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RESEARCH TOPIC FROM JAMS:

Where did the Li-enriched metasomatic agent come from? Metasomatic albitite from the Iwagi Islet, Southwest Japan

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Metasomatism is a process in which pre-existing rocks undergo compositional and mineralogical transformations associated with chemical reactions by reaction fluids (so-called metasomatic agents) penetrating the protolith. The study of metasomatic rocks is essential for understanding the nature and origin of metasomatic agents and is of great interest in a wide range of geological sciences, including petrology, mineralogy, and geochemistry.

In Setouchi Province of southwest Japan, metasomatic rocks containing pyroxene, garnet, amphibole, and biotite are distributed along an approximately E–W trend, and these rocks are associated with Late Cretaceous granites (Fig. 1; Murakami 1976). The metasomatic rocks are mostly small masses, and the textures of the weakly metasomatized ones are similar to those of the adjacent granites. They commonly occur along shear zones with abundant quartz veins. We can find one such metasomatic rock, albitite, in the Iwagi Islet. Unlike other metasomatites found in the region, the albitites here are characterized as being enriched in lithium (500 ppm; Imaoka et al. 2021a). 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 mineralogical characteristics of peculiar Li-minerals have been investigated in particular detail (Imaoka et al. 2021b: Imaoka and Nagashima 2022), as they are significant for understanding the formation and evolution of albitites here. They are considered to originate from precipitation from a fluid enriched in Li and Na at low to moderate temperatures (Imaoka et al. 2017). The Iwagi albitites are known as the type locality of four Li-analog minerals: sugilite $KNa_2(Fe^{3+}, Mn^{3+}, Al)_2Li_3Si_{12}O_{30}$ (Murakami et al. 1976), katayamalite $KLi_3Ca_7Ti_2(SiO_3)_{12}(OH)_2$ (Murakami et al. 1983), murakamiite $LiCa_2Si_3O_8(OH)$ (Imaoka et al. 2017; Nagashima et al. 2018), and ferro-ferri-holmquistite $\square Li_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH)_2$ (Nagashima et al. 2022).

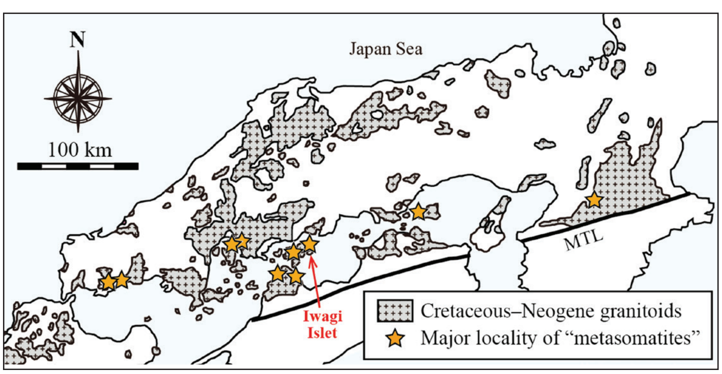

Figure 1 Distribution of metasomatites in Setouchi Province, SW Japan (after Murakami 1976).

Characteristics and formation of the Iwagi albitite (Imaoka et al. 2021a)

The Iwagi albitites form small bodies that are several tens of centimeters to tens of meters in size, disseminated in a host granite of Late Cretaceous age (ca. 90 Ma). There are no clear intrusive margins between the albitites and surrounding albitized granite, and the boundaries are instead gradational between the two rock types, reflecting the different degrees of interaction between host granite and fluids (Table 1). The albitization process decreases the ratio of quartz and K-feldspar and increases that of plagioclase based on the modal compositions. Aegirine and Li-bearing minerals form as accessory phases with albitization. The Li-concentrated minerals vary with albitization. In the weakly albitized specimens preserving the texture of the host granite, aggregates of blue, acicular, ferro-ferri-holmquistites are observed as a replacement for the biotite (Fig. 2). However, sugilite, katayamalite, and murakamiite–pectolite series minerals associated with aegirine are observed as Li-enriched phases in the complete albitites (Fig. 3). The albitites have various replacement textures as a result of Na–Li metasomatism, and they also show conspicuous strain-induced textures. According to bulk analyses, the albitite was particularly enriched in Li, Na, and Fe, whereas K, Si, and LREEs were depleted relative to the host granite. Metasomatic minerals, formed by the replacement reaction by dissolution–reprecipitation processes associated with Na- and Li-rich hydrothermal fluids, occur as infilling of the vugs and pores formed by the dissolution of quartz and K-feldspar. Moreover, the $^{40}Ar/^{39}Ar$ plateau age of katayamalite is 90.91 ± 0.23 Ma (Imaoka, unpublished), indicating that the albitization was a Late Cretaceous event.

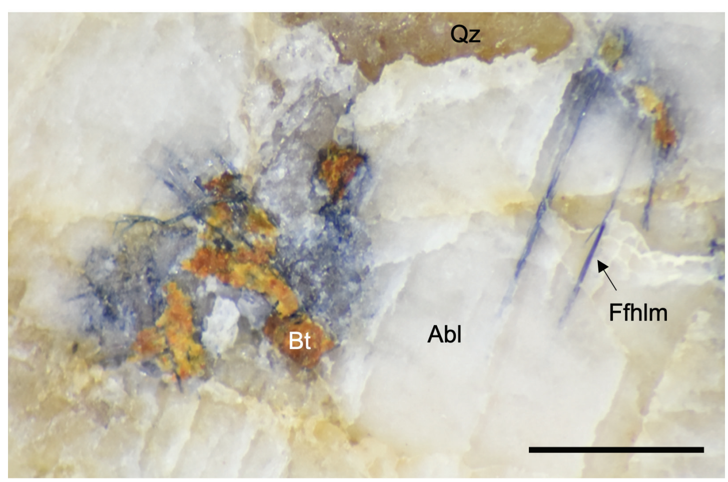

Figure 2 Photomicrograph showing the representative occurrence of ferro-ferri-holmquistite (Ffhlm) in the weakly albitized granite. Blue acicular Ffhlm crystals occur as a replacement for the biotite, Bt (strongly altered). Abl, albite, Qz, quartz. Scale bar = 1 mm.

The δ^7Li isotope variation was given special focus in this study. Because the reaction temperature changes the Li isotope ratio between fluid and solid phases (e.g., Wunder et al. 2006), δ^7Li values provide clues to understanding the albitization process. The δ^7Li values of murakamiite and Li-rich pectolite showed a wide range, from –9.1‰ to +0.4‰ (average = –2.9‰), and their heterogeneity was observed on the sub-millimeter-scale within a single crystal. Such large δ^7Li fractionation and δ^7Li values < 0‰ suggest low- to moderate-temperature environments (e.g., Wunder et al. 2007; Tomascak et al. 2016). In addition to δ^7Li isotope values, considering the syntheses of pectolite-bearing assemblages (Karup-Møller 1969), the weight loss of murakamiite–pectolite determined by DTA-TG (Imaoka et al. 2017), and the stability field

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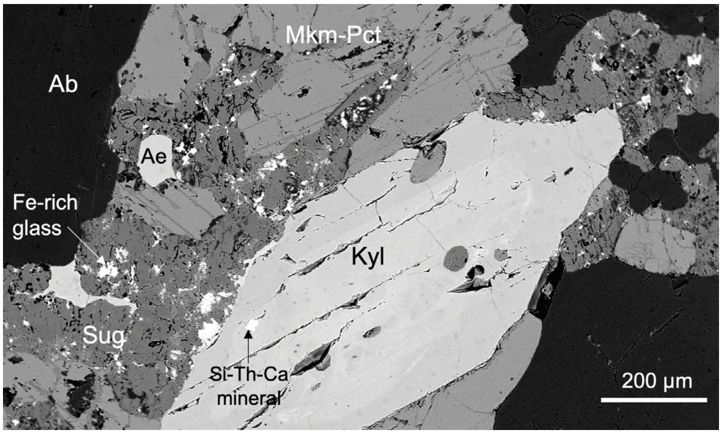

Figure 3 Back-scattered electron image of katayamalite (Kyl), murakamiite–pectolite series mineral (Mkm-Pct), sugilite (Sug) associated with aegirine (Ae) in the metasomatized albitite.

of aegirine, a typical coexisting phase with murakamiite–pectolite (Redhammer et al. 2000), the hydrothermal fluid–rock interaction that formed the Iwagi albitite was estimated to be 300–600 °C. The very low δ^7Li 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 δ^7Li values. Exceptionally low δ^7Li values, as low as −5‰ to +2‰, have been reported from the deep crustal fluids (Nishio et al. 2010), and interestingly these fluids show significant Li enrichment. Therefore, the deep crustal fluids meet the requirement for the parental fluids of murakamiite–pectolite, and they were likely involved in the formation of the Iwagi albitite. Strain-induced textures observed in the thin sections imply that Li–Na-enriched and low-δ^7Li fluids derived from the subduction zone migrated upward along the shear zone after granite emplacement. Deformation-induced fracturing of the rock could have facilitated fluid circulation and the occurrence of the metasomatic rocks along the E–W trending lineament.

The metasomatic Iwagi albitite likely tells us about the locus for large-scale fluid movements within the crust. Further studies on the metasomatites distributed in this region are mandatory.

Table 1 VARIATION OF MINERAL ASSEMBLAGES WITH ALBITIZATION*

Degree of albitization	Original granite				→
Quartz	X	X			
Microcline	X	X			
Plagioclase	X				
Biotite	X	X			
Albite		X	X	X	X
Aegirine-augite		X	X	X	X
Ferro-ferri-holmquistite		**X**			
Sugilite			**X**	**X**	**X**
Katayamalite				**X**	**X**
Murakamiite–pectolite					**X**

* Li-analogue minerals are written in bold.

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