Dalyite $(K_2ZrSi_6O_{15})$ and Zektzerite $(LiNaZrSi_6O_{15})$ in Aegirine-bearing Albitite from Iwagi Islet, SW Japan

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Abstract

The rare potassium zirconium silicate dalyite and lithium sodium zirconium silicate zektzerite have been found in Cretaceous aegirine albitite from Iwagi Islet, Southwest Japan. Electron microprobe analyses of the dalyite and zektzerite yielded the following empirical formulas based on 15 oxygens: $(K_{1.93}Ba_{0.01})_{\Sigma 1.94}(Zr_{0.99}Hf_{0.02})_{\Sigma 1.01}Si_{5.98}O_{15}$ and $Na_{1.03}(Zr_{0.96}Hf_{0.02}Y_{0.01}Sc_{0.01})_{\Sigma 1.00}Li_{1.02}(Si_{5.95}Al_{0.04})_{\Sigma 5.99}O_{15}$, respectively. The occurrence of porous zircon, dalyite, and mantles of zektzerite on resorbed zircon in the albitite suggests that those zirconosilicate minerals are the products of metasomatic mineral replacement reactions by Na-, K-, and Li-rich hydrothermal fluids. This is the first documented occurrence of dalyite and zektzerite in the Japanese Islands.

Key words: dalyite, zektzerite, albitite, Li-metasomatism, Iwagi Islet

I. Introduction

Dalyite, K₂ZrSi₆O₁₅, was first discovered in peralkaline granite xenolith from Ascension Island (Van Tassel, 1952). Since then, it has been reported as an accessory mineral in a variety of peralkaline silica-oversaturated rocks, including peralkaline granites, syenites, pegmatites, charoitites, lamproites, lamprophyres, fenites, and carbonatites (see Jeffery *et al.*, 2016 and references therein). It is often associated with chevkinite-(Ce), aegirine, quartz, and britholite.

Zektzerite, LiNa (Zr,Ti,Hf) $\mathrm{Si_6O_{15}}$, is a very rare mineral that occurs in peralkaline granites and syenites in association with arfvedsonite, ferrorichterite, astrophyllite, okanoganite, elpidite, aegirine, riebeckite, pyrochlore, sogdianite, and zircon. It was first found in miarolitic cavities in the agpaitic granite of the Golden Horn batholith, Washington (Dunn *et al.*, 1977).

It also occurs in a block of peralkaline pegmatite in the moraine of the Dara-i-Pioz glacier, northern Tajikistan (Grew *et al.*, 1993), in the fluorite-bearing biotite syenogranite of the Cretaceous Del Salto pluton in the Patagonian batholith, Aysén Province, Chile (Welkner *et al.*, 2002), in the nepheline syenite pegmatite at Virikkollen, Haneholmveien, and Sandefjord in Norway, as euhedral crystals at Ampasibitika on the Ampasindava Peninsula, Madagascar, and as gemmy crystals up to 3 cm across at Mt Malosa in Malawi¹⁾.

The peculiar metasomatic rocks (albitites) on Iwagi Islet (34°15′47″N, 133°9′39″E), Ehime Prefecture, Japan, have been studied by Sugi and Kutsuna (1944), Taneda (1950, 1952), and Murakami and Matsunaga (1966). They contain rare (unusual) Li-rich silicates, including katayamalite (KLi₃Ca₇Ti₂(SiO₃)₁₂(OH)₂; Murakami *et al.*, 1983; Andrade *et al.*, 2013), sugilite (Na₂K(Fe³⁺,Mn³⁺,Al)₂Li₃Si₁₂O₃₀; Kato *et al.*,

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1976; Murakami *et al.*, 1976; Armbruster and Oberhänsli, 1988), and murakamiite (Lianalogue of pectolite, LiCa₂Si₃O₈(OH); Imaoka *et al.*, 2017), and their mineralogical diversity is unique. During our chemical and mineralogical studies of the albitites from Iwagi Islet, we found the rare Zr-bearing minerals dalyite and zektzerite. In this paper, we will describe the occurrence and chemical compositions of these minerals and discuss their metasomatic formation.

II. Geological setting

Small bodies of metasomatites are distributed in the Setouchi area, SW Japan (Fig. 1a). They are known from seventeen areas and occur in the granitoids of the Cretaceous Ryoke and San-yo belts. The modes of occurrence, petrography, and major element chemistry of some of these metasomatites have been described by Murakami (1976 and references therein), Murakami and Matsunaga (1966), and Minakawa et al. (1978). According to Murakami (1976), the metasomatites commonly form small bodies less than 100 m across that are pipe-like, irregular sheets, or ovoid in shape.

The geology of Iwagi Islet and its peculiar albitites has recently been described in detail by Imaoka et al. (2021). Thus, only an outline of the geology of the islet is provided in this paper. The Ryoke metamorphic rocks, made up of schistose hornfelses derived from slates and sandstones, are the oldest rocks on the islet. These occur in the central summit area of the islet, and in the southwestern coastal area. Granitoids intrude the Ryoke rocks and are distributed extensively throughout the islet. They can be divided into three types, coarse-, medium-, and fine-grained biotite granite, in order of emplacement (Fig. 1b). The coarsegrained biotite granite occurs in the eastern and northern parts of the islet as sheets in the topographically lower part of the mediumgrained granite, and the sheets are accompanied by pockets or dikes of aplite and pegmatite. The fine-grained granite forms a sheet in the upper part of the medium-grained granite around Mt Sekizen-san. Dikes of granophyre, diorite porphyry, and granite porphyry cut these granites.

The albitites occur as many small discrete masses in the coarse-grained biotite granite around the summit of Mt Kuresaka in the eastern part of the islet (Fig. 1c). The largest body of albitite is several tens of meters in diameter, and small albitite bodies, up to several tens of centimeters to meters wide are generally oriented more-or-less N-S, and irregularly distributed over an area of $1.5 \times 0.8 \; \mathrm{km^2}$. The relationships between the albitites and the surrounding coarse-grained granite are transitional, so that albitized granite and quartz albitite can be found between them. No intrusive contact was found between them.

III. Petrography

Sample IWG-23, a dalyite-zektzerite-bearing albitite, was collected from the top of Mount Kuresaka at the eastern end of Iwagi Islet. Albite is the dominant mineral in the albitite, and white to transparent albite and black aegirine are visible to the naked eye. The minerals present include albite (99.7%), alkali-feldspar (0.2%), quartz (0.1%), and agairine (<0.1%). The albite (0.2-6 mm) is subhedral-anhedral, and it forms aggregates of numerous, small, granular crystals at the boundaries of large, broken, and deformed albite grains. Magmatic quartz shows variable degree of dissolution and changed to secondary opal (SiO2·nH2O) (Imaoka et al., 2021), which is termed "dequartzification" (e.g., Cathelineau, 1986; Boulvais et al., 2007; Nishimoto et al., 2014; Figs. 2a, b, and c). They present in some vug and pore (Figs. 2a, b, and c). Even with this sample, quartz (0.5-1.7 mm) is opalized, and occurs as prismatic and/or spherical crystals associated with aegirine and an unknown Si-Fe-K-Al mineral. The aggirine (0.01-0.3 mm) occurs as anhedral aggregates and/or independent euhedral-anhedral grains, and it is often associated with the opalized quartz and unknown Si-Fe-K-Al mineral (Fig. 2a). Small amounts of Kfeldspar occur as anhedral crystals included in

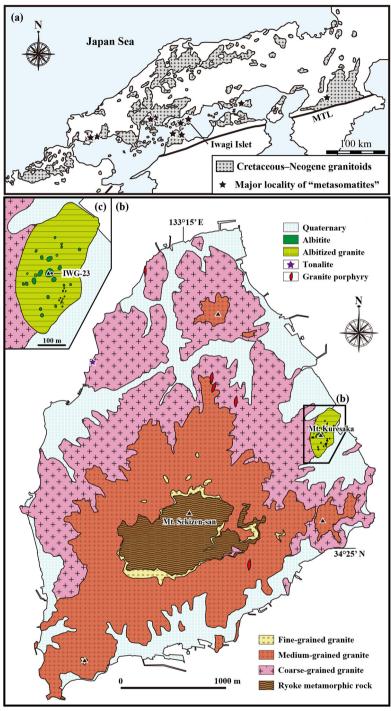
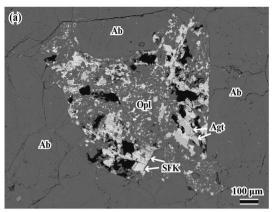
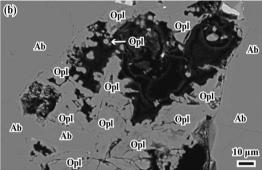


Fig. 1 (a) Distribution of metasomatic rocks in Setouchi Province, SW Japan. (b) Geological map of Iwagi Islet, Ehime Prefecture, Japan (Imaoka *et al.*, 2021). (c) Enlarged view of the area around Mount Kuresaka showing the occurrence of small masses of albitite, along with the location of the studied dalyite–zektzerite-bearing albitite sample no. IWG-23.





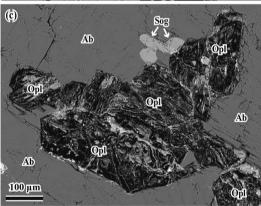
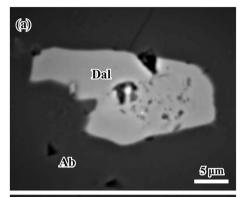


Fig. 2 Backscattered electron images showing the dissolution of magmatic quartz. (a) Opalized quartz filling a vug with aegirine-augite and a minute Si-Fe-K-Al-mineral. (b) Opal filling a vug that formed among albite crystals. (c) Opalized quartz that exhibits a fine fibrous mesh texture and a sogdianite-like mineral. Abbreviations: Opl = opal, Ab = albite, Agt = aegirine-augite, Sog = sogdianite-like mineral, SFK = Si-Fe-K-Al mineral.



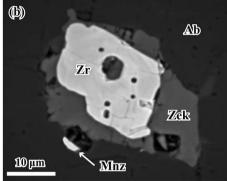


Fig. 3 Backscattered electron images of an anhedral dalyite crystal filling an interstitial space (a), and zektzerite including porous zircon (b) from the albitite on Iwagi Islet, Ehime Prefecture, Japan. Abbreviations: Dal = dalyite, Zr = zircon, Zek = zektzerite, Ab = albite, Mnz = monazite.

the quartz and albite.

The accessory minerals present include a sogdianite-like mineral (Fig. 2c), zircon, fluorapatite, calcite, britholite-(Ce), monazite-(Ce), turkestanite, dalyite (Fig. 3a), zektzerite (Fig. 3b), and unknown Si-Fe-K-Al and Si-Th-Ca minerals. The sogdianite-like mineral (4-110 um) is heterogeneous in appearance, and often associated with the opalized quartz. The zircons (3-40 µm) are euhedral-anhedral, and often enclosed by the sogdianite-like mineral. Porous zircon is commonly observed (Fig. 3b). The fluorapatite (3-15 µm across) occurs as euhedralanhedral crystals in the albite, and it is often associated with K-feldspar. The calcite (12-30 um across) occurs in the albite with the K-feldspar. The britholite-(Ce) (2-22 µm) occurs as

anhedral grains at the grain boundaries of the quartz and K-feldspar. The monazite-(Ce) (4–11 µm across) is heterogeneous in appearance, and it occurs in the albite, often associated with zircon. The dalyite was observed as an anhedral colorless grain 14×29 µm in size enclosed by the albite (Fig. 3a). The zektzerite (10–65 µm) occurs either as independent grains enclosed by the albite or as grains within the albites that enclose grains of zircon (Fig. 3b). The unknown Si-Fe-K-Al mineral (3.8–17 µm) is anhedral. The unknown Si-Th-Ca mineral (3.8–17 µm) is heterogeneous in appearance and occurs as anhedral crystals within the quartz.

IV. Mineral chemistry

The chemical compositions of the minerals were determined on a polished section using a JXA-8230 electron microprobe analyzer (EMPA) at Yamaguchi University, Japan. The operating conditions were as follows: an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1 µm. Wavelength-dispersion spectra were collected with LIF, PET, and TAP crystals to identify interfering elements, and to locate the best wavelengths for background measurements. The probe standards used for the measured elements are described in Nagashima et al. (2013). The measured intensities of $EuL\alpha_1$ and $GdL\alpha_1$ were corrected for peakoverlap interference of $PrL\beta_2$ for Eu and $LaL\beta_2$ and $CeL\gamma_1$ for Gd using JEOL software. The microprobe data were processed by an on-line computer using the ZAF correction method. The analytical errors estimated from the reproducibility observed in multiple measurements were $\pm 2\%$ for major elements and $\pm 5\%$ for trace elements.

1) Dalyite (K₂ZrSi₆O₁₅)

Representative analyses of the dalyite are listed in Table 1. The composition can be summarized as follows: SiO_2 62.0 wt.%, K_2O 15.7 wt.%, ZrO_2 21.0 wt.%, and HfO_2 0.74 wt.%. The low contents of Ti and Hf (up to 0.01 and 0.02 apfu, respectively), indicate that the replacement of Zr by Ti and Hf is limited. The insignificant concentrations of Ba and Na (up to

0.01 and 0.01 apfu, respectively) also indicate a limited substitution for K (Table 1). From the analyses, the empirical formula based on 15 O apfu is $(K_{1.93}Na_{0.01}Ba_{0.01})_{\Sigma_{1.95}}(Zr_{0.99}Hf_{0.02}Ti_{0.01})_{\Sigma_{1.02}}Si_{5.98}O_{15}$, which is close to the ideal formula of dalyite. Jeffery *et al.* (2016) classified dalyites based on K \leftrightarrow Na substitution within the polyhedral sites into Group 1, with an abundance of Na (0.12–0.19 apfu), and Group 2, with significantly lower concentrations of Na (< 0.015–0.03 apfu). The Iwagi dalyite belongs to Group 2.

2) Zektzerite (NaZrLiSi₆O₁₅)

Representative analyses of the zektzerite are listed in Table 1, and we note that the Li₂O value (2.82 wt.%) is taken from Dunn et al. (1977). The chemical composition can be summarized as follows: SiO₂ 66.3 wt.%, Na₂O 5.9 wt.%, ZrO2 21.9 wt.%, Li2O 2.82 wt.%, and trace amounts of HfO₂ (0.75 wt.%), Al₂O₃ (0.35 wt.%), and FeO (0.09 wt.%). Only minor substitution of hafnium for zirconium is indicated. The empirical formula based on 15 O apfu is $Na_{1.03}(Zr_{0.96}Hf_{0.02}Y_{0.01}Sc_{0.01})_{\Sigma_{1.00}}Li_{1.02}$ (Si_{5.95}Al_{0.04})_{25.99}O₁₅. X-ray diffraction data and analytical data of Li contents are not available due to the small size and low modal ratio of the mineral, but no minerals with the same element ratio are known other than zektzerite.

V. Discussion

Mineral replacement reactions take place primarily by dissolution-reprecipitation processes associated with fluid-rock interactions and metasomatism (Putnis, 2002), and important evidence for these processes is the presence of pores (including micropores) in the metasomatic minerals. Recent experimental studies confirmed that reactions between minerals and a fluid phase commonly involve a pseudomorphic replacement via an interface-coupled dissolution-reprecipitation process (e.g., Labotka et al., 2004; Putnis et al., 2007; Niedermeier et al., 2009). Albitization in granites causes an overall change in bulk composition dominated by the production of Na-rich minerals in the rock with a concomitant removal of K by the fluid. Engvik et al. (2008) suggested that

Table 1 Representative chemical compositions of dalyite and zektzerite in an albitite (IWG-23) from Iwagi Islet, Ehime Prefecture, Japan.

Dalyite (23-081)				Zektzerite (23-032)			
Oxide (wt.%)		O = 15		Oxide (wt.%)		O = 15	
SiO_2	62.00	Si	5.976	SiO_2	66.32	Si	5.949
TiO_{2}	0.09	Ti	0.007	TiO_{2}	0.00	Ti	0.000
$\mathrm{Al_2O_3}$	0.02	Al	0.002	Al_2O_3	0.35	Al	0.037
$\mathrm{Cr_2O_3}$	0.00	$\mathbf{Cr}^{^{3+}}$	0.000	$\mathrm{Cr_2O_3}$	0.03	$\mathbf{Cr}^{^{3+}}$	0.002
V_2O_3	0.05	V^{3+}	0.003	V_2O_3	0.00	V^{3+}	0.000
FeO	0.04	$\mathrm{Fe}^{^{2+}}$	0.003	FeO	0.09	$\mathrm{Fe}^{^{2+}}$	0.007
MnO	0.03	$\mathrm{Mn}^{^{2+}}$	0.002	MnO	0.00	Mn^{2^+}	0.000
MgO	0.02	Mg	0.002	MgO	0.00	Mg	0.000
BaO	0.15	Ba	0.006	BaO	0.03	Ba	0.001
Na_2O	0.06	Na	0.011	Na_2O	5.91	Na	1.028
K_2O	15.67	K	1.927	K_2O	0.01	K	0.001
${ m ZrO_2}$	21.02	\mathbf{Zr}	0.988	${ m ZrO_2}$	21.94	\mathbf{Zr}	0.960
HfO_2	0.74	$_{ m Hf}$	0.020	HfO_2	0.75	$_{ m Hf}$	0.019
$\mathrm{Sc_2O_3}$	0.01	Sc	0.001	$\mathrm{Sc_2O_3}$	0.02	Sc	0.002
Y_2O_3	0.00	Y	0.000	Y_2O_3	0.18	Y	0.009
La_2O_3	0.00	La	0.000	La_2O_3	0.05	La	0.002
$\mathrm{Ce_2O_3}$	0.04	Ce	0.001	$\mathrm{Ce_2O_3}$	0.03	Ce	0.001
Pr_2O_3	0.01	\Pr	0.000	Pr_2O_3	0.05	\Pr	0.002
$\mathrm{Sm}_2\mathrm{O}_3$	0.05	Sm	0.002	$\mathrm{Sm}_2\mathrm{O}_3$	0.00	Sm	0.000
$\mathrm{Lu}_2\mathrm{O}_3$	0.00	Lu	0.000	$\mathrm{Lu}_2\mathrm{O}_3$	0.21	Lu	0.006
$\mathrm{Nb_2O_5}$	0.03	Nb	0.001	$\mathrm{Nb_2O_5}$	0.07	Nb	0.003
ThO_2	0.00	Th	0.000	ThO_2	0.03	Th	0.001
UO_2	0.02	U	0.000	UO_2	0.00	U	0.000
$\mathrm{Li_2O}$	n.d.	Li	-	$\mathrm{Li_2O}$	2.82	Li	1.017
F	0.11	Total	8.954	F	0.08	Total	9.047
$-O \equiv F$	0.05	F	0.033	$-\mathrm{O} \equiv \mathrm{F}$	0.04	F	0.023
Total	100.11			Total	98.97		

an interface-coupled dissolution–reprecipitation mechanism is responsible for the coupled exchange of Na^+ and Si^{4+} for Ca^{2+} and Al^{3+} during the albitization of plagioclase.

Pseudomorphs are clear examples of dissolution-reprecipitation (Putnis, 2002). The key feature of a pseudomorph is the preservation of the shape (and volume) of the parent crystal (Putnis, 2002). In the Iwagi albitite, magmatic quartz was dissolved (Fig. 2), and the resulting vugs were often filled by metasomatic minerals such as opal, aegirine, murakamiite, Li-rich pectolite, and sugilite (Imaoka *et al.*, 2021)

that may resemble pseudomorphs.

The principal Zr-bearing minerals in the Iwagi albitites include zircon $(ZrSiO_4)$, sogdianite-like minerals (Fig. 2c), dalyite $(K_2ZrSi_6O_{16}; Fig. 3a)$, zektzerite (LiNaZrSi_6O_{15}; Fig. 3b), baddeleyite (ZrO_2) , and gittinsite $(CaZrSi_2O_7)$ (Imaoka, unpublished data). Among these, zircon is the most ubiquitous in all the samples we studied. The most important observations we made on the petrography and chemistry of the zirconium-bearing minerals in the albitites are as follows: (1) porous zircon is commonly observed in the albitite (Fig. 3b), but not in the host biotite

granite where the zircons have well-developed crystal shapes and show oscillatory zoning indicating a magmatic origin, (2) mantles of zektzerite on porous zircon are found in the albitite (Fig. 3b), and (3) the dalvite occurs in a small pore in the albitite (Fig. 3a), and its composition is close to the ideal, with a low Na content (< 0.015 to 0.03 apfu). Observation (1) suggests that the early crystallized zircon in the host granite became unstable and porous due to the instability of zircon in alkalineperalkaline solutions and fluids (Watson, 1979; Geisler et al., 2007; Grimes et al., 2009). Observation (2) implies that the zircons were readily dissolved during albitization and that the chemical compositions of the Li-Na-rich fluids were different enough to induce the resorption of the early zircon. From observation (2) we conclude that the zektzerite is a metasomatic rather than a magmatic mineral. We propose the following metasomatic reaction for the formation of zektzerite in an open system:

$$\begin{split} &ZrSiO_4 + 5SiO_2 + Li^+ + Na^+ + 2OH^-\\ &zircon \quad quartz\\ &= LiNaZrSi_6O_{15} + H_2O \\ &zektzerite \end{split} \tag{1}$$

The observed dissolution of magmatic quartz (Fig. 2) is consistent with the above reaction, according to which SiO_2 (quartz) is consumed.

The occurrence of anhedral dalyite in a small pore (observation 3) indicates that it formed as a result of metasomatism by the interstitial solution trapped in the pore. The formation of dalyite in the albitite can be explained by the following reaction:

$$\begin{split} &ZrSiO_4 + 5SiO_2 + 2K^+ + 2OH^-\\ &zircon \quad quartz\\ &= K_2ZrSi_6O_{15} + H_2O\\ &dalyite \end{split} \tag{2}$$

The observed dissolution of magmatic quartz (Fig. 2) also provides evidence for this proposed reaction. It is possible to estimate the amounts of primary high-temperature phases (K-feldspar, quartz, and zircon) that were dissolved, as the modal amounts of K-feldspar and

quartz in the albitite are only 0.2% and 0.1%, respectively, indicating that the original large amounts of K-feldspar (20–38%) and quartz (36–45%) in the host granite were lost during an outflow of $K^{\scriptscriptstyle +}$ and SiO_2 and an inflow of $Li^{\scriptscriptstyle +}$ and $Na^{\scriptscriptstyle +}$ in hydrothermal fluids, thereby facilitating the growth of zektzerite and dalyite.

Jeffery et al. (2016) divided dalvite into two types based on the Na ↔ K substitution: the sodic Group 1 type is characterized by relatively high Na contents (0.12-0.19 apfu) and the potassic Group 2 type by low Na contents (< 0.015-0.03 apfu). Generally, the dalyite found within peralkaline granites and syenites is defined by a higher K

Na substitution relative to the dalyite found in highly potassic rocks (Jeffery et al., 2016). It seems strange at first that the dalyite in the sodic Iwagi albitite is the potassic Group 2 type dalyite. Harris and Rickard (1987) also noted that the Straumsvola dalvite has no Na content, despite the rock having a high Na₂O/K₂O ratio of 1.35 (Na₂O = 6.00, $K_2O = 4.44$ wt.%). They suggested that dalyite is stable near the liquidus for a wide range of K concentrations. From such data and suggestions, the chemical compositions of the Straumsvola and Iwagi dalyites may reflect another potential control (e.g., temperature) in addition to whole-rock chemistry.

Imaoka et al. (2021) inferred that the large Li isotope fractionation of murakamiite and Lirich pectolite on Iwagi Islet could be attributed to metasomatic hydrothermal fluid-rock interactions at 300-600°C. Dalyite has been synthesized hydrothermally at 340°C and 600 bars (Caruba et al., 1970), which would suggest that the metasomatic formation of dalyite took place at a relatively low temperature during the paragenetic sequence of events that formed the albitite. Under such low-temperature conditions, dalyite of potassic Group 2 is stable, and very limited substitution of Na for K can occur. The dalyite occurring in metasomatic rocks such as the Iwagi albitite shows more limited miscibility than that shown by the same minerals in igneous rocks.

With regard to dalyite: (1) on Iwagi Islet it

occurs only in the metasomatic albitite, and it does not occur in the host granite; (2) dalyite on the Azores was inferred to be the last mineral to crystallize (Ridolfi et al., 2003), as in our samples; (3) Furnes et al. (1982) suggested that dalyite in the ultrapotassic Sunnfjord dike was either metasomatic in origin or, if magmatic, that it had been altered by metasomatism; and (4) analytical data, possibly recording metasomatism, frequently exhibit Na contents below the detection level (Jeffery et al., 2016). Taking these results and our data into account, we conclude that the dalyite in the Iwagi albitite is metasomatic in origin.

In summary, the Iwagi albitites record the Zr-mineral replacement reactions that occurred via dissolution-reprecipitation and changed the original magmatic mineralogy of the host granite during hydrothermal activity.

Acknowledgments

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Notes

1) http://www.mindat.org/min-4390.html [Cited 2020/ 10/16].

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岩城島産エジリンアルビタイト中のデーリー石とゼッツェル石

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愛媛県岩城島の白亜紀エジリンアルビタイトより稀な K-Zr 珪酸塩鉱物であるデーリー石と Li-Na-Zr 珪酸塩鉱物であるゼッツェル石が見いだされた。デーリー石とゼッツェル石の EPMA 分析結果からそれぞれ $(K_{1.93}Ba_{0.01})_{\Sigma 1.94}(Zr_{0.99}Hf_{0.02})_{\Sigma 1.01}$ $Si_{5.98}O_{15}$ および $Na_{1.03}(Zr_{0.96}Hf_{0.02}Y_{0.01}Sc_{0.01})_{\Sigma 1.00}$ $Li_{1.02}(Si_{5.95}Al_{0.04})_{\Sigma 5.99}O_{15}$ の実験式が得られる。多

孔質ジルコン、デーリー石、および不安定なジルコンを被覆するゼッツェル石の産状から、このアルビタイトは熱水活動時期における Na、K、Liに富んだ流体によるジルコニウム鉱物の分解と沈殿による交代反応の記録をよく保存している。これは日本列島におけるデーリー石とゼッツェル石産出の最初の報告である。

キーワード:デーリー石、ゼッツェル石、アルビタイト、リチウム交代作用、岩城島

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