LETTER

Sr-Pb isotope compositions of lawsonites in a Pacheco Pass metagraywacke, Franciscan Complex, California

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Lawsonite, jadeite, and glaucophane are iconic minerals within a Pacheco Pass metagraywacke of the Franciscan Complex, California. Those minerals and the associated quartz form the distinctive very low-temperature and high-pressure metamorphic lawsonite-jadeite-glaucophane assemblage, which is diagnostic of 'cold' oceanic subduction zones. In this paper, we evaluate the ability of lawsonite geochemistry to trace protoliths with in-situ trace element and Sr-Pb isotope analyses in lawsonite from the Pacheco Pass blueschist-facies metagraywacke, a classical example of trench-fill sediments in subduction zones. Initial Sr isotope ratios are relatively high (87 Sr/ 86 Sr = 0.7071-0.7074), and initial Pb isotope ratios are 206 Pb/ 204 Pb = 18.74-19.66, 207 Pb/ 204 Pb = 15.58-15.70, and 208 Pb/ 204 Pb = 38.41-39.34, which range from a MORB trend to a cluster on the EMII component. These geochemical signatures suggest the protolith of the metagraywacke mainly contained material derived from continental volcaniclastic rocks and quartzofeldspathic sediments. There is also a possibility that the protolith contains plume-related oceanic island basalt that reached or intruded into the fore-arc sedimentary sequence of California. Considering the maximum depositional age of the metagraywacke at ~ 102 Ma, the subduction of the Farallon Plate beneath the continental crust of the North American Plate might have carried alkali basalt with OIB-like isotopic signatures to the Franciscan trench.

Our study proves the advantage of in-situ lawsonite Sr-Pb isotope analyses to characterize protoliths of metamorphic rocks. The results would manifest that the Sr-Pb isotopic signature of Ca-Al silicate minerals, such as lawsonite, and possibly epidote and pumpellyite, in various types of metamorphic/metasomatic rocks, would be an effective tool for investigating convergent margins.

Keywords: Lawsonite, Blueschist metamorphism, Sr-Pb isotope, Pacheco Pass, Franciscan Complex

INTRODUCTION

Lawsonite [CaAl₂Si₂O₇(OH)₂·H₂O] is an index Ca-Al hydrous silicate mineral confined to blueschist-facies and low-temperature eclogite-facies rocks (Tsujimori et al., 2006; Tsujimori and Ernst, 2014). Lawsonite is a good geochemical tracer of fluid-mediated processes in subduction zones (e.g., Vitale Brovarone et al., 2014; Martin et al., 2014; Fornash et al., 2018; Hara et al., 2018). Lawsonite in a subducting slab plays an important role in the transfer of trace elements and H₂O into great depths of the mantle, because lawsonite contains up to ~ 11.5 wt% H₂O

and is stable along a cold geothermal gradient (cf. Okamoto and Maruyama, 1999; Poli and Schmidt, 2002). Since lawsonite has high concentrations of trace elements such as Sr, Pb, U, Th, and light rare earth elements (LREEs) and especially acts as a major sink for Sr and Pb in the host rocks (e.g., Martin et al., 2014), the Sr-Pb isotope compositions of lawsonite can represent whole-rock isotopic characteristics (Hara et al., 2018).

Hara et al. (2018) described the Sr-Pb isotope compositions of lawsonites in eclogite-facies metabasalts and metachert from South Motagua Mélange (SMM), Guatemala. Using a laser ablation-multipole collector-inductive coupled plasma mass spectrometry (LA-MC-ICPMS), they obtained well-constrained geochemical signatures reflecting protoliths, and/or multiple inputs

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from paleo-seawater, and sediment-derived synmetamorphic fluids. In-situ Sr-Pb isotope analyses in lawsonite provide information that cannot be recognized by petrographical observations as well as conventional wholerock geochemistry, for example, isotopic variation correlated with petrographic textures.

In this paper, we describe the Sr-Pb isotope compositions of lawsonites in a blueschist-facies jadeite-bearing metagraywacke from Pacheco Pass in the Franciscan Complex and discuss the geological significance of the isotope compositions. Mineral abbreviations in this paper follow Whitney and Evans (2010).

GEOLOGIC OUTLINE

The Franciscan Complex of northern California is a classic, well-studied, Pacific-type convergent plate boundary sequence, which includes jadeite-glaucophane-facies metamorphic units (e.g., Ernst, 1970, 1984, 2017; Wakabayashi, 2017). The complex is subdivided into three subparallel belts; Eastern, Central mélange, and Coastal belts that display the different times of deposition, accretion, and exhumation. The Franciscan Eastern Belt is a high-pressure/low-temperature (HP/LT) metamorphic belt characterized by the occurrence of low-grade blueschist-facies rocks with exotic tectonic blocks of coarse-grained blueschist, amphibolite, and eclogite (Ernst, 2017).

The Franciscan jadeite-bearing metagraywacke occurs in the Yolla Bolly terrane of the Eastern Belt. The Franciscan metagraywacke contains a broad spread of Late Jurassic-Cretaceous detrital zircon grains coming from the Sierra Nevada volcanic-plutonic arc (e.g., Ernst et al., 2009; Snow et al., 2010; Dumitru et al., 2015). The jadeite- and lawsonite-bearing metagraywacke in the Pacheco Pass area has been intensively studied, particularly in regards to their metamorphic mineral parageneses (e.g., Ernst, 1965, 1971, 1993; Terabayashi and Maruyama, 1998; Radvanec et al., 1998; Ernst and McLaughlin, 2012). In the Pacheco Pass area, peak P-T conditions reached ~ 200-300 °C at \geq 0.7-0.8 GPa, and a depositional/accretionary maximum age was estimated as ~ 102 Ma based on detrital zircon U-Pb ages of metaclastic rocks (Ernst et al., 2009).

SAMPLE DESCRIPTION

We collected a sample of blueschist-facies jadeite- and lawsonite-bearing metagraywacke from a stratigraphically coherent metasedimentary section in the Pacheco Pass area of the northern Diablo Range, California Coast Ranges (Ernst, 1971, 1993; Terabayashi and Maruyama, 1998; Radvanec et al., 1998; Ernst et al., 2009) (Fig. 1). The Pacheco Pass metagraywacke is relatively coarsegrained metaclastic rock (Fig. 2a), consisting mainly of quartz, chlorite, jadeite, phengite, lawsonite, glaucophane, titanite and containing rare detrital zircon and chromian spinel. Detrital clastic grains of plagioclase, up to ~ 1 mm, are commonly replaced by composite aggregates of jadeite with quartz and lawsonite, and lithic fragments of mafic volcanics are replaced by chlorite, lawsonite, phengite, and glaucophane. Most lawsonites occur as subhedral grains with semi-rectangular shapes of ~ 50-120 µm in length (Figs. 2b and 2c).



Figure 1. A map showing northern California emphasized Pacheco Pass area. The base map was created using Google Earth and the USGS's California geologic map data (https://mrdata.usgs.gov/ geology/state/state.php?state=CA). Color version is available online from https://doi.org/10.2465/jmps.190727.



Figure 2. Photomicrographs of metagraywacke. (a) Scanned image. (b) Plane-polarized light image. (c) Back scattered image with analyzed spot (40 μm in diameter). Color version is available online from https://doi.org/10.2465/jmps.190727.

METHOD

We prepared both an ordinary thin-section ($\sim 30 \ \mu m$ in thickness) for petrographic observation and a polished thick-section ($\sim 180 \ \mu m$ in thickness) for LA-ICPMS analyses. All the data were obtained from lawsonite crystals in one thick-section prepared from the collected metagraywacke sample.

Concentrations of major elements and trace elements were analyzed by using LA-ICPMS which involves an OK Laboratory OK-Fs2000K 266 nm femtosecond laser ablation system with ~ 12 J·cm⁻² laser fluence, coupled to a modified Element XR sector-field (SF)-ICPMS (Thermo Fisher Scientific), located at JAMSTEC. The spot size was 40 μ m in diameter, and the repetition rate was 15 Hz (Fig. 2c). For technical details, see Kimura and Chang (2012).

In-situ LA-MC-ICPMS Sr-Pb isotope analyses of lawsonites were performed at JAMSTEC, using an OK Laboratory OK-EX2000 193 nm nanosecond excimer laser with ~ 10 mJ·cm⁻² fluence, coupled to a MC-ICPMS (Neptune, Thermo Fisher Scientific) (Kimura et al., 2013a, 2013b). In both Sr-Pb isotope analyses, the spot sizes were 200 μ m in diameter and the repetition rates were 10 Hz.

RESULTS

Major and trace element compositions

Overall, the analyzed lawsonites are characterized by high concentration of trace elements, especially REEs in Supplementary Table S1 (available online from https:// doi.org/10.2465/jmps.190727). Although the trace element composition of lawsonites shows variation among the analyzed grains, primitive mantle (PM)-normalized spider-diagram shows enrichment in LREE (Fig. 3). LREE- and middle (M) REE-enriched patterns with smooth depletion of heavy (H) REE are the characteristic feature of lawsonite in the low-grade, garnet-free blueschist (e.g., Spandlar et al., 2003); this feature is different from the eclogite-facies lawsonite with strong depletion in HREE (e.g., Martin et al., 2014; Hara et al., 2018). The trace-element patterns of the Pacheco Pass lawsonites show negative Pb peaks (Fig. 3). Note that the Pb concentrational range of the lawsonite overlaps with those of whole-rock data of Franciscan metagraywackes (Fig. 3).

Sr and Pb isotopic compositions

Strontium and lead isotope compositions (${}^{87}Sr/{}^{86}Sr$, ${}^{206}Pb/{}^{204}Pb$, ${}^{207}Pb/{}^{204}Pb$, ${}^{208}Pb/{}^{204}Pb$, ${}^{207}Pb/{}^{206}Pb$, ${}^{208}Pb/{}^{206}Pb$, and ${}^{208}Pb/{}^{207}Pb$) of lawsonites are listed in Tables 1 and 2. The Pacheco Pass lawsonites have relatively high initial Sr isotope ratios: ${}^{87}Sr/{}^{86}Sr = 0.7071-0.7074$ (Fig. 4). Because of the negligible Rb content of lawson-



Figure 3. PM-normalized spider-diagram of lawsonites in metagraywacke. For comparison, those of Franciscan metagraywacke (Ghatak et al., 2013), Cascade arc (Rowe et al., 2009), N-MORB, OIB (Sun and McDonough, 1989), and Global Subducting Sediment (GLOSS, Plank and Langmuir, 1998) are also shown. Normalization factors are from McDonough and Sun (1995). Color version is available online from https://doi.org/ 10.2465/jmps.190727.

 Table 1. Initial Sr isotope ratios of lawsonites in metagraywacke

Spot ID	⁸⁷ Sr/ ⁸⁶ Sr*
MkAn-1**	0.70347 ± 0.00008
MkAn-2	0.70331 ± 0.00008
GW-LSr01	0.70713 ± 0.00005
GW-LSr02	0.70735 ± 0.00012
GW-LSr03	0.70742 ± 0.00008
GW-LSr04	0.70740 ± 0.00008

* Errors after \pm are given as 2 standard error.

** MkAn is a standard material.

ite, the Sr isotope ratios are hardly changed during 102 m.y. and the analyzed Sr isotope ratios can be considered as initial ratios. Granodiorites from the Sierra Nevada batholith present more similar whole-rock trace element and Sr-Pb isotope compositions to Franciscan metagray-wackes in other localities than the Pacheco Pass area (Ghatak et al., 2013). However, the Sr isotope compositions of the Pacheco Pass lawsonites show a different trend compared to those of the whole-rock granodiorites from Sierra Nevada volcanic-plutonic arc (Fig. 4). Moreover, the Sr isotopes are clearly different from the whole-rock data of Franciscan metagraywackes in the literature.

The Pacheco Pass lawsonites have enriched initial Pb isotope ratios: ${}^{206}\text{Pb}/{}^{204}\text{Pb} = 18.74-19.66$, ${}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.58-15.70$, and ${}^{208}\text{Pb}/{}^{204}\text{Pb} = 38.41-39.34$. These values range from a mid-ocean ridge basalt (MORB) trend to enriched mantle (EM) II-like basalt (Figs. 5a and 5b). These initial Pb isotopic values are similar to the whole rock data of Cascade sediment (Church, 1976; Prytulak et al., 2006), the Franciscan metagraywacke, Catalina mélange rock, and granodiorites from the Sierra Nevada batholith (Chen and Tilton, 1991; King et al., 2007; Ghatak et al., 2013) (Figs. 5c and 5d). Note that the Pacheco Pass lawsonites are especially enriched in ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ values compared with the whole-rock data of Franciscan rocks (Fig. 5d).

Table 2. Analyzed and initial (102 Ma) Pb isotope ratios of lawsonites in metagraywacke

Spot ID	$^{206}Pb/^{204}Pb^{*}$	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
BCR-2G_1**	18.76 ± 0.02	15.62 ± 0.01	38.72 ± 0.04	0.8326 ± 0.0002	2.0639 ± 0.0003	2.4788 ± 0.0004
BCR-2G_2	18.76 ± 0.01	15.62 ± 0.01	38.72 ± 0.03	0.8328 ± 0.0001	2.0645 ± 0.0002	2.4790 ± 0.0003
BCR-2G_3	18.78 ± 0.02	15.64 ± 0.02	38.76 ± 0.05	0.8326 ± 0.0001	2.0640 ± 0.0002	2.4789 ± 0.0003
BCR-2G_4	18.75 ± 0.02	15.62 ± 0.02	38.71 ± 0.04	0.8327 ± 0.0001	2.0646 ± 0.0002	2.4791 ± 0.0004
BCR-2G_5	18.77 ± 0.02	15.62 ± 0.01	38.73 ± 0.03	0.8324 ± 0.0001	2.0635 ± 0.0003	2.4790 ± 0.0003
GW-LPb01	19.93 ± 0.37	15.78 ± 0.28	40.01 ± 0.73	0.7912 ± 0.0032	2.0057 ± 0.0055	2.5347 ± 0.0060
GW-LPb02	19.41 ± 0.09	15.61 ± 0.07	38.91 ± 0.18	0.8045 ± 0.0013	2.0076 ± 0.0023	2.4949 ± 0.0023
GW-LPb03	19.52 ± 0.13	15.68 ± 0.11	39.21 ± 0.27	0.8031 ± 0.0007	2.0081 ± 0.0011	2.5001 ± 0.0015
GW-LPb04	19.63 ± 0.11	15.54 ± 0.09	39.66 ± 0.28	0.7944 ± 0.0023	2.0244 ± 0.0027	2.5515 ± 0.0056
GW-LPb05	20.64 ± 0.15	15.80 ± 0.05	40.63 ± 0.19	0.7673 ± 0.0036	1.9746 ± 0.0053	2.5699 ± 0.0062
GW-LPb06	19.78 ± 0.13	15.71 ± 0.10	39.80 ± 0.26	0.7935 ± 0.0026	2.0099 ± 0.0037	2.5311 ± 0.0044
GW-LPb07	20.02 ± 0.12	15.75 ± 0.10	40.06 ± 0.25	0.7869 ± 0.0010	2.0013 ± 0.0016	2.5436 ± 0.0023
GW-LPb08	19.65 ± 0.17	15.66 ± 0.13	39.31 ± 0.33	0.7978 ± 0.0010	2.0012 ± 0.0014	2.5100 ± 0.0029

Spot ID	²⁰⁶ Pb/	²⁰⁷ Pb/	²⁰⁸ Pb/	²⁰⁷ Pb/	²⁰⁸ Pb/
1	²⁰⁴ Pb _(i) ***	²⁰⁴ Pb(i)	²⁰⁴ Pb _(i)	²⁰⁶ Pb(i)	²⁰⁶ Pb(i)
BCR-2G 1**		—			
BCR-2G_2		—		_	
BCR-2G_3	_	_			
BCR-2G_4					
BCR-2G_5		—		_	
GW-LPb01	19.20	15.74	39.52	0.82	2.06
GW-LPb02	18.70	15.57	38.42	0.83	2.05
GW-LPb03	18.80	15.65	38.72	0.83	2.06
GW-LPb04	18.91	15.50	39.17	0.82	2.07
GW-LPb05	19.89	15.77	40.13	0.79	2.02
GW-LPb06	19.05	15.68	39.31	0.82	2.06
GW-LPb07	19.29	15.72	39.57	0.81	2.05
GW-LPb08	18.93	15.63	38.82	0.83	2.05

* Errors after \pm are given as 2 standard error.

** BCR-2G is a standard material.

*** Subscript (i) represents initial isotope ratio.



Figure 4. Box plot showing initial Sr isotope ratios of lawsonites in metagraywacke. Bold lines show medians and 'n' represents the number of data. For comparison, Sr isotope ratios of eclogitefacies lawsonites in SMM metamorphic rocks (Hara et al., 2018), whole-rock Sr isotope ratios of Franciscan metagraywacke (Ghatak et al., 2013), Sierra Nevada batholith (>102 Ma data, Chen and Tilton, 1991), Cascade arc [Downloaded from the geochemical database GEOROC (http://georoc.mpch-mainz.gwdg. de) and extracted basalt data], and MORB, EMI, and EMII (Stracke et al., 2003) are shown.

In comparison with lawsonites in the eclogite-facies metabasaltic and metasedimentary rocks from SMM in Guatemala (Hara et al., 2018), the blueschist-facies lawsonites in the Pacheco Pass metagraywacke show more heterogeneous and enriched Pb isotope ratios (Figs. 5a and 5b). The enriched Pb in the Pacheco Pass metagraywacke can be distinguished from depleted Pb isotope ratios reported from some Franciscan high-grade metabasites (Saha et al., 2005) (Figs. 5c and 5d).

NEW INSIGHTS

Hara et al. (2018) demonstrated that lawsonite may be a successful geochemical tracer to decipher the protolith tectonic provenance as well as fluid-derived input. They reported both protolith-derived and secondary fluid-modified Sr-Pb isotopic signatures from eclogite-facies lawsonites in SMM eclogites (Figs. 4 and 5). The preservation of multi-stage isotope records in natural lawsonites inferred that isotopic signatures in lawsonite would be not easily erased by near-surface alteration and/or weathering. Our new study also confirmed the advantage of in-situ Sr-Pb isotope study of lawsonite to characterize protoliths of metamorphic rocks.

Lawsonites from the Pacheco Pass blueschist-facies metagraywacke have enriched Sr-Pb isotope ratios inherited from clastic fragments with geochemical provenances from a complex debris deliver system. The relatively heterogeneous Pb isotope ratios would reflect the different isotopic components in a multi-provenance sedimentary protolith, such as oceanic basalt, volcaniclastic and/ or quartzofeldspathic sediments deposited in a trench. Notably, the enriched Pb isotope compositions suggest a possibility of geochemical input from EMII-like basaltic fragments during deposition of sedimentary protolith. In such geochemical scenario, we can estimate that the subduction of the Farallon Plate at ~ 102 Ma (depositional age of the metagraywacke protolith; Ernst et al., 2009) beneath the North American Plate would have conveyed a plume-related seamount alkali basalt to the trench. Small-scale alkali intrusions near a trench setting were reported in the eastern belt of the Franciscan Complex (Mertz et al., 2001). Such basaltic intrusions would



Figure 5. Binary plots showing initial Pb isotope ratios of lawsonites in metagraywacke. (a) and (c) ²⁰⁶Pb/²⁰⁴Pb versus ²⁰⁷Pb/²⁰⁴Pb diagram. (b) and (d) ²⁰⁶Pb/²⁰⁴Pb versus 208Pb/204Pb diagram. For comparison, in (a) and (b), possible components are shown: MORB, EMI, EMII, and HIMU (Stracke et al., 2003), GLOSS (Plank and Langmuir, 1998), Cascade arc [Downloaded from the geochemical database GEOROC (http:// georoc.mpch-mainz.gwdg.de) and extracted basalt data], Cascade sediment (Church, 1976; Prytulak et al., 2006), and eclogite-facies lawsonites in SMM metamorphic rocks (Hara et al., 2018). In (c) and (d), GLOSS and Franciscan rocks are shown: metagraywacke (Ghatak et al., 2013), metamorphic rocks (Saha et al., 2005), Catalina mélange rocks (King et al., 2007), and Sierra Nevada batholith (>102 Ma data, Chen and Tilton, 1991).

be another candidate of the enriched Pb isotope compositions recorded in lawsonite.

As described above, the Sr isotope compositions of lawsonites in the Pacheco Pass metagraywacke show the minor involvement with the Sierra Nevada volcanic-plutonic arc that have provided trench-fill quartzofeldspathic sediments (Fig. 3). Instead, the high Sr isotope ratios in lawsonites are consistent with a sedimentary-dominant protolith for the Pacheco Pass metagraywacke. The Sr isotope values might have also been influenced by fluids before and during metamorphism. However, it is difficult to evaluate the effect of fluid interaction in lawsonite due to the geochemical complexity of a trench-fill sediment and slab fluid. In any case, this study proposes that the Sr-Pb isotope composition of Ca-Al hydrous silicate minerals, such as lawsonite, would be the best available geochemical tool so far to investigate convergent margin processes.

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SUPPLEMENTARY MATERIALS

Color versions of Figures 1-3 and Supplementary Table S1 is available online from https://doi.org/10.2465/jmps.190727.

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Figure 1

Figure 1. A map showing northern California emphasized Pacheco Pass area. The base map was created using Google Earth and the USGS's California geologic map data (https://mrdata.usgs.gov/geology/state/state.php?state=CA)



Figure 2

Figure 2. Photomicrographs of metagraywacke. (a) Scanned image.(b) Plane-polarized light image. (c) Back scattered image with analyzed spot (40 μm in diameter).



Figure 3. PM-normalized spider-diagram of lawsonites in metagraywacke. For comparison, those of Franciscan metagraywacke (Ghatak et al., 2013), Cascade arc (Rowe et al., 2009), N-MORB, OIB (Sun and McDonough, 1989), and Global Subducting Sediment (GLOSS, Plank and Langmuir, 1998) are also shown. Normalization factors are from McDonough and Sun (1995).

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Lawsonite in Pacheco Pass metagraywacke												
Spot ID	BHVO-2G-1*	BHVO-2G-2	BHVO-2G-3	BHVO-2G-4	BHVO-2G-5	GW-LTr01	GW-LTr02	GW-LTr03	GW-LTr04	GW-LTr05	GW-LTr06	GW-LTr07
SiO2 (wt%)	48.23	49.10	48.15	49.11	49.01	44.02	44.61	42.04	43.17	44.17	42.51	41.28
TiO2	2.86	2.85	2.91	2.83	2.80	0.11	0.21	0.09	0.21	0.09	1.00	0.06
Al2O3	12.99	12.63	12.96	13.06	13.00	34.64	33.75	36.12	35.15	34.31	33.92	36.21
FeO	13.00	12.88	13.07	12.35	12.52	0.25	0.24	0.24	0.39	0.41	1.21	0.53
MnO	0.20	0.20	0.20	0.19	0.19	0.02	0.03	0.02	0.02	0.02	0.03	0.04
MgO	7.45	7.33	7.58	7.52	7.43	0.02	0.02	0.02	0.02	0.02	0.11	0.05
CaO	12.26	12.08	12.15	12.00	12.15	20.89	21.08	21.43	21.01	20.94	21.10	21.75
Na2O	2.22	2.14	2.19	2.16	2.14	0.02	0.02	0.02	0.01	0.02	0.04	0.06
K2O	0.53	0.54	0.54	0.53	0.52	0.01	0.00	0.00	0.00	0.00	0.05	0.00
P2O5	0.25	0.25	0.24	0.25	0.24	0.02	0.02	0.02	0.01	0.02	0.03	0.02
Sc (ppm)	35.2	34.6	35.9	34.0	33.1	4.05	2.59	5.62	9.22	3.07	32.6	3.18
V	358	357	358	355	346	99.9	36.9	71.7	158	42.9	555	19.8
Cr	293	298	299	294	278	6.40	8.10	4.40	2.89	0.435	189	2.91
Co	54.9	52.7	53.7	50.6	52.4		0.052	0.298	0.057	0.110	12.5	0.320
Ni	141	137	148	141	136	_	0.177	_	_	_	13.5	_
Cu	144	143	139	132	138	0.042	1.51	2.87	1.93	0.082	5.75	0.864
Zn	128	129	129	123	121	3.32	3.27	1.50	3.81	2.37	6.40	5.51
Ga	24.0	23.8	23.9	23.2	22.2	54.7	43.7	60.8	58.4	65.8	84.1	63.9
Rb	9.96	10.2	10.2	9.38	9.53	0.226	0.286	_	0.246	0.109	0.964	_
Sr	445	437	433	411	405	1700	1160	1680	1400	2440	2110	2620
Y	26.3	26.9	26.5	24.7	25.2	81.7	33.7	102	133	54.8	321	33.5
Zr	183	182	178	174	168	0.636	1.94	2.58	3.89	1.04	92.1	2.05
Nb	19.5	19.3	18.9	18.0	18.2	1.40	1.56	1.29	2.03	2.14	13.7	2.50
Ba	141	139	141	135	132	101	168	114	115	152	178	288
La	17.1	16.7	16.3	16.4	15.7	159	19.8	282	359	46.8	577	30.7
Ce	43.1	42.0	41.7	39.1	37.7	282	32.3	501	633	76.3	1440	54.5
Pr	5.85	5.70	5.47	5.50	5.15	27.9	3.28	54.3	64.5	8.29	205	6.04
Nd	27.3	25.2	27.6	25.0	24.5	92.2	11.7	166	217	29.0	932	21.0
Sm	7.36	6.89	5.95	6.78	5.93	13.9	2.84	25.2	35.7	5.57	232	3.77
Eu	2.22	2.09	2.33	2.08	1.85	3.96	0.979	6.71	10.3	2.13	61.2	1.57
Gd	7.36	7.63	6.46	6.15	6.88	12.5	2.45	21.2	29.9	4.41	216	1.87
Tb	0.967	0.851	0.953	0.908	0.893	1.74	0.465	2.81	4.26	0.812	23.5	0.619
Dy	5.39	5.89	5.51	5.29	5.54	13.7	4.23	18.8	25.6	6.84	91.7	4.01
Ho	1.16	1.03	1.01	0.992	0.932	3.30	0.947	3.92	4.84	1.55	11.6	0.899
Er	2.63	2.65	2.61	2.63	2.15	9.15	3.52	9.65	10.9	4.74	20.9	2.66
Tm	0.404	0.298	0.366	0.274	0.371	1.14	0.566	0.900	1.15	0.615	1.92	0.380
Yb	1.95	2.34	1.87	1.84	1.87	5.46	4.21	4.91	5.87	3.57	11.2	1.52
Lu	0.267	0.239	0.314	0.270	0.218	0.513	0.437	0.537	0.690	0.401	1.52	0.158
Hf	4.43	4.29	4.13	4.05	4.03	_	0.000	0.158	0.096	_	2.36	0.070
Та	1.09	1.05	1.04	1.07	1.05	_	0.097	0.051	0.001	0.004	0.924	_
Pb	1.75	1.84	1.71	1.84	1.60	2.84	3.00	4.19	2.33	4.03	8.70	5.47
Th	1.07	1.14	1.14	1.06	1.03	4.63	2.25	7.07	2.14	1.28	85.5	0.602
U	0.450	0.455	0.430	0.443	0.456	2.14	0.826	2.26	2.32	0.865	10.6	0.385

*BHVO-2G is a standard material for the trace element analysis by LA-ICPMS.

**"—" means below detection limit.

Note: Analytical precision of trace element analysis was as following:

% RDs (percent relative deviations) <1% to <10% in the concentration range between 0.1 ppm to 3000 ppm;

% RDs = 10–30% in the concentration range between 0.008 ppm to 0.1 ppm (Kimura & Chang, 2012).