Chemical and lithium isotope characteristics of murakamiite and Li–rich pectolite from Iwagi Islet, Southwest Japan

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We report in situ major and trace element and Li isotope analyses of murakamiite and Li–rich pectolite in an albitite and whole–rock analyses of the albitite and host granite from Iwagi Islet, SW Japan. The albitite forms small bodies that are several tens of centimeters to tens of meters in size, disseminated in a host granite of Late Cretaceous age. The studied murakamiite–bearing albitite contains albite, sugilite, aegirine–augite, quartz, murakamiite–Li–rich pectolite, microcline, katayamalite, and accessory minerals. It shows conspicuous strain-induced textures. The murakamiite and Li–rich pectolite form a solid solution with Li × 100/(Li + Na) atomic ratios ranging from 44.2 to 60.1, and the Na line profiles show a zoning structure in which Na decreases from core to rim. Major and trace element compositions of murakamiite–pectolite normalized to that of albitite indicate the enrichments of some elements, particularly in Mn, Ca, Li, Sr, and REEs, roughly on the same order of magnitude (~ 10 times). The albitite–normalized element concentrations vary systematically with ionic radius of the element; the normalized concentrations of cations with the same valence roughly form a simple convex parabolic curve when plot against the ionic radius. This indicates that the element partitioning of murakamiite and pectolite during metasomatism to form albitite took place under a strong control of crystal structure, quasi-equilibrated with metasomatic fluids and coexisting minerals. The δ7Li values of murakamiite and Li–rich pectolite show a wide range from −9.1 to +0.4‰ (average −2.9‰), and no obvious correlation with Li contents was observed. These δ7Li values should have resulted from hydrothermal fluid–rock interactions at the temperatures of 300–600 °C. The very low δ7Li values down to −9.1‰ may have originated from intra-crystalline Li isotope diffusion, or involvement of deep–seated, Li-Na-enriched subduction–zone fluids with low δ7Li values.

Keywords: Murakamiite, Li–rich pectolite, Metasomatism, Li isotopes, Iwagi Islet, Japan

INTRODUCTION

Murakamiite, LiCa2Si3O8(OH) (JMA 2016–066), a Li-analog of pectolite NaCa2Si3O8(OH), is a new mineral that was recently discovered in an aegirine–augite albitite exposed on Iwagi Islet (34°15′47″N, 133°9′39″E), Ehime Prefecture, Japan (Imaoka et al., 2017). The murakamiite is triclinic, belongs to the space group Pl̅, and is a new member of the hydropyroxyenoids with three-periodic SiO4 tetrahedra (Nagashima et al., 2018). Iwagi Islet is also known as the type locality of two other Li-bearing minerals, sugilite, KNa2(Fe3+,Mn3+,Al)3Li3Si12O30 (Murakami et al., 1976; Kato et al., 1976; Armbuster and Oberhänsli, 1988) and katayamalite, KLi3Ca7Ti2(SiO3)12(OH)2 (Murakami et al., 1983; Andrade et al., 2013). Lithium, an alkali element with an ionic radius smaller than Na, is known to be highly mobile during fluid–rock interactions (Brenan et al., 1998). The peculiar Li-minerals in Iwagi Islet are considered to originate from Li metasomatism of an igneous precursor and result from precipitation from a fluid enriched in Li and Na at low– to moderate-temperatures (hydrothermal stages) (Imaoka et al., 2017). The murakamiite-bearing albitite in this study contains 500 ppm Li (Table 1). Such a high–Li albitite is unusual amongst metasomatic rocks in Setouchi Province of SW Japan, and

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such rocks are also rare worldwide. The mechanism to form the Li-rich albitite and the origin of the Li-rich fluid are still unknown.

It has been reported that some geothermal waters show unusual Li enrichment and the ability to precipitate Li-rich mineral resources, such as the Chilean Lhasen geothermal resources of the Andes (Gianni et al., 2005), Punta Plateau of Argentina (Simone et al., 2004) and Kawu area of the Tibetan Plateau (Tan et al., 2018). We can expect, therefore, that the Li-rich mineral murakamiite in Iwagi Islet was also precipitated during geothermal fluid activity, and that a detailed study of the mineral will provide important information regarding the processes of Li metasomatism and the source of Li.

In this paper, we present major and trace element and Li isotope compositions of murakamiite and Li-rich pectolite from Iwagi Islet, as well as major and trace element compositions of a host albitite and granite. For murakamiite and Li-rich pectolite, we carried out in situ analyses using the techniques of laser ablation-inductively coupled plasma–mass spectrometry (LA–ICP–MS), laser ablation–multiple collector–inductively coupled plasma–mass spectrometry (LA–MC–ICP–MS), and micro-milling (MM)–MC–ICP–MS. Using these data, we discuss the mode of Li-Na substitution, factors controlling minor and trace element compositions, and Li isotope characteristics of the murakamiite and Li-rich pectolite, and also the Li metasomatism to generate these minerals.

### GEOLOGICAL BACKGROUND

Metasomatic rocks that contain pyroxene, garnet, amphibole, and biotite are distributed in Setouchi Province, SW Japan, along an approximately E-W trend. These rocks are associated with Late Cretaceous granites (Murakami, 1976) (Fig. 1). The metasomatic rocks occur mostly as small masses that grade into the surrounding granitic rocks. The textures of the weakly metasomatized rocks are similar to those of the surrounding granites and, in

| Sample | Detection limit | Murakamiite-bearing albitite | Coarse-grained biotite granite |
|--------|----------------|-----------------------------|--------------------------------|
| IWG-168 | 0.01 | 67.74b) | 78.66b) |
| T-69 | 0.01 | 0.052b) | 0.048b) |
| Fe2O3 (T) a) | 0.01 | 1.91b) | 0.81b) |
| MnO | 0.01 | 0.047b) | 0.016b) |
| MgO | 0.01 | 0.10b) | 0.03b) |
| CaO | 0.01 | 1.99b) | 0.43b) |
| Na2O | 0.01 | 10.44b) | 3.10b) |
| K2O | 0.01 | 0.35b) | 4.60b) |
| P2O5 | 0.01 | 0.01b) | 0.008b) |
| LOI | | 0.26b) | 1.01 |
| Total | | 99.25b) | 100.17 |

**Table 1. Chemical compositions of samples of murakamiite-bearing albitite (IWG-168) and host granite (T-69) from Iwagi Islet**

**Figure 1. Distribution of metasomatitic rocks in Setouchi Province, SW Japan.**
many places, the original grain size of granite, magmatic foliation, and associated aplites and pegmatites are preserved. The metasomatic rocks commonly occur along shear zones with abundant quartz veins. Textures and structures due to shearing are observed in both the metasomatites and surrounding granites.

The geology of Iwagi Islet and petrology of the albitites have been described by Mitsuchi (1931), Sugi and Kutuna (1944), Taneda (1950, 1952), Umegaki et al. (1954), and Murakami and Matsunaga (1966). According to these studies, the Ryoke Metamorphic Rocks, consisting of hornfelsed slate and sandstone, comprise the oldest formation on the islet. The Ryoke Metamorphic Rocks crop out around Mount Sekizenn-san and in the southwestern coastal area of the islet. Granites intrude the Ryoke Metamorphic Rocks and are widespread throughout the islet. According to our study, the granites can be divided into three types: coarse-, medium-, and fine-grained (Fig. 2a). The coarse-grained granite occurs mainly as sheets in the western, eastern, and northern parts of the islet, and mainly in the topographically lower parts of the medium-grained granite. The coarse- and fine-grained granites are associated with pockets or dikes of aplite, pegmatite, and holmquistite-bearing quartz vein. The fine-grained granite forms tabular bodies that intruded into the upper part of the medium-grained granite around Mount Sekizen-san. These granites are thus vertically stacked sheet-like bodies that can be explained by a sheet-on-sheet model (Menand, 2008). The main mineral assemblages of these granites are identical and

Figure 2. (a) Geological map of Iwagi Islet, Ehime Prefecture, Japan (this study), along with the sampling location of the studied coarse-grained biotite granite (T-69). (b) Enlarged view of the area around Mount Kuresaka showing the occurrence of small masses of albitites, together with the sampling location of the studied murakamite-bearing albitite (IWG-168).
The albitites in Iwagi Islet have been described as ‘aegirine syenite’ since the paper of Sugi and Kutuna (1944), but the name ‘aegirine syenite’ is misleading because: (1) these rocks contain only very small amounts of K-feldspar (max 5.0 vol%) but large amounts of albite (70.2–99.7 vol%) and thus cannot be classified as syenite in the nomenclature of plutonic rocks given by the IUGS Subcommission (1973) and (2) they are not ordinary plutonic igneous rocks but rather are metasomatic rocks, as indicated by the early studies by Murakami and Matsu-naga (1966) and Murakami (1976). We also present several lines of evidence that support this, as described in the next chapter. Therefore, we have renamed these rocks ‘albitite’ following the recommendations of the IUGS Subcommission on the systematics of metamorphic rocks (Zharikov et al., 2007).

**OCCURRENCE AND PETROGRAPHY OF THE ALBITITES**

The albitites occur as numerous small discrete masses in albitized granite, which gradually grade into a normal coarse-grained granite around the summit of Mount Kure-saka in the eastern part of the islet (Figs. 2a and 2b). The largest body of albitite is several tens of meters in diameter, and small albitite bodies, up to several tens of centimeters or meters wide, are irregularly distributed over an area of 300 × 200 m². There are no clear intrusive margins between the albitites and surrounding albitized granite, and the boundaries are instead gradational with diffuse zones of quartz albitite between the two rock types.

The albitites on Iwagi Islet have various replacement textures as a result of Na-Li metasomatism, which involved dissolution and precipitation of minerals in response to the introduction and/or removal of chemical components during the interaction of the host granite with aqueous fluids. The textures of the albitites were formed by the following processes: (1) plagioclase is often replaced by fluorite (Fig. 3g), sericite, and epidote, (2) zircon is euhedral in the host granite and albitized granite (Fig. 3h) but is anhedral and porous in the metasomatic rocks (e.g., Geisler et al., 2007; Sarangua et al., 2019), (3) zircon is surrounded by sogdianite (KZr2Li3Si12O30) as described by Furumoto et al. (2012), and (4) the Li–Mg amphibole holmquistite that is a characteristic metasomatic mineral (Grew, 2020) is observed in albitized granite (Fig. 3i). This is the first reported occurrence of holmquis-tite in Japan. The chemical compositions, mineralogical changes, and chemical reactions related to each texture are beyond the scope of this paper.

The albitites in Iwagi Islet are thus metasomatic rocks, and therefore petrographically and geochemically heterogeneous. We identified the following metasomatic rock types based on the characteristic mineral assemblages of the metasomatites of Iwagi Islet, from the initial host rock to the inner part of metasomatism: (1) the original coarse-grained granite (quartz + microcline + plagioclase + biotite), (2) albitized granite (microcline + albite + quartz ± biotite ± aegirine ± holmquistite), (3) quartz albitite (albite + quartz + microcline + aegirine; (4) hedenbergite albitite (albite + quartz + microcline + hedenbergite ± andradite), (5) sugilite albitite (albite + sugilite + aegirine-augite), (6) katayamalite albitite (albite + aegirine-augite + katayama-lite ± sugilite), and (7) murakamiite–bearing albitite (albite + sugilite + aegirine-augite + murakamiite + pectolite + katayamalite). These types of metasomatic alteration occur on the scale of centimeters to meters.

The studied murakamiite–bearing albitite (Fig. 4, sample no. IWG-168) collected at the top of Mount Kure-saka (Fig. 2b) is fresh (lack of surficial weathering) and contains albite (79.8 vol%; Ab92.6Or5.8Ab99.6Or1.3An0.1), sugilite (8.8 vol%) partially replaced by unidentified hydrous Ca-rich and Ca–Fe–rich altered silicates, aegirine-augite (3.0 vol%; Ae45.8Jd16.5Di35.5–Ae71.1JD2.9Di27.8), quartz (2.7 vol%), murakamiite and Li-rich pectolite (2.4 vol%), microcline (0.3 vol%; Or96.4Ab1.2An0.2–Or97.7Ab2.7), and katayamalite (0.1 vol%). Accessory minerals include zircon, britholite–(Ce), ekanite-like mineral, fluorapatite, and titanite. Conspicuous strain-induced textures are ex-hibited by the aegirine-augite, katayamalite, and primary albite grains. Figure 5a shows the occurrences of mura-kamiite (or pectolite) and albite in a thin-section. The
Murakamiite (or pectolite) crystals occur in a vug with aegirine–augite. Albite is the major constituent, and it occurs as subhedral to anhedral crystals that are 0.1 to 5.0 mm in diameter. The following three types of albite occur (as noted by Murakami and Matsunaga, 1966): (1) large subhedral crystals with or without simple twinning (Ab1; Fig. 5b), (2) large anhedral crystals with fine lamellae of polysynthetic albite twinning as well as cross-hatched twinning (chessboard-twinned albite) (Ab2; Figs. 5b and, 5c), and (3) newly formed granular albite crystals in aggregates that replace large albite grains along their boundaries (Ab3; Fig. 5b). Undulose extinction, deformation twinning (Ab4; Fig. 5c), and healed microstructures are the most common deformation features. Curved twin lamellae are also observed.

**ANALYTICAL METHODS**

Whole-rock major and trace element abundances (including Li) were determined for a murakamiite–bearing albite (IWG-168) and the host coarse-grained granite (sample no. T-69). Two-dimensional Na analysis was carried out for murakamiite (or pectolite) crystals in a thin section of IWG-168. Major and trace element abundance (including Li) and Li isotope ratios were also measured.
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for 95 and 61 spots, respectively, from 49 grains of murakamiite and Li-rich pectolite separated from IWG-168. Crystals separated from IWG-168 were cast in epoxy resin and polished to expose their midsections for analysis.

Electron microprobe analyses

To reveal possible variation in the Li ↔ Na substitution at the large polyhedron (the M3 sites) within a single crystal of murakamiite (or pectolite), X-ray mapping and line analyses of Na were conducted using a JXA-8230 electron probe micro analyzer (EPMA) at Yamaguchi University, Yamaguchi, Japan. The operating conditions were as follows: accelerating voltage of 15 kV, beam current of 20 nA, and beam diameter of 1 µm. Wavelength-dispersive spectra were collected with a TAP crystal to identify interfering elements, and to locate the best wavelength of Na for background measurements. The microprobe standard used for the Na analyses was albite.

Whole-rock major and trace element analyses

Analyses of major and some trace elements (Cr, Ni, Cu, and Zn) were undertaken at Hiroshima University, Hiroshima, Japan, using a fully automated wavelength dispersive Rigaku zsx-101e X-ray fluorescence (XRF) system, equipped with a 3 kW generator and a Rh-W dual anode X-ray tube. Analytical conditions and precision are given in Kanazawa et al. (2001).

Other trace elements, except for Li, were analyzed at Actlabs, Canada, using a Perkin-Elmer Sciex ELAN 9000 ICP-MS, after sample digestion by Li metaborate/tetraborate fusion (code 4B2-research). The errors and analytical precision of the ICP-MS analyses are present-ed on the Actlabs website (http://www.actlabs.com/), and the accuracy of the analyses was monitored by analysis of international reference materials (e.g., W2, WMG1, STM1, DNC1, BIR1, and SY3). Based on the rock standard STM1, accuracy was typically better than 5%, except for La and Er (<10%) and Pr (<30%).

Lithium abundances in the rocks were determined by inductively coupled plasma optical emission spectros-copy (ICP-OES) (Perkin-Elmer Optima 8300) at Yama-
The major and trace element concentrations of murakamiite and Li-rich pectolite were simultaneously determined using LA-ICP-MS, following the method of Kimura and Chang (2012). The analytical setup consisted of a 200 nm femtosecond LA system (OK Fs2000K; OK Lab, Tokyo, Japan) coupled to a quadrupole ICP-MS (iCAP-Qc; Thermo Fisher Scientific, Bremen, Germany) at the Research Institute for Marine Geodynamics, Japan Agency for Marine–Earth Science and Technology (IMG/JAMSTEC), Yokosuka, Japan. The laser fluence on the sample surface was ~ 6 J·cm⁻², and the samples were ablated using a rotation raster protocol with a 20 µm diameter laser beam and 10 Hz laser pulse repetition rate moving at a rate of 11.5 µm s⁻¹ along the circumference of a circle with a radius of 10 µm. Ablation craters that were 30 µm in diameter and 15 µm in depth were created after 60 s of ablation. The U.S. Geological Survey (USGS) standard reference glass GSE-1G was used as the external calibration standard, and the standard glasses GSD-1G and BHVO-2G from USGS, NIST 610 and NIST 612 from the National Institute of Standards and Technology (NIST), and JR-1 natural obsidian glass from the Geological Survey of Japan (GSJ) were analyzed together with the murakamiite to assess the data quality. The major and trace element analyses of minerals (2RSD) of multiple measurements. Better than ±3%, as estimated from the reproducibility (2RSD) of multiple measurements.

Major and trace element analyses of minerals

The major and trace element concentrations of murakamiite and Li-rich pectolite were simultaneously determined using LA-ICP-MS, following the method of Kimura and Chang (2012). The analytical setup consisted of a 200 nm femtosecond LA system (OK Fs2000K; OK Lab, Tokyo, Japan) coupled to a quadrupole ICP-MS (iCAP-Qc; Thermo Fisher Scientific, Bremen, Germany) at the Research Institute for Marine Geodynamics, Japan Agency for Marine–Earth Science and Technology (IMG/JAMSTEC), Yokosuka, Japan. The laser fluence on the sample surface was ~ 6 J·cm⁻², and the samples were ablated using a rotation raster protocol with a 20 µm diameter laser beam and 10 Hz laser pulse repetition rate moving at a rate of 11.5 µm s⁻¹ along the circumference of a circle with a radius of 10 µm. Ablation craters that were 30 µm in diameter and 15 µm in depth were created after 60 s of ablation. The U.S. Geological Survey (USGS) standard reference glass GSE-1G was used as the external calibration standard, and the standard glasses GSD-1G and BHVO-2G from USGS, NIST 610 and NIST 612 from the National Institute of Standards and Technology (NIST), and JR-1 natural obsidian glass from the Geological Survey of Japan (GSJ) were analyzed together with the murakamiite to assess the data quality (Supplementary Table S1; available online from https://doi.org/10.2465/jmps.200721). To validate the Li analytical precision including the uncertainties on the measurements of both the unknown and calibration standard are estimated to be better than 1.48% (1RSE).

Li isotope analyses of minerals

Lithium isotopic compositions were determined with a MC-ICP-MS (Thermo Fisher Scientific NEPTUNE) coupled to a 193 nm ultraviolet excimer laser (OK ExLA 2000; OK Lab, Tokyo, Japan) at the IMG/JAMSTEC. A 50 µm radius × 50 µm depth cylindrical crater was generated by 60 s of ablation using a 1 Hz laser repetition rate at ~ 6 J·cm⁻² laser fluence. These analytical conditions were used for all analyses. All samples were measured by the standard-sample bracketing method. The collection and reduction of data followed the procedures described by Kimura et al. (2016), which involves a novel ablation volume correction (AVC) method. The published Li isotope ratio of NIST 610 (Kasemann et al., 2005) was used for normalization of the standard-sample bracketing analyses. The Li isotope results are reported in δ⁷Li notation as:

$$δ^{7}\text{Li} = \frac{[\text{Li}^{7}/\text{Li}^{6}]_{\text{sample}}/[\text{Li}^{7}/\text{Li}^{6}]_{\text{SVEC standard}} - 1]}{[\text{Li}^{7}/\text{Li}^{6}]_{\text{SVEC standard}}} \times 1000$$

relative to NIST SRM 8545 (L-SVEC standard; 7Li/6Li = 12.173; Li carbonate; Flesch et al., 1973). Repeated analyses of the NIST 610 standard yielded an analytical precision of <1‰ at the 2SE level (Supplementary Table S3; available online from https://doi.org/10.2465/jmps.200721). Our results for various rock and mineral standards fall within the ranges of previously published values (Kimura et al., 2016). The Li isotopic compositions were determined nearby or at the same sites as the LA-ICP-MS (iCAP-Qc) analyses.

To cross-check the data obtained by LA-MC-ICP-MS, we also conducted solution-based Li isotope analyses, using a micro-milling (MM) device (Geomill326; pit size = 120 µm) and a MC-ICP-MS (Thermo Fisher Scientific NEPTUNE) at the Kochi Institute for Core Sample Research, JAMSTEC, Kochi, Japan. Sample powders containing 2-20 ng Li were collected by MM and digested with HF-HNO₃. Lithium in the sample was then chemically separated with a two-step cation exchange procedure (Nishio et al., 2010, 2015). δ⁷Li values of the samples were obtained by a standard-sample bracketing technique using the NIST SRM 8545 standard. Typically within-run analytical precision was ±0.1‰ (2SE), and the reproducibility was ±0.3‰ (2SD).

RESULTS

Na distribution in murakamiite (or Li-rich pectolite) crystal

The backscattered electron (BSE) image of murakamiite (or pectolite) examined X-ray intensity of Na is shown in Figure 6a. The X-ray intensity map of Na in murakamiite (or pectolite) (monomineralic aggregate of two grains) is
shown in Figure 6b. The murakamiite (or pectolite) grains display a variation of Na intensity distribution, indicating various Li ↔ Na substitution within a single grain crystal. The murakamiite has a perfect {100} and {001} cleavage (Imaoka et al., 2017), and the cleavage fractures, i.e., the brittle fractures by separation across well-defined crystallographic planes, are well-developed (Fig. 6a). The Na intensity line profiles of murakamiite were examined for two different directions, i.e., along A–B (parallel to the cleavage; murakamiite–1) and C–D–E lines (across the cleavage; murakamiite–1 and –2) (Fig. 6a). The profile parallel to the cleavage shows a clear zoning structure in which Na content decreases from core to rim (A–B line). Across-the-cleavage profile (C–D–E line) also show Na content roughly decreasing from core to rim, although the variations are somewhat irregular especially in murakamiite–2, with abundant cleavage fractures reflecting that the mineral is brittle with a splintery fracture (Fig. 6c).

**Whole-rock major and trace elements in albite and granite**

The whole-rock major and trace element compositions of the murakamiite-bearing albite (IWG–168) and host coarse-grained biotite granite (T–69) are listed in Table 1 and plotted on a multi-element diagram normalized to upper continental crust in Figure 7. The host granite has a relatively evolved composition with high SiO$_2$ (78.66 wt%), K$_2$O/Na$_2$O > 1, and low MgO (0.03 wt%) and TiO$_2$ (0.048 wt%). The murakamiite-bearing albite and the host granite show similar concentrations of Ti, P, Ga, Sr, Y, Zr, Hf, heavy REEs (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Th, and U. However, the albite is enriched in Al, Fe, Mn, Mg, Ca, Na, Li, Cr, Zn, and Nb and depleted in Si, K, Rb, Sn, Cs, Ba, light REEs, and Tl relative to the host granite.

The chondrite-normalized REE patterns of the murakamiite-bearing albite and host granite are shown in Figure 8. Both rocks exhibit relatively flat REE patterns with similar, large negative Eu anomalies (Eu/Eu$^*$ = 0.121 for albite; Eu/Eu$^*$ = 0.126 for host granite). (La/Yb)$_N$ and (Dy/Yb)$_N$ ratios are 1.55 and 0.97 for albite, and 0.868 and 0.896 for granite, respectively.

**Figure 6.** (a) Backscattered electron (BSE) image of two murakamiite or pectolite grains and other phases indicated by the rectangle in Figure 4a together with the analytical area and line profiles shown in (b) and (c). Mur, murakamiite or pectolite; Ab, albite; Agt, aegirine-augite; Sug, altered sugilite; P, pore. (b) X-ray intensity map (Na-K$\alpha$) for the murakamiite grain indicated by the rectangle in (a). The map shows a spatial variations of Na distribution, which also indirectly indicates a spatial variation of Li within the grain due to Li ↔ Na substitutions. (c) Na intensity profiles of murakamiite along A–B and C–D–E lines of (a), f, cleavage fracture.
Major and trace elements in murakamiite and Li-rich pectolite

The analyses of 16 representative grains obtained by LA-ICP-MS on murakamiite and Li-rich pectolite are listed in Table 2. The murakamiites analyzed in this study have Li × 100/(Li + Na) atomic ratios ranging from 50.6 to 60.1 (Table 2). These murakamiites are associated with and coherently intergrown with Li-rich pectolites that have Li × 100/(Li + Na) ratios of 44.2 to 49.5. Figure 9 shows the relationship between Na and Li in atoms per formula unit (apfu) calculated on the basis of nine atoms of oxygen for murakamiite and Li-rich pectolite. The Na and Li of the murakamiites and Li-rich pectolites plot on an ideal line of Na + Li = 1.0, thus indicating a simple Na ↔ Li substitution at M3 site in this solid solution.

In addition to the inter-grain compositional variations described above, variations in Li2O contents within a single grain were observed in the LA-ICP-MS analyses (Table 3). Nine of the 49 grains showed variations within an individual grain of up to 0.36 wt% (grain no. 26), which exceeds the analytical error. This is consistent with the presence of compositional zoning of Na in murakamiite observed by EPMA (Fig. 6).

δ7Li values of murakamiite and Li-rich pectolite

δ7Li values of the murakamiites and Li-rich pectolites are given in Table 3 and Figure 10. The accuracy of the LA-MC-ICP-MS analyses was verified by comparing with the MM-MC-ICP-MS analyses. The milling position of 83-a_MM in grain no. 83 was close to spot 83-4 of the LA-MC-ICP-MS analyses (Supplementary Fig. S1; available online from https://doi.org/10.2465/jmps.200721.). δ7Li values obtained by the two methods agree with each other within the analytical uncertainty: −7.1 ± 1.5‰ by LA-MC-ICP-MS versus −6.56 ± 0.30‰ by MM-MC-ICP-MS. The data for grain no. 15 (−5.1 ± 1.3‰ versus −5.85 ± 0.30‰) are also the same within analytical error. However, the values obtained by LA-MC-ICP-MS and MM-MC-ICP-MS are distinct for grain no. 1 (−2.4 ± 1.2‰ versus −4.97 ± 0.30‰) and no. 62 (−2.0 ± 1.0‰ versus −4.71 ± 0.30‰) exceeding analytical errors (Table 3), suggesting Li isotope heterogeneity within a single crystal.

In fact, for 10 of the 49 analyzed grains, large variations within an individual grain were observed by LA-MC-ICP-MS, which reaches 6.4‰ in grain no. 24 (i.e.,
−9.1 ± 1.8‰ to −2.7 ± 1.4‰; Table 3). Thus, in situ LA−MC−ICP−MS analyses revealed significant δ⁷Li heterogeneity at sub−millimeter–scale within a single crystal. In total, 49 grains of murakamiite and Li−rich pectolites from a single albitite sample IWG−168 show a very wide range of δ⁷Li values from −9.1 to +0.4‰ (average −2.9‰). No obvious correlation was observed between δ⁷Li values and Li contents, and no significant difference was observed between δ⁷Li values of murakamiite and Li−rich pectolite (Fig. 10).

**DISCUSSION**

**Crystal structure control on element partitioning into murakamiite and Li−rich pectolite**

Chemical compositions of murakamiite and Li−rich pectolite are plotted on a multi−element diagram normalized to the whole−rock composition of the murakamiite−bearing albitite in Figure 11. No significant compositional difference is observed between murakamiite and Li−rich pectolite there, but both minerals are characterized by marked enrichments in Mn, Ca, Li, Sr, and REEs (Y and La−Lu) roughly on the same order of magnitude (~ 10 times) relative to the whole−rock albitite composition. This suggests selective uptake of these elements into murakamiite−pectolite during the metasomatism to form Li−rich albitite. It is noteworthy that large negative Eu anomaly found in Figure 8 disappears here, showing the normalized Eu value consistent with those of Sm and Gd.

To examine the effects from ionic radius, average values of element concentrations in murakamiite and Li−rich pectolite normalized to albitite plot against ionic radii of Shannon (1976) in Figure 12. Here we used ionic radii for 6−coordination alone for all monovalent, divalent and trivalent cations, considering the expected coor−

| Mineral     | Analysis spot | Li-rich pectolite | Murakamiite |
|-------------|---------------|-------------------|-------------|
| SiO₂ (wt%)  | 75 67 16 M7−1 5M−1 22 | 55.37 55.61 55.30 55.52 55.54 55.31 55.53 55.46 55.29 55.70 |
| TiO₂        | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 |
| Al₂O₃       | 0.00 0.00 0.00 0.07 0.10 0.00 0.00 0.00 0.00 0.00 |
| FeO         | 0.29 0.31 0.31 0.35 0.33 0.32 0.37 0.36 0.33 0.35 |
| MnO         | 0.79 0.81 0.82 0.72 0.78 0.75 0.82 0.77 0.77 0.79 0.82 0.78 0.82 |
| MgO         | 0.02 0.03 0.03 0.10 0.10 0.04 0.04 0.04 0.04 0.03 0.04 0.02 0.03 0.04 |
| CaO         | 34.10 33.68 33.56 33.72 33.08 33.76 33.58 33.45 33.96 33.76 33.84 34.13 33.82 33.85 34.10 33.74 |
| Na₂O        | 5.20 5.09 5.05 4.94 4.91 4.75 4.70 4.59 4.40 4.35 4.20 4.18 4.13 3.98 3.92 3.78 |
| K₂O         | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 |
| Li₂O        | 1.98 2.07 2.12 2.12 2.24 2.25 2.32 2.38 2.38 2.43 2.47 2.49 2.55 2.65 2.72 2.74 |
| H₂O²        | 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 2.80 |
| O=          | 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 |
| Si          | 2.981 2.995 2.977 2.990 3.006 2.995 2.996 3.003 2.992 2.999 2.998 2.996 2.992 2.985 2.999 |
| Ti          | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 |
| Al          | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 |
| Fe²⁺        | 0.03 0.04 0.04 0.03 0.04 0.03 0.04 0.04 0.04 0.03 0.04 0.04 0.03 0.04 0.03 0.04 |
| Mn²⁺        | 0.03 0.03 0.03 0.03 0.06 0.03 0.33 0.33 0.36 0.03 0.38 0.35 0.35 0.35 0.36 0.36 0.36 0.38 |
| Mg          | 0.00 0.02 0.03 0.03 0.08 0.08 0.03 0.03 0.03 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.03 0.03 |
| Ca          | 1.987 1.957 1.949 1.959 1.914 1.958 1.946 1.935 1.968 1.954 1.957 1.977 1.956 1.957 1.972 1.946 |
| Na          | 0.548 0.535 0.530 0.520 0.515 0.499 0.493 0.481 0.461 0.455 0.439 0.438 0.432 0.416 0.410 0.395 |
| K           | 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 |
| Li          | 0.433 0.452 0.462 0.463 0.487 0.489 0.505 0.517 0.518 0.527 0.535 0.542 0.554 0.574 0.590 0.594 |
| H           | 1.016 1.013 1.012 1.012 1.009 1.011 1.011 1.009 1.010 1.009 1.008 1.009 1.008 1.008 1.006 1.006 |
| Sum         | 7.017 7.005 7.005 7.005 6.996 7.004 7.008 6.999 7.003 6.996 6.993 7.006 7.000 7.006 7.006 7.002 6.998 |

Li × 100/(Li+Na) 44.2 45.8 46.6 47.1 48.6 49.5 50.6 51.8 52.9 53.7 54.9 55.3 56.2 58.0 59.0 60.1

* Determined by TG-DTA analysis. Data was measured using mixture of murakamiite (about 71 vol%) and pectolite (about 29 vol%) (Imaoka et al., 2017)
dination in the crystal structure of murakamiite–pectolite. In this diagram, monovalent, divalent and trivalent cations all draw separate, systematic convex parabolic curves with maxima at around Li$^+$, Mn$^{2+}$–Ca$^{2+}$ and Y$^{3+}$–Ho$^{3+}$ (Fig. 12). These regularities of the curves indicate that the ionic size is a major factor controlling the murakamiite (or pectolite)/albitite ratio of an element. This diagram looks like a PC–IR diagram (e.g., Matsui et al., 1977; Wood and Blundy, 2014), in which partition coefficients of elements between mineral and melt plot against ionic radii of elements, and crystal structure control of the partition coefficient appears there. In our Figure 12, murakamiite/albitite element ratio is used instead of mineral/melt partition coefficient in PC–IR diagram. Assuming that the whole–rock composition of the albitite represents the element resource available for metasomatism to form murakamiite and other minerals, and that the elements are redistributed in equilibrium among the coexisting minerals through the interaction with metasomatic fluid, the murakamiite/albitite element ratio can be regarded as an analogue of murakamiite/albititic fluid partition coefficient of the element. If this is the case, Figure 12 exhibits the characteristics of element partitioning in murakamiite–pectolite during metasomatism, largely controlled by its crystallographic property.

In the detailed view, it is possible to draw a monovalent curve passing through the plots from Li$^+$ through Na$^+$ to Rb$^+$. The Li$^+$ ↔ Na$^+$ substitutions are valid between the murakamiite and pectolite as described above. The curve indicates that Rb$^+$ (1.52 Å) is too large to re-

| Mineral | Li-rich pectolite | Murakamiite |
|---------|-------------------|-------------|
| Sc (ppm) | 5.6–6.5 | 9.0–9.0 |
| V | n.d.–6.5 | n.d.–9.0 |
| Cr | n.d.–3.3 | 0.39–0.4 |
| Co | n.d.–0.4 | 0.4–0.4 |
| Ni | 0.1–1 | 0.5–n.d. |
| Cu | n.d.–2 | 0.23–n.d. |
| Zn | 7.2–6.8 | 10.7–32.3 |
| Ga | 0.9–1.4 | 1.7–1.3 |
| Rb | 0.28–0.24 | 0.14–0.08 |
| Sr | 352–376 | 380–407 |
| Y | 1240–1330 | 1295–1510 |
| Zr | 2.58–2.40 | 3.59–2.38 |
| Nb | n.d.–0.3 | 0.12–0.05 |
| Cs | n.d.–0.1 | 0.01–0.00 |
| Ba | 0.15–0.01 | 0.74–0.14 |
| La | 39.8–44.1 | 60.3–52.9 |
| Ce | 174–190 | 285–211 |
| Pr | 26.7–32.8 | 47.0–32.7 |
| Nd | 146–174 | 233–162 |
| Sm | 72.4–83.4 | 93.4–71.6 |
| Eu | 3.06–3.82 | 4.29–2.95 |
| Gd | 118–136 | 144–118 |
| Tb | 25.9–30.0 | 28.0–24.8 |
| Dy | 197–220 | 215–194 |
| Ho | 46.4–49.6 | 49.3–44.0 |
| Er | 135–155 | 138–125 |
| Tm | 21.5–22.6 | 22.0–19.7 |
| Yb | 145–151 | 138–125 |
| Lu | 20.5–21.3 | 17.8–16.2 |
| Hf | 0.47–0.31 | 0.36–0.35 |
| Ta | 0.07–0.08 | 0.08–0.07 |
| W | 0.25–0.45 | 0.42–0.31 |
| Pb | 0.16–0.65 | 0.55–1.43 |
| Th | 0.09–0.15 | 0.07–0.67 |
| U | 1.17–0.71 | 1.62–1.19 |

n.d., not detected.

Table 2. (Continued)
suggests that divalent cations such as Mg$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, and Sr$^{2+}$ sub-
stitution in murakamiiite. On the other hand, Figure 12 shows the chemical characteristics re-
lated to pectolite solid solution on a Na$^+$ versus Li$^+$ diagram (atomic proportions) showing the ideal straight-line substitution vector.



\textbf{Figure 9.} Chemical compositions of the murakamiite-Li-rich pecto-
lite solid solution on a Na$^+$ versus Li$^+$ diagram (atomic proportions) showing the ideal straight-line substitution vector.

place Na$^+$, but the substitution of smaller Li$^+$ (0.76 Å) for Na$^+$ is preferable in murakamiite/pectolite structure. But Li$^+$ cannot locate at exactly the same position of Na$^+$ in the large polyhedra due to smaller ionic radius (Naga-
shima et al., 2018). The ionic radius of Li$^+$ of 0.76 Å is smaller than that of Na$^+$ (1.02 Å), and it therefore prefers a position in a smaller coordinated polyhedron within the large eight-coordinated polyhedron (Nagashima et al., 2018).

Divalent cations also show a roughly smooth convex parabolic curve passing through Mn$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Ni$^{2+}$ on the left side and Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ on the right side, with a maximum around Mn$^{2+}$ and Ca$^{2+}$. The murakamiite structure provides two cation positions, namely the M1 and M2 positions. It is established that Ca$^{2+}$ ions prefer the M1 position whereas Mn$^{2+}$ ions prefer the M2 position (Nagashima et al., 2018). It is likely to be the reason why Mn$^{2+}$ and Ca$^{2+}$ show similarly high murakamiite/albitite ratios, and thus the curve for divalent cations may have two maxima at Mn$^{2+}$ and Ca$^{2+}$. The Ca$^{2+}$ ↔ Mn$^{2+}$ substitutions are common in hydrous pyroxenoids, and the substitutions occur between the murakamiite Li$_3$Ca$_2$Si$_3$O$_9$(OH) and tanoahaitiite LiMn$_2$ Si$_3$O$_9$(OH) (Nagase et al., 2012) as well as among the pectolite Na$_3$CaY$_2$Si$_3$O$_9$H and schizolite NaCaMnSi$_3$O$_8$(OH) (the same mineral species to the ‘marshallsussmanite’; Grice et al., 2019), and serandite NaMn$_2$Si$_3$O$_8$(OH) (Fig. 13). A relatively high murakamiite/albitite ratio ob-
served for Sr$^{2+}$ suggests the favorable Ca$^{2+}$ ↔ Sr$^{2+}$ sub-
stitution in murakamiite. On the other hand, Figure 12 suggests that divalent cations such as Mg$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Ni$^{2+}$ ions are too small (0.69–0.78 Å), and Ba$^{2+}$ is too large (1.35 Å) to be accommodated to the crystal structure of murakamiite favorably.

The trivalent cations also show a roughly smooth convex parabolic curve passing through heavy REEs$^{3+}$, Sc$^{3+}$, Ga$^{3+}$, Cr$^{3+}$, and Al$^{3+}$ on the left side and middle REEs$^{3+}$ and light REEs$^{3+}$ on the right side, with a max-
imum at Y$^{3+}$ and Ho$^{3+}$. The trivalent curve runs sub-
parallel to the divalent curve on the left side. The maximum at Y$^{3+}$ and Ho$^{3+}$ indicates that about 0.90 Å is the most favorable ionic radius for the crystallographic position among the trivalent cations in murakamiite. Trivalent cat-
ions incorporated into divalent cation sites require coupled substitution for keeping charge balance. Although currently we have no direct evidence for the presence of trivalent cations in the murakamiite structure, the het-
erovalent (coupled) substitution, such as NaYCa$_2$ is the-
oretically possible among the M1, M2, and M3 positions in murakamiite. Indeed, in the newly-found barrydaw-
somite-(Y), Na$_{0.5}$Ca$_{1.5}$Y$_{0.5}$Si$_3$O$_9$H is related to pectolite by a heterovalent coupled substitution: Na$_2$Si$_2$O$_5$H + ½[NaYCa$_2$] = Na$_{0.5}$Ca$_{1.5}$Y$_{0.5}$Si$_3$O$_9$H, which is the first hy-
dropyroxenoids with stoichiometric trivalent species of REEs (Mitchell et al., 2015).

In summary, it is suggested that murakamiite-pecto-
lite in Figure 12 shows the chemical characteristics re-
flecting the major substitution schemes of hydrous pyrox-
enoids. This implies that murakamiite-pectolite was crys-
tallized in quasi-equilibrium with the bulk albitite com-
position, and that the element re-distribution via fluid took place extensively during metasomatism to form al-
bite. Thus, it can be concluded that the minor and trace element compositions of murakamiite and Li-rich pecto-
lite were generated through quasi-equilibration with flu-
ids and coexisting minerals such as albite and sugilite under a strong control of crystal structure.

**Origin of Li isotope variation in murakamiite and Li-rich pectolite**

The murakamiite and Li-rich pectolite grains from a single albitite sample IWG-168 show a very wide range of $\delta^{7}\text{Li}$ values from −9.1 to +0.4‰, and also show large intra-
crystal $\delta^{7}\text{Li}$ variations up 6.4‰. In general, large Li iso-
topic fractionations occur in relatively low- to moderate-
temperature environments, including weathering (e.g., Pistiner and Henderson, 2003; Rudnick et al., 2004b; Ushikubo et al., 2008) and hydrothermal alteration (e.g., Chan et al., 2002; Bouman et al., 2004; Wunder et al., 2007). In contrast, little Li isotopic fractionation occurs during high-temperature (>800 °C) igneous differentiation (e.g., Tomascak et al., 1999, 2016; Teng et al., 2004).
Table 3. Li concentrations and isotope ratios of the Li-rich pectolites and murakamiites from Iwagi Islet

| Analyzed grain-spot | Li$_2$O (wt%) ± 1SE | $\delta^7$Li (%) ± 2SE | Analyzed grain-spot | Li$_2$O (wt%) ± 1SE | $\delta^7$Li (%) ± 2SE |
|---------------------|---------------------|------------------------|---------------------|---------------------|------------------------|
| LA–ICP–MS           |                     |                        | MM–MC–ICP–MS with chemical separation |                     |                        |
| 01-1                | 2.49 0.04           | -2.4 1.2               | 01-1                | 2.35 0.03           | -4.8 1.3               |
| 01-2                | n.d.                | -1.1 1.4               | 03-1                | 2.35 0.03           | -5.9 1.4               |
| 05-1                | 2.55 0.04           | -2.0 1.0               | 03-2                | n.d.                | -4.6 1.3               |
| 06-1                | 2.33 0.03           | -0.4 1.4               | 03-3                | n.d.                | -7.1 1.5               |
| 06-2                | n.d.                | -1.0 1.2               | 03-4                | n.d.                | -4.7 1.6               |
| 08-1                | 2.16 0.03           | -3.0 1.4               | 03-5                | n.d.                | -4.3 1.0               |
| 08-2                | n.d.                | -5.4 1.5               | 89-1                | 2.87 0.04           | -5.7 1.4               |
| 15-1                | 2.32 0.03           | -5.1 1.3               | 92-1                | 2.79 0.04           | -2.1 1.4               |
| 16-1                | 2.12 0.03           | -2.7 1.1               | 92-2                | 2.76 0.04           | -0.4 1.4               |
| 17-1                | 2.71 0.04           | -4.0 1.0               | 94-1                | n.d.                | -5.1 1.0               |
| 20-1                | 2.10 0.03           | -6.1 1.2               | 94-2                | 2.04 0.03           | -5.1 1.1               |
| 20-2                | n.d.                | -1.1 1.3               | 99-1                | 2.44 0.04           | -1.5 1.4               |
| 24-1                | 2.43 0.04           | -9.1 1.8               | 100-1               | 2.08 0.03           | -1.1 1.3               |
| 24-2                | n.d.                | -2.7 1.4               | 100-2               | n.d.                | -0.7 1.4               |
| 26-1                | 2.45 0.04           | -6.7 2.8               | 100-3               | n.d.                | -1.8 1.5               |
| 26-2                | 2.81 0.04           | -8.7 2.5               | 100-4               | n.d.                | -1.4 1.4               |
| 26-3                | 2.58 0.04           | -3.5 1.4               | 100-5               | n.d.                | -1.8 1.4               |
| 26-4                | n.d.                | -2.6 1.9               | 101-1               | 2.17 0.03           | -3.1 1.3               |
| 26-5                | 2.48 0.04           | -3.6 1.8               | 101-2               | n.d.                | -1.4 1.4               |
| 30-1                | 2.85 0.04           | -6.2 1.9               | 102-1               | 2.76 0.04           | -4.1 1.5               |
| 30-2                | 2.76 0.04           | -0.7 1.3               | 102-2               | n.d.                | -1.6 1.5               |
| 31-1                | 2.21 0.03           | -6.6 1.8               | 102-3               | n.d.                | -2.7 1.4               |
| 31-2                | n.d.                | -1.9 1.4               | 102-4               | n.d.                | -4.1 1.4               |
| 33-1                | 2.04 0.03           | -2.7 1.3               | 103-1               | 2.35 0.03           | -3.0 1.5               |
| 34-1                | 2.69 0.04           | -1.5 1.2               | 103-2               | n.d.                | -1.7 1.4               |
| 34-2                | 2.76 0.04           | -3.5 1.8               | 104-1               | n.d.                | -2.8 1.4               |
| 38-1                | 2.65 0.04           | -2.5 1.2               | 104-4               | n.d.                | -2.9 1.1               |
| 41-1                | 2.44 0.04           | -3.6 1.1               | 105-1               | 2.35 0.03           | -4.7 1.1               |
| 41-2                | n.d.                | 0.1 1.2                | 105-2               | 2.25 0.03           | -1.3 1.3               |
| 49-1                | 2.18 0.03           | -0.7 1.0               | 106-1               | n.d.                | -2.0 1.4               |
| 50-1                | 2.62 0.04           | -2.4 1.1               | 106-2               | n.d.                | -0.6 1.5               |
| 52-1                | 2.35 0.03           | -2.0 1.0               | 107-1               | 2.64 0.04           | -2.2 1.2               |
| 52-2                | n.d.                | -1.2 1.4               | 107-2               | n.d.                | -1.4 1.4               |
| 53-1                | 2.40 0.04           | -5.0 0.9               | 108-1               | 2.33 0.03           | -2.6 1.5               |
| 53-2                | 2.33 0.03           | -3.7 1.1               | 108-2               | 2.40 0.04           | -4.3 1.6               |
| 53-3                | 2.37 0.04           | -2.6 1.2               | 109-1               | 2.19 0.03           | -0.3 1.3               |
| 54-1                | 2.47 0.04           | -1.1 1.1               | 109-2               | n.d.                | 0.2 1.2                |
| 54-2                | 2.34 0.03           | -1.0 1.2               | 111-1               | n.d.                | -1.7 1.1               |
| 55-1                | 2.35 0.03           | -3.6 1.3               | 111-2               | n.d.                | -1.0 1.0               |
| 55-2                | n.d.                | -3.5 1.1               | 113-1               | 2.19 0.03           | -0.3 1.1               |
| 62-1                | n.d.                | -2.0 1.0               | 113-2               | 2.39 0.04           | -1.6 1.2               |
| 64-1                | 2.20 0.03           | -4.0 1.0               | 117-1               | 2.08 0.03           | -0.5 1.1               |
| 64-2                | 2.21 0.03           | -4.9 1.2               | 117-2               | 2.19 0.03           | -0.3 1.2               |
| 65-1                | 2.51 0.04           | -2.6 1.1               | 118-1               | 2.00 0.03           | -3.4 1.3               |
| 65-2                | 2.22 0.03           | -2.5 1.2               | 01-a_MM             | 2.49                | -4.97 0.30             |
| 66-1                | 2.16 0.03           | -1.5 1.1               | 15-a_MM             | 2.32                | -5.85 0.30             |
| 66-2                | n.d.                | -0.5 1.1               | 39-a_MM             | 2.43                | -3.72 0.30             |
| 69-1                | 2.41 0.04           | -1.2 1.0               | 62-a_MM             | 2.17                | -4.71 0.30             |
| 69-2                | 2.60 0.04           | -2.2 1.1               | 83-a_MM             | 2.35                | -6.56 0.30             |
| 70-1                | 2.41 0.04           | -2.7 1.1               | 85-a_MM             | 2.43                | -4.35 0.30             |
To evaluate the processes to cause the \( \delta^7\text{Li} \) characteristics observed for murakamiite and Li–rich pectolite, we consider the following three constraints. (1) Only low–to moderate–temperature processes can fractionate Li isotopes sufficiently to generate materials with \( \delta^7\text{Li} < 0\% \) (e.g., Tomascak et al., 1999; Rudnick et al., 2004a, 2004b; Teng et al., 2004). (2) Thermogravimetric analysis of murakamiite and Li–rich pectolite revealed that the weight loss begins at 710 and 630 °C, respectively, and completes at 730 °C (Yagi et al., 1968; Imaoka et al., 2017). Pectolite–bearing assemblages can form at temperatures of 300 ± 50 °C and pressure of 300 bars (Karup–Møller, 1969). The lowest temperature under which aegirine is stable, is reported to be 300 °C at 1 kbar (Redhammer et al., 2000). Pressure–temperature estimates for the Wessels mine where sugilite occurs are 270–420 °C at 0.2–1.0 kbar (Dixon, 1989). Thus, murakamiite and Li–rich pectolite coexistent with aegirine and sugilite is inferred to have formed at 300–600 °C. (3) The texture of albittes (Figs. 3 and 5) indicates that murakamiite and Li–rich pectolite are products of metasomatism. Based on these lines of evidence, we infer that the large Li iso-
tago fractionation should be attributed to metasomatic hydrothermal fluid–rock interactions at 300–600 °C.

Experimentally determined Li isotopic fractionation between clinopyroxene and aqueous fluids (Wunder et al., 2006) predicts that the solid phase has 5.6 and 2.8‰ lighter δ7Li values than the coexisting fluid at 300 and 600 °C, respectively. Assuming these Li isotope fractionations are valid for the murakamiite (pectolite)–fluid system, the δ7Li values of the fluids equilibrated with the above murakamiite–pectolite crystals (−9.1 to +0.4‰) are estimated to be −3.5 to +6.0‰ at 300 °C and −6.3 to +3.2‰ at 600 °C. Thus, the large δ7Li variation observed in murakamiite–pectolite can result from (1) initial δ7Li variation in parental fluids, (2) crystallization of minerals at varied temperatures, and (3) contribution of variably evolved fluids with elevated δ7Li produced through successive precipitation of minerals having lower δ7Li values. In either case, involvement of fluids with δ7Li value as low as −6.3 to −3.5‰ is required to fully explain the δ7Li values of murakamiite–pectolite. However, few marine and continental hydrothermal fluids and groundwaters with δ7Li < 0‰ have been reported (Tomascak et al., 2016). One explanation is that the very low δ7Li values observed in murakamiite–pectolite (down to −9.1‰) originated from diffusion–induced Li isotope fractionation in sub–millimeter to millimeter scale (e.g., Richter et al., 2003, 2014; Lundstrom et al., 2005), not from equilibration processes. Considering the large intra–grain δ7Li variation observed in murakamiite–pectolite (e.g. −9.1 to −2.7‰ in grain no. 24), this scenario cannot be ruled out.

Alternatively, it is possible that the fluids with exceptionally low δ7Li values were involved in the genesis of murakamiite–pectolite. The δ7Li values for some of the deep crustal fluids below the Ontake volcano, Central Japan, are reported to be as low as −5 to +2‰ (Nishio et al., 2010), and thus fulfill the requirement for parental fluids of murakamiite–pectolite. Interestingly, these deep crustal fluids show significant Li enrichment, with high Li/Na ratios up to 2.0 × 10⁻³ (cf. 1.5 × 10⁻⁵ in seawater). These Li/Na ratios are apparently consistent with the values for the Arima–type deep–seated brines (2.6 × 10⁻³ in Arima and 7.3 × 10⁻³ in Kashiio: Kusuda et al., 2014; Ishikawa et al., 2014) and also comparable to that for the murakamiite–bearing albite (6.4 × 10⁻³). The Arima–type fluids are suggested to have been derived from dehydration of subducted oceanic slab (Kusuda et al., 2014). Thus, highly Li–Na enriched, low–δ7Li subduction–zone fluids might migrate upward along the shear zone after the emplacement of granite to generate the Li–Na metasomatism that formed the zoned albrite containing murakamiite–pectolite. Clear strain–induced textures exhibited by albite (Fig. 5), aegirine–augite, and katayamalite are the products of dynamic recrystallization. Deformation–induced fracturing of the rock could have facilitated fluid circulation, and the occurrence of the metasomatic rocks along the E–W–trending lineament (Fig. 1) suggests this was the locus for large–scale fluid movement in the crust. This resulted in mass transfer and associated formation of a metasomatic mineral assemblage. Further research is required to constrain the origin and nature of the Li–bearing minerals and their parental Na–Li–rich fluids associated with metasomatism of the Iwagi Islet granites.

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SUPPLEMENTARY MATERIALS

Supplementary Tables S1–S3 and Supplementary Figure S1 are available online from https://doi.org/10.2465/ jmps.200721.

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