MORB and OIB fields are from Zindler and Hart (1986); $^{87}Sr/^{86}Sr$ ratio of the Ordovican to Carboniferous (O–C) seawater is from Veizer (1989), and $^{87}Sr/^{86}Sr$ ratio of the global subducting sediments (GLOSS) can be high as much as 0.73 (Plank and Langmuir, 1998).

The δ^{26}Mg values of southwestern Tianshan eclogites vary widely from -0.37 ± 0.05 to $+0.26 \pm 0.04$ (Table 2), equal to or higher than unaltered oceanic basalts and eclogites of continental basalt protolith, both of which have homogeneous Mg isotopic compositions around the normal mantle value (-0.25 ± 0.07; Fig. 2). Garnets in southwestern Tianshan eclogites yield δ^{26}Mg values varying from -1.75 ± 0.07 to -1.10 ± 0.07, and omphacites have δ^{26}Mg values ranging from -0.04 ± 0.05 to $+0.46 \pm 0.07$ (Table 2), with corresponding inter-mineral Mg isotope fractionation ($\Delta^{26}Mg_{Cpx\text{-}Grt} = \delta^{26}Mg_{Cpx} - \delta^{26}Mg_{Grt}$) in the range of 1.23–1.98. Temperatures estimated using garnet-clinopyroxene Mg isotope geothermometer range from 485 °C to 675 °C (Huang et al., 2013; W.Y. Li et al., 2016b), which are in rough agreement with the peak and retrograde metamorphic temperatures for the Tianshan eclogites (e.g.,Du et al., 2014a, 2014b). Six mica schists from southwestern Tianshan have bulk δ^{26}Mg values ranging from -0.11 ± 0.05 to $+0.23 \pm 0.02$ (Table 2).

5. Discussion

The overprint of fluid–rock interactions on the southwestern Tianshan eclogites/blueschists has been confirmed by many petrological and geochemical studies (John et al., 2008; van der Straaten et al., 2008, 2012; Beinlich et al., 2010; Lü et al., 2012; J.-L. Li et al., 2016a; Zhang et al., 2016). Depending on the nature and abundance of fluids in a subduction channel, the initial composition of an eclogite can be altered to various degrees after fluid–rock interactions. In this section, we first focus on the trace element and Sr-Nd isotopes to characterize the source and nature of the fluids, and then decipher how fluid–rock interactions may have influenced the Mg isotopic systematics of the eclogites. Finally, we discuss the Mg isotope geochemistry of slab-

Table 1
The Sr and Nd isotopic compositions of the eclogites from southwestern Tianshan.

Sample	Rb(ppm)	Sr(ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	2sigma	$^{87}Sr/^{86}Sr_{(320Ma)}$	Sm(ppm)	Nd(ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2sigma	$\varepsilon Nd_{(320Ma)}$
H902-7	31.1	332	0.271	0.707198	0.000006	0.7060	9.35	37.6	0.150	0.512418	0.000007	-2.4
300-1	89.2	203	1.275	0.712858	0.000045	0.7071	5.74	23.1	0.150	0.512682	0.000011	2.8
H902-4	3.9	115	0.099	0.709964	0.000004	0.7095	3.35	11.5	0.176	0.512903	0.000016	6.0
H902-5	8.5	47.0	0.523	0.710863	0.000004	0.7085	0.67	1.94	0.207	0.512841	0.000026	3.5
305-1^{a}	0.8	92.3	0.024	0.706988	0.000006	0.7069	1.51	4.47	0.204	0.513122	0.000012	9.2
305-2 ^{a}	1.4	181	0.022	0.706855	0.000006	0.7068	2.01	5.46	0.222	0.513209	0.000016	10.1
305-3 ^{a}	9.1	273	0.097	0.707012	0.000007	0.7066	1.32	4.23	0.188	0.512966	0.000024	6.8
305-4 ^{a}	5.0	42.8	0.338	0.709384	0.000008	0.7078	2.40	6.56	0.221	0.513201	0.000016	10.0
X3-1 ^{a}	1.1	175	0.018	0.706961	0.000008	0.7069	2.43	6.92	0.212	0.513172	0.000007	9.8
8-12	4.0	297	0.039	0.711889	0.000008	0.7117	3.09	9.50	0.196	0.512917	0.000009	5.4
H608-6	5.4	149	0.105	0.711467	0.000003	0.7110	3.14	10.2	0.186	0.512775	0.000019	3.1
8-4	2.6	128	0.058	0.711301	0.000007	0.7110	2.34	7.37	0.191	0.513043	0.000034	8.1
8-9	0.4	112	0.011	0.707053	0.000004	0.7070	3.92	13.2	0.179	0.513076	0.000013	9.2
8-20	4.4	170	0.075	0.706122	0.000007	0.7058	5.11	16.3	0.189	0.513108	0.000017	9.5

Samples marked with a superscript “a” are carbonated eclogites enclosed in marbles, and all the others are the eclogites enclosed in mica schists.

Table 2
Magnesium isotopic compositions of the eclogites and mica schists and their mineral separates from southwestern Tianshan.

Sample	Rock/mineral	δ^{26}Mg(‰)	2SD	δ^{25}Mg(‰)	2SD
Eclogites/blueschists					
H902-7	Bulk rock	0.27	0.08	0.16	0.05
	Replicate	0.24	0.06	0.14	0.08
	average	0.25	0.05	0.15	0.04
	Grt	−1.37	0.07	−0.69	0.06
	Cpx	0.46	0.07	0.27	0.06
300-1	Bulk rock	0.25	0.05	0.16	0.04
	Replicate	0.28	0.07	0.15	0.05
	average	0.26	0.04	0.16	0.04
H902-4	Bulk rock	−0.10	0.05	−0.03	0.04
	Grt	−1.61	0.07	−0.88	0.06
	Duplicate	−1.70	0.07	−0.87	0.05
	average	−1.66	0.05	−0.87	0.04
	Cpx	0.09	0.05	0.02	0.07
	Replicate	0.05	0.05	0.04	0.07
	average	0.07	0.04	0.03	0.05
H902-5	Bulk rock	−0.10	0.06	−0.04	0.05
	Grt	−1.58	0.07	−0.78	0.07
	Duplicate	−1.47	0.09	−0.77	0.06
	average	−1.54	0.06	−0.78	0.04
	Cpx	0.06	0.05	0.01	0.07
H907-21	Bulk rock	−0.19	0.06	−0.11	0.05
	Grt	−1.45	0.09	−0.76	0.06
	Cpx	−0.04	0.05	−0.05	0.07
305-1[a]	Bulk rock	−0.09	0.05	−0.07	0.05
	Grt	−1.10	0.07	−0.58	0.05
	Cpx	0.14	0.07	0.09	0.05
305-2 [a]	Bulk rock	0.02	0.08	0.02	0.05
	Grt	−1.17	0.06	−0.60	0.05
	Duplicate	−1.16	0.06	−0.64	0.05
	Replicate	−1.16	0.09	−0.59	0.06
	average	−1.16	0.04	−0.62	0.03
	Cpx	0.11	0.07	0.04	0.05
305-3 [a]	Bulk rock	−0.19	0.06	−0.10	0.03
305-4 [a]	Bulk rock	−0.28	0.05	−0.16	0.04
X3-1 [a]	Bulk rock	0.01	0.06	−0.01	0.05
	Grt	−1.16	0.06	−0.63	0.04
	Duplicate	−1.15	0.09	−0.60	0.06
	average	−1.16	0.05	−0.62	0.03
8-12	Bulk rock	−0.26	0.05	−0.13	0.04
8-19	Bulk rock	−0.33	0.05	−0.19	0.05
	Grt	−1.54	0.07	−0.79	0.06
	Replicate	−1.52	0.06	−0.75	0.06
	Duplicate	−1.51	0.07	−0.80	0.06
	average	−1.52	0.04	−0.78	0.03
	Cpx	0.27	0.07	0.13	0.05
8-26	Bulk rock	−0.31	0.05	−0.16	0.05
H608-6	Bulk rock	−0.25	0.05	−0.11	0.04
	Grt	−1.56	0.07	−0.81	0.05
8-3	Bulk rock	−0.24	0.05	−0.13	0.04
	Grt	−1.51	0.09	−0.83	0.06
8-4	Bulk rock	−0.17	0.05	−0.10	0.05
	Replicate	−0.19	0.06	−0.09	0.05
	average	−0.18	0.04	−0.10	0.04
	Grt	−1.67	0.07	−0.87	0.07
	Duplicate	−1.65	0.09	−0.87	0.06
	average	−1.66	0.06	−0.87	0.04
8-5	Bulk rock	−0.26	0.05	−0.13	0.04
	Grt	−1.34	0.07	−0.70	0.06
8-7	Bulk rock	−0.34	0.06	−0.15	0.05
8-9	Bulk rock	−0.12	0.06	−0.05	0.05
8-20	Bulk rock	−0.37	0.05	−0.16	0.05
	Grt	−1.75	0.07	−0.89	0.05
	Cpx	−0.02	0.07	−0.03	0.05
H710-3	Bulk rock	−0.16	0.05	−0.03	0.05
A314-3 [a]	Bulk rock	−0.15	0.08	−0.08	0.05
	Grt	−1.53	0.07	−0.80	0.05
	Cpx	0.45	0.05	0.26	0.07
105-1	Bulk rock	−0.03	0.07	−0.03	0.06
105-12	Bulk rock	0.00	0.07	0.02	0.06
106-14 [a]	Bulk rock	−0.19	0.07	−0.12	0.06
110-3	Bulk rock	0.08	0.07	0.01	0.06
Q316-10	Bulk rock	−0.09	0.04	−0.04	0.02
A300-3	Bulk rock	0.00	0.03	0.00	0.03
a300-16	Bulk rock	−0.11	0.04	−0.05	0.02
H902-10	Bulk rock	−0.33	0.02	−0.16	0.02
k984-1	Bulk rock	−0.05	0.06	−0.02	0.03
H902-2-1	Bulk rock	0.15	0.01	0.07	0.01
Mica schist					
106-3B	Bulk rock	−0.18	0.07	−0.08	0.06
	Duplicate	−0.13	0.08	−0.05	0.05
	Average	−0.16	0.05	−0.06	0.04
986-1	Bulk rock	−0.11	0.08	−0.02	0.05
305-5	Bulk rock	−0.16	0.05	−0.08	0.04
Q314-1	Bulk rock	0.23	0.02	0.13	0.03
Q316-4	Bulk rock	−0.25	0.02	−0.13	0.01
H865-1	Bulk rock	−0.13	0.03	−0.06	0.01

Samples marked with a superscript “a” are carbonated eclogites enclosed in marbles, and all the others are the eclogites enclosed in mica schists; Grt = garnet; Cpx = clinopyroxene; 2SD = two times the standard deviation of the population of n ($n > 20$) repeat measurements of the standard during an analytical session; replicate: repeat sample dissolution, column chemistry and instrument analysis of Mg isotopic ratios; duplicate: repeat measurement of Mg isotopic ratios on the same solution.

derived fluids in the subduction channel and their influences on the sub-arc peridotites.

5.1. Geochemical evidence for fluid–rock interactions

Trace element and Sr-Nd isotope geochemistry suggest interactions of eclogites with metamorphic fluids. The fluids are mainly derived from subducted sediments, with limited contributions from serpentinites or altered oceanic crusts. Most eclogites are variably enriched in LILEs (e.g., Ba, Cs, Rb, and K) and Pb (Fig. 3), which can be produced during either ancient seafloor alteration or subduction-zone fluid–rock interactions. Bebout (2007) documented that significant enrichments of Ba and Pb in metabasaltic rocks can be most directly associated with metasomatism because these two elements are only slightly enriched in altered oceanic basalts during seafloor alteration relative to other LILEs. The consistently high Ba/Rb, high Ba/K and low Ce/Pb of our eclogites are thus indicative of HP/UHP fluid–rock interactions rather than ancient seawater alteration (Fig. 3a, b, c). Furthermore, these eclogites have extremely high initial ^{87}Sr/^{86}Sr ratio up to 0.7117 (Fig. 1), a signature that cannot be attributed to pre-subduction seawater alteration because the Ordovican-Carboniferous seawater has much lower ^{87}Sr/^{86}Sr ratios of 0.7075–0.7090 (Veizer, 1989). The high ^{87}Sr/^{86}Sr$_{320Ma}$ ratios thus must have resulted from interactions of the eclogites with fluids during metasomatism, and the fluids might be derived from subducted sediments whose ^{87}Sr/^{86}Sr ratios can be as high as 0.73 (Plank and Langmuir, 1998). In contrast to Sr isotopes, Nd isotopes appear to behave conservatively during the metasomatism (King et al., 2006). Due to the low mobility of REE during metamorphic dehydration under relatively low P-T conditions (Kessel et al., 2005), slab-derived fluids would contain too little Nd to affect the Nd isotopic systematics of eclogites (van der Straaten et al., 2012), such that the eclogites retain their depleted Nd isotopic signatures (Fig. 1). In accordance with the high ^{87}Sr/^{86}Sr ratios, most eclogites contain very low concentrations of Co and Ni evolving from oceanic basalts towards the GLOSS (global subducting sediments; Fig. 3d), pointing towards again interactions of the eclogites with sediment-derived fluids. Some eclogites however have Ni and Co contents overlapping or slightly higher than oceanic basalts (Fig. 3d). This indicates the possible contributions of altered oceanic crust-derived or serpentinite-derived fluids (e.g., van der Straaten et al., 2012), although subducted sediments must be the dominant source for fluids that have interacted with the eclogites.

The geochemical signatures of sediment-derived fluids might vary significantly in response to the mineralogical heterogeneity of subducting sediments. The eclogites display a series of geochemical

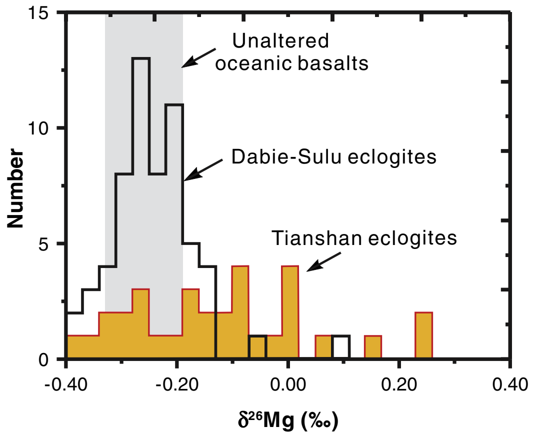

Fig. 2. Histogram of δ^{26}Mg values for the eclogites from southwestern Tianshan. δ^{26}Mg values of the eclogites with continental origin are from Li et al. (2010) and Wang et al. (2014a, 2014b). δ^{26}Mg values of the unaltered oceanic crust are from Teng et al. (2010).

features indicative of two compositionally different fluid components (Fig. 4). As shown in Rb/Sr vs. Pb* (an index of enrichment of Pb; $Pb^* = 2^*Pb_N/[Ce_N + Pr_N]$) and Ba/Pb vs. Pb* diagrams, the enrichment of Pb in eclogites is not always associated with the enrichment of LILEs (Fig. 4a and b). The observed decoupling patterns may indicate two major fluid components: one enriched in LILEs relative to Pb (e.g., high Rb/Sr and Ba/Pb but low Pb*), and the other enriched in Pb relative to LILEs (e.g., high Pb* but low Rb/Sr or Ba/Pb). The roughly positive correlation between Pb* and $^{87}Sr/^{86}Sr_{320Ma}$ (Fig. 4c), suggests that the high-Pb component also contains a significant amount of radiogenic Sr that has elevated the $^{87}Sr/^{86}Sr$ value of eclogites. Some carbonated eclogites are extremely enriched in elemental Sr but have relatively low $^{87}Sr/^{86}Sr$ values of 0.7066–0.7078 (Supplementary Fig. S2), suggesting that the surrounding marbles are not the source of high-$^{87}Sr/^{86}Sr$ fluid. Instead, the high-$^{87}Sr/^{86}Sr$ fluid component must be sourced from other metasediments, such as mica schists. The high-LILEs component, on the other hand, might contain too little Sr to modify the Sr isotopic composition of eclogites, as reflected by the decoupling relationship between $^{87}Sr/^{86}Sr_{320Ma}$ and Rb/Sr (Fig. 4d): the high-Rb/Sr eclogites display low $^{87}Sr/^{86}Sr_{320Ma}$ values, whereas the low-Rb/Sr samples are characterized by highly radiogenic Sr isotopic compositions (Fig. 4d). All these observations support that the eclogites were infiltrated by two fluid components. The distinct geochemical signatures of the two fluid components are consistent with the fact that LILEs and Sr-Pb are hosted in different hydrous minerals in subducted sediments: mica-group minerals are the dominant host for LILEs, whereas epidote-group minerals (and to a less extent carbonate minerals and paragonite) are the major host of Pb and Sr (e.g., Bebout et al., 2007, 2013; Busigny et al., 2003; Xiao et al., 2012). As a result, fluid dehydrated from mica-group minerals would have high Rb/Sr and Ba/Pb ratios, whereas fluid released from epidote-group minerals in metasediments could be enriched in Pb and Sr (as well as $^{87}Sr/^{86}Sr$). It is possible that varying modal mineralogy in the subducted sediments (e.g., mica-group minerals are abundant in metapelites and epidote-group minerals are abundant in greywackes) can result in decomposition of mica- and epidote-group minerals in different proportions along the subduction P-T path and generate the two fluid components in the subduction channel. During crustal subduction, biotite is thought to be completely decomposed at P = 1.3–1.5 GPa, at which the epidote-group minerals such as epidote and zoisite are still stable (Poli and Schmidt, 2002). Therefore, decomposition of biotite at the early stage during crustal subduction could release a significant amount of fluid that is enriched in LILEs. At a higher pressure above 2.5 GPa, epidote and zoisite might become unstable (Carswell, 1990; Poli and Schmidt, 2002). Metamorphic dehydration at this stage could thus release abundant Sr and Pb to the fluids. Such fluids, when released from subducting oceanic crust, would migrate upward along the subduction channel, infiltrate the

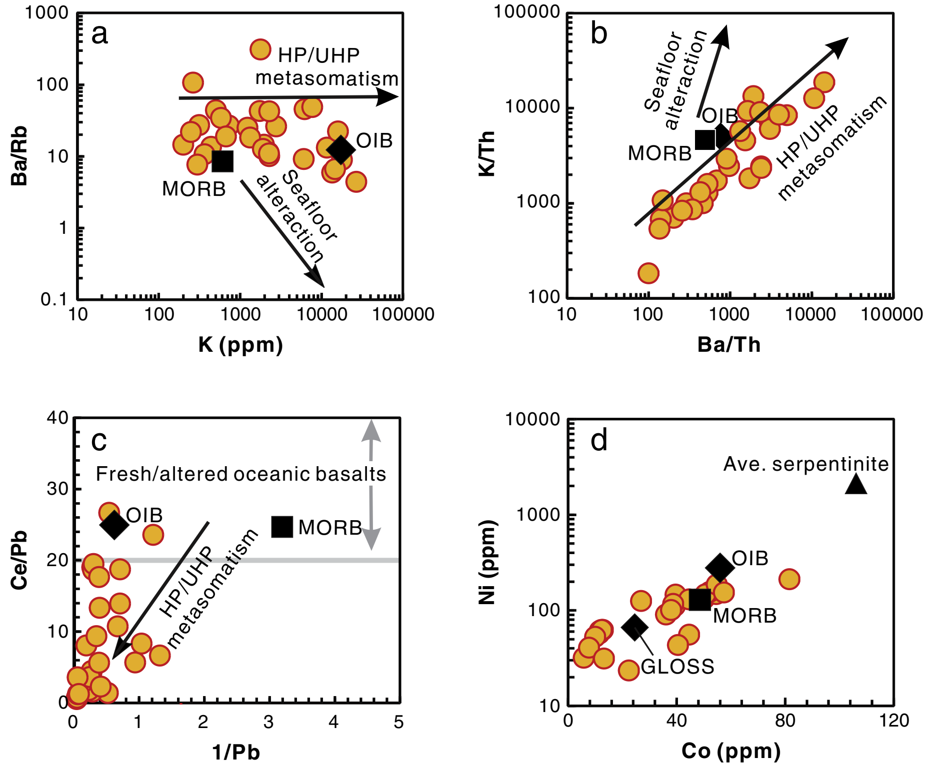

Fig. 3. Ba/Rb vs. K (a), K/Th vs. Ba/Th (b), and Ce/Pb vs. 1/Pb (c) diagrams to differentiate between ancient seawater alteration and metamorphic metasomatism after Bebout (2007). The Ni vs. Co diagram (d) indicates that most eclogites have lower Ni and Co concentration than oceanic basalts. Data of MORB and OIB are from Sun and McDonough (1989); the Ni and Co of average serpentinite are from data compiled by van der Straaten et al. (2008).

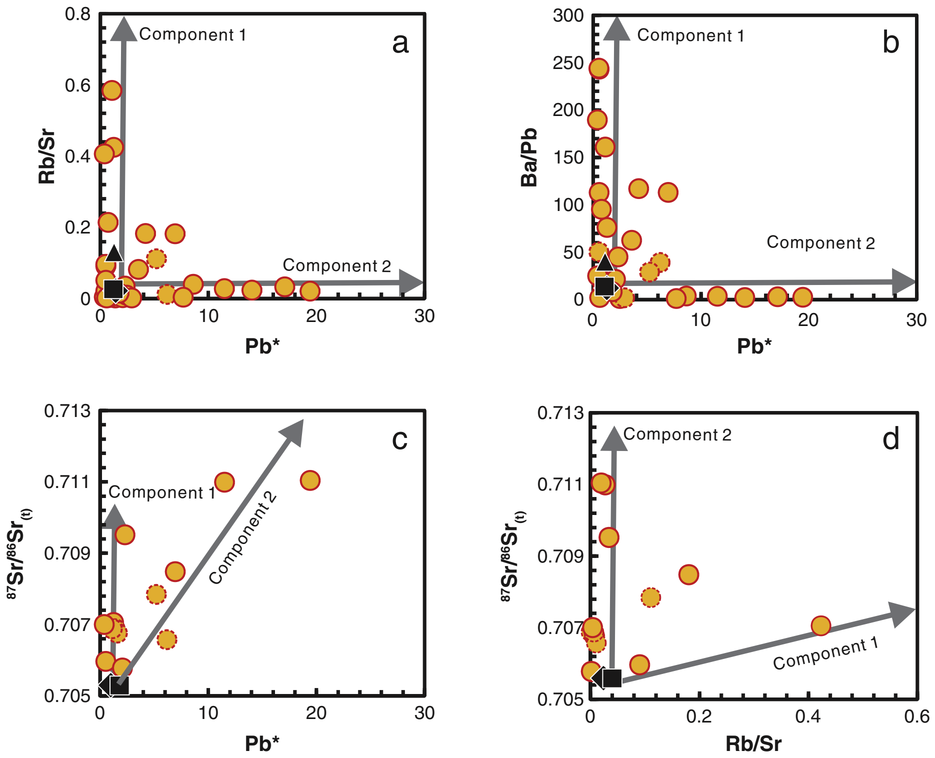

Fig. 4. Rb/Sr vs. Pb* (a), Ba/Pb vs. Pb* (b), $^{87}Sr/^{86}Sr_{(t)}$ vs. Pb* (c) and $^{87}Sr/^{86}Sr_{(t)}$ vs. Rb/Sr (d) diagrams to indicate the two fluid components. The Pb* represents an indices of enrichment of Pb in the eclogites: $Pb^* = 2^*Pb_N/(Ce_N + Pr_N)$. The higher the Pb*, the more enrichment of Pb for the eclogites. The carbonated eclogites are marked as dashed outline. The black triangle in panels a and b represents the average altered oceanic crust (super composite of Ocean Drilling Program Site 801) in Kelley et al. (2003). Black square and diamond represent the composition of MORB and OIB, respectively. The component 1 is enriched in LILEs, which might be derived from dehydration of mica-group minerals. The component 2 is enriched in Pb and $^{87}Sr/^{86}Sr$, likely released from epidote-group minerals.

exhuming eclogites and impart their distinct geochemical signatures to the eclogites via fluid–rock interactions.

5.2. Constraining the mechanisms of Mg isotopic variations in the eclogites

The eclogites have varying Mg contents (MgO = 3.2 to 9.7 wt.%) at a given SiO_2 content, and more variable and systemically heavier Mg isotopic composition than fresh oceanic basalts (Fig. 5). The simplest explanation for the low MgO and high $\delta^{26}Mg$ of eclogites is physical/mechanical mixing with a high-$\delta^{26}Mg$ sedimentary component at some point before or during the exhumation of the eclogites. However, this is very unlikely because binary mixing calculation, using the highest $\delta^{26}Mg$ value of the six mica schists as an endmember (Q-314), suggests that at least >60% of sedimentary component is required to produce the Mg isotopic compositions of most eclogites (Fig. 5), such that the eclogites would have anomalously high SiO_2 contents (>55 wt.%). In addition, the SiO_2 of eclogites does not correlate with neither $^{87}Sr/^{86}Sr_{320Ma}$ nor εNd(t) (Supplementary Fig. S3), further supporting that binary mixing between basalt (or eclogite) and sediment (or metasediment) might not be the case. Magnesium is fluid-mobile, thus, processes like ancient seawater alteration, prograde metamorphism (e.g., release of Mg into metamorphic fluids and eclogite-host isotopic exchanges), and retrograde fluid–rock interactions (e.g., interaction with metamorphic fluid during exhumation), could potentially account for the observed Mg isotopic variations. Next, we endeavor to explore how Mg isotopes behave during these processes, based on which, we highlight the importance of subduction channel fluids in generating Mg isotopic variations in exhumed eclogites.

5.2.1. Seafloor alteration cannot explain the Mg isotopic signatures

Seafloor alteration produces even larger Mg isotopic variations, with Mg isotopes likely fractionated in a different manner from that observed in the eclogites, as shown in Fig. 5. Altered oceanic crusts (AOC) from two different sites have been reported for Mg isotopic compositions (Huang et al., 2015; Teng, 2017). Carbonate-barren AOC samples recovered from IODP site 1256 in the eastern equatorial Pacific retain a mantle-like $\delta^{26}Mg$ value as for fresh oceanic basalts (Fig. 5; Huang et al., 2015), based on which Huang et al. (2015) concluded that seafloor alteration causes limited Mg isotope fractionation, regardless of alteration temperature and water/rock ratio. At the other site (ODP site 801) in western Pacific, extensively altered AOC samples have highly variable $\delta^{26}Mg$ values ranging from −2.76 to +0.21 (Fig. 5), with low $\delta^{26}Mg$ values being associated with carbonate enriched samples and high $\delta^{26}Mg$ values associated with clay-rich samples (Teng, 2017). Due to carbonate dilution effect (Tipper et al., 2006), the AOC samples from ODP site 801 are distributed in a trend in which $\delta^{26}Mg$ values decrease as MgO decreases (Fig. 5). Different from AOC, none of the studied eclogites (32 in total) show enrichment of light Mg isotopes, although they contain variable abundances of carbonate minerals. Furthermore, neither heavily nor less altered AOC could account for the roughly negative correlation between $\delta^{26}Mg$ and MgO for the eclogites (Fig. 5). Thus, ancient seawater alteration is unlikely to be the cause of the variable and systemically heavier Mg isotopic compositions of the eclogites.

5.2.2. The role of prograde metamorphic dehydration and eclogite-host isotopic exchange

Magnesium isotope fractionation during prograde metamorphic dehydration or eclogite-host isotopic exchange cannot account for the Mg isotopic variations in our eclogites. It is possible that dehydrated fluids have distinct Mg isotopic compositions from the rock where the fluids are from. However, since the fraction of Mg partitioning into the fluid phases is so small compared to that inherited by metamorphic minerals during prograde metamorphism, metamorphic dehydration

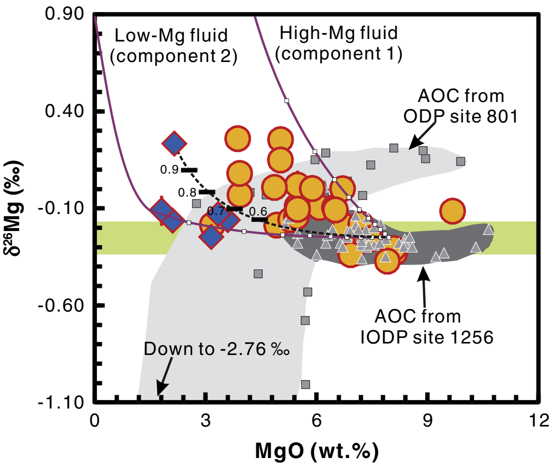

Fig. 5. The variation of δ^{26}Mg values as a function of MgO content for the eclogites (yellow circle) and mica schists (blue diamond) from southwestern Tianshan. The compositions of altered oceanic crust (AOC) from ODP site 801 and IODP site 1256 are from Huang et al. (2015) and Teng (2017). The co-variation between δ^{26}Mg and MgO for the eclogites can be roughly modeled as fluid–rock interactions of the eclogites with compositionally different two fluid components. We assume that the component 1, because of its origin from Mg-rich mica-group minerals or to a less extent talc, have δ^{26}Mg = +1.00 and MgO = 1 wt.%; the component 2, released from Mg-poor epidote-group minerals, contain very little Mg (assuming MgO = 0.05 wt.%). Although we assign a value of +1.00 for the δ^{26}Mg of the low-MgO component 2, the change of this value will not affect the modeling significantly, as the component 2 contains too little Mg so as not to influence the Mg isotopic composition of the eclogites. Thus, the two purple curves with increment of 10% represent the fluid–rock interaction of an eclogite (δ^{26}Mg = −0.25; MgO = 8 wt.%) with high-MgO and low-MgO fluid components, with the partition coefficient of MgO between fluid and eclogite, $D_{\text{eclogite/fluid}} = 4$. The black dotted curve represents binary mixing between sediments and basalts, which suggests that >60% of sedimentary component is required to produce the Mg isotopic composition of the eclogites. The green bar represents the normal mantle δ^{26}Mg value (Teng et al., 2010).(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

causes insignificant Mg isotope fractionation (<±0.07) on a bulk-rock scale (Li et al., 2014; Teng et al., 2013; W.-Y. Li et al., 2011b; Wang et al., 2014b, 2015a, 2015b). Local isotopic exchange between eclogite and its host rock can potentially change the original mantle-like Mg isotopic compositions of the eclogites (Wang et al., 2014a). To which direction the Mg isotopes of the eclogites fractionate depends on the types of host rock. For example, eclogite-host isotopic exchange would make eclogite boudins in carbonates/marbles isotopically lighter, whereas those enclosed in mica schists heavier (Wang et al., 2014a). However, no systemic relationship between δ^{26}Mg and host rock type was observed for the southwestern Tianshan eclogites. On the opposite, the carbonated eclogites (those enclosed in marbles) in our study are enriched in heavy Mg isotopes (δ^{26}Mg = −0.28 to +0.02; Table 2), which we interpret below as a result of infiltration of external fluids derived from metasediments.

5.2.3. Response of Mg isotopic systematics in the eclogites to fluid–rock interactions

Thus, our favored interpretation of the Mg isotopic variation is fluid–rock interaction in a subduction channel. The fluids must be enriched in heavy Mg isotopes, and pervasively reactive in interacting with the eclogites because the eclogites have systemically heavier Mg isotopic compositions (Fig. 2), regardless of their diverse host rock types. Below, we discuss how the two fluid components may have affected the Mg isotopic compositions of the eclogites.

The two fluid components, due to their derivation from different hydrous minerals, have different impacts on the Mg isotopic systematics of eclogites. In the plots of δ^{26}Mg vs. Pb* and δ^{26}Mg vs. ^{87}Sr/^{86}Sr$_{320\text{Ma}}$ (Fig. 6a and b), the high-Pb* and ^{87}Sr/^{86}Sr$_{320\text{Ma}}$ samples retain a mantle-like δ^{26}Mg value, suggesting that the infiltration of high-Pb and ^{87}Sr/^{86}Sr fluid component had limited influences on the Mg isotopic composition of eclogites. Being the dominant source of high-Pb and ^{87}Sr/^{86}Sr component, the epidote-group minerals contain little Mg (e.g., Guo et al., 2012), and thus the fluid dehydrated from them is unable to modify the Mg isotopic composition of the eclogites (although the exact δ^{26}Mg value of any epidote-group mineral has not been reported so far). The low-Pb* and ^{87}Sr/^{86}Sr$_{320\text{Ma}}$ samples, on the other hand, have variably high δ^{26}Mg values (Fig. 6a and b). As expected, eclogites with high-Rb/Sr and Ba/Pb ratios have high δ^{26}Mg values (Fig. 6c and d). Because of the complexity of the fluid system and the uncertainty of its Mg concentration and Mg isotopic composition, we are not expecting to see good correlations between δ^{26}Mg and indices of enrichment of LILEs (such as Rb/Sr and Ba/Pb). However, the general patterns shown in Fig. 6c and d suggest that the high-LILEs component carries a significant amount of isotopically heavy Mg that has elevated the δ^{26}Mg values of the eclogites. Mica-group minerals, as the major source of high-LILE component, are enriched in MgO, and in addition their δ^{26}Mg values are characteristically high. For instance, biotites in metapelites from the Ivrea Zone in NW Italy have δ^{26}Mg values ranging from −0.08 to +1.10 (Wang et al., 2015b), and phengites in eclogites from the Dabie orogen have δ^{26}Mg values of +0.30 to +0.59 (W.-Y. Li et al., 2011). Therefore, eclogites metasomatized by the mica-derived fluid could gain high-δ^{26}Mg signatures. It is also important to note that in Fig. 6c and d, a part of low-Rb/Sr and Ba/Pb samples has slightly high δ^{26}Mg value, which we interpret as the possible influence of the talc-derived fluid, as the talc in serpentinite is depleted in LILEs but enriched in heavy Mg (δ^{26}Mg = +0.06 to +0.30; Beinlich et al., 2014). Without good constraints on the Mg isotopic composition of fluid and the partition coefficient of MgO between fluid and eclogite, it is not yet possible to give a perfect fluid–rock interaction model for the whole dataset of the eclogites. However, the rough negative correlation between δ^{26}Mg and MgO for the eclogites can be generally modeled as interactions of eclogites with high-MgO (e.g., dehydrated from mica-group minerals or talc) and low-MgO fluid components (e.g., dehydrated from epidote-group minerals) under a variety of water/rock (fluid/eclogite) ratios (Fig. 5).

5.3. The origins of isotopically heavy fluids in subduction channel

Fluids in subduction channels are likely to have heavy Mg isotopic compositions, although different subducted lithologies themselves show highly variable δ^{26}Mg values. The subducted abyssal peridotites have slightly high δ^{26}Mg values of −0.25–+0.10 (Liu et al., 2017). The subducted sediments and altered oceanic crusts have large variations in δ^{26}Mg values (−2.76‰ to +0.92‰), with low δ^{26}Mg associated with carbonated rocks and with high δ^{26}Mg associated with carbonate-free rocks (Hu et al., 2017; Huang et al., 2015; Li et al., 2010; Teng, 2017; Teng et al., 2016; Wang et al., 2015a). One might expect that subsolidus decarbonation or carbonate dissolution during metamorphism could release light Mg isotopes, making the sediment-derived fluids isotopically light. However, decarbonation is an inefficient process for carbonated sediments/basalts along the P-T paths of oceanic subduction (Dasgupta and Hirschmann, 2010; Gorman et al., 2006). Carbonate species dissolved in metamorphic fluid is thought to be mainly $CaCO_3$ (Ague and Nicolescu, 2014; Kelemen and Manning, 2015; Li et al., 2017). Therefore, the presence of carbonate minerals in subducted rocks has negligible influence on the Mg isotopic composition of dehydrated fluids (Li et al., 2017). By contrast, breakdown of hydrous minerals might control the Mg concentration and Mg isotopic composition of dehydrated fluids. Reported δ^{26}Mg values for Mg-rich hydrous minerals, such like mica-group minerals and talc, are higher than the normal mantle value (Beinlich et al., 2014; W.-Y. Li et al., 2011; Wang et al., 2015b), and thus it is very likely that the dehydrated fluids are enriched in heavy Mg isotopes. For example, a recent study suggested that the fluid derived from talc and antigorite in serpentinite is likely characterized by

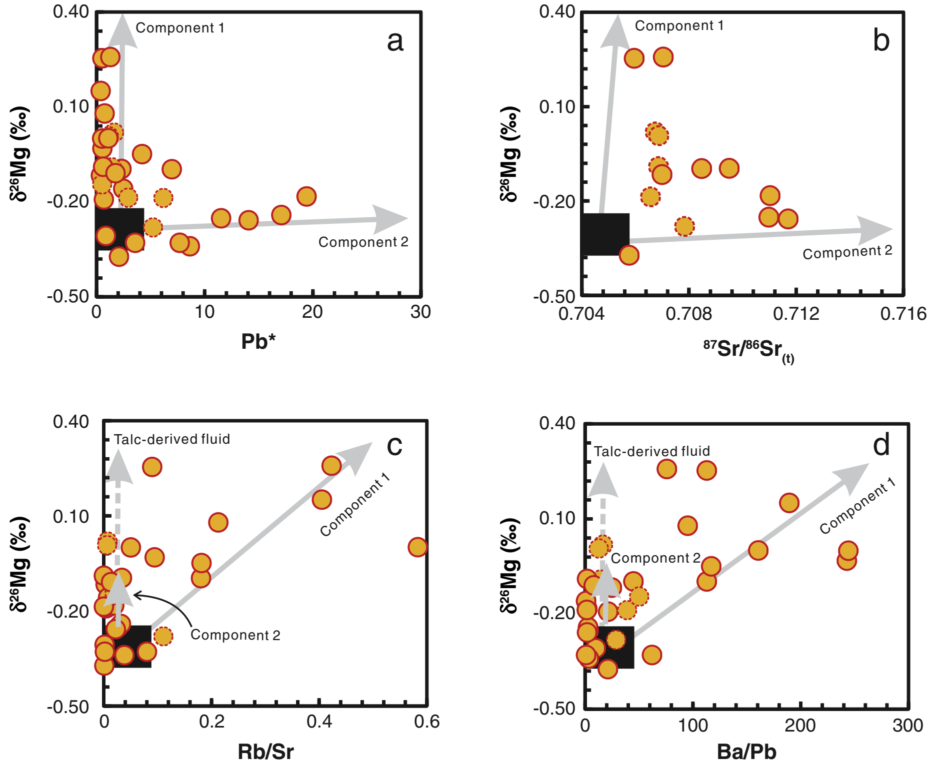

Fig. 6. δ^{26}Mg vs. Pb* (a), δ^{26}Mg vs. ^{87}Sr/^{86}Sr$_{(t)}$ (b), δ^{26}Mg vs. Rb/Sr (c), and δ^{26}Mg vs. Ba/Pb (d) diagrams showing the influence of the two fluid components on the Mg isotopic systematics of eclogites (shown as solid arrows). The carbonated eclogites are marked as dashed outline. The high-LILE fluid component contains a considerable amount of isotopically heavy Mg to shift the δ^{26}Mg of eclogites towards a higher value, whereas the high-^{87}Sr/^{86}Sr and -Pb fluid component contains little heavy Mg to influence the Mg isotopic systematics of eclogites. Some low-Rb/Sr and -Ba/Pb samples also have slightly heavy Mg isotopic compositions, which might point towards the contributions of fluids dehydrated from talc in serpentinite (shown as dashed arrows; Beinlich et al., 2014).

high-Mg and high-δ^{26}Mg, and could be responsible for the high δ^{26}Mg values of white schists in Western Alps (Chen et al., 2016).

5.4. Implications on Mg isotopic systematics in sub-arc peridotites

Fluids in subduction channels can infiltrate the mantle wedge, inducing fluid-peridotite interactions and potentially modifying the Mg isotopic composition of associated peridotites. Only a few Mg isotopic data have been reported so far for mantle wedge peridotites, and they are indeed enriched in heavy Mg isotopes: six arc peridotites from Avacha Volcano in Kamchatka analyzed by Pogge von Strandmann et al. (2011) have δ^{26}Mg values ranging from -0.25 to -0.06, higher than the normal mantle value (-0.25 ± 0.07; Teng et al., 2010). Although the actual mechanism responsible for the Mg isotopic variations in these peridotites is still uncertain, their high δ^{26}Mg values are consistent with petrological and geochemical evidence suggesting that these peridotites have been affected by upward fluid migration from the subducting slab (Ionov and Seitz, 2008). Most recently, Li et al. (2017) found that island arc or back arc basin basalts from circum-Pacific arcs, including Kamchatka, Philippines, Costa Rica and Lau Basin have generally high δ^{26}Mg values ranging from -0.35 to $+0.06$. Teng et al. (2016) reported the Martinique arc lava δ^{26}Mg values of -0.25 to -0.10. Those values overlap the Avacha peridotites and are systemically higher than normal oceanic basalts and peridotites, consistent with the interpretation that isotopically heavy fluids released from the subducted slab incorporate into the mantle wedge (Li et al., 2017; Teng et al., 2016). All the three cases suggest that massive flux of dehydrated fluid into the sub-arc mantle could facilitate extensive fluid-peridotite interaction and shift the δ^{26}Mg of sub-arc peridotite towards higher values.

6. Conclusions

To reveal the nature of fluid–rock interactions in subduction channels and the influence of subduction-zone fluids on the Mg isotopic systematics in exhumed rocks, we present major and trace elements, and Sr-Nd-Mg isotopic data for the eclogites and mica schists from southwestern Tianshan, China. The following conclusions can be drawn:

(1) The eclogites have high Ba/Rb and Ba/K but low Ce/Pb ratios, suggesting the overprint of subduction-zone metamorphic metasomatism. The highly radiogenic Sr isotopic composition (^{87}Sr/^{86}Sr$_{320Ma}$ = 0.7058–0.7117; higher than that of coeval seawater), together with the varying and mostly low Ni and Co concentrations, further indicate that the eclogites have interacted with fluids mainly released from subducted sediments, with limited contributions from altered oceanic crust- or serpentinite-derived fluids.

(2) The positive correlation between ^{87}Sr/^{86}Sr and Pb*, and the bidirectional patterns in ^{87}Sr/^{86}Sr - Rb/Sr, Pb* - Rb/Sr, and Pb* - Ba/Pb spaces, suggest interaction of the eclogites with compositionally different two fluid components: the high-LILEs component which could be derived from dehydration of mica-group minerals, and the high-Pb and ^{87}Sr/^{86}Sr component likely released from epidote-group minerals in subducted sediments.

(3) The highly variable and systemically heavy Mg isotopic compositions of eclogites (δ^{26}Mg = -0.37 to $+0.26$) resulted from fluid–rock interactions in the subduction channel. The high-LILE component, dehydrated from Mg-rich mica-group minerals or to a less extent from talc, contains a considerable amount of Mg that has shifted the δ^{26}Mg of the eclogites towards higher values. The high-Pb and ^{87}Sr/^{86}Sr component, dehydrated from Mg-

poor epidote-group minerals, has little Mg so as not to influence the Mg isotopic composition of the eclogites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.lithos.2017.08.004.

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