

Original paper

Cathodoluminescence characterization of feldspar minerals from granite-syenite rocks in Iwagijima Island, Ehime Prefecture, Japan

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Abstract: In Iwagijima Island, aegirine syenite was emplaced in the Ryoke granite during late Cretaceous time by a hydrothermal metasomatism. The syenite and related rocks show various types of petrographic textures in response to the process of hydrothermal alteration, e.g., feldspar minerals. We have conducted to clarify the feldspar with a variety of metasomatic alteration in the granite-syenite by using cathodoluminescence (CL) imaging and spectroscopy. Feldspar exhibits a variety of CL colors depending on kinds of impurity elements and their concentrations, and defect densities related to Si-Al ordering and other structural disorder. The feldspar in the unaltered granites shows apple green and blue CL emissions. The former is identified to plagioclase (Ab₈₀ An₂₀) characterized by Mn²⁺ activator at 560 nm, and the latter to alkali feldspar (Or₉₀ Ab₁₀) by defect center at 420 nm related to Al-O-Al. Altered granite has albite with red CL emission at around 750nm, and alkali feldspar within homogeneous color of red to violet-blue emissions at around 400 nm and 720 nm. These CL emissions in a red region can be assigned to Fe³⁺ activator. The feldspar in syenite is mostly altered to albite with an enhanced red emission at around 750 nm. Therefore, the disappearance of blue emission in alkali feldspar in syenite implies that alkali-rich (sodium-rich) hydrothermal metasomatism for the formation of syenite could act at relatively high temperature above 250 °C successively after granitic magmatism.

Introduction

Iwagijima Island belonging to the Geiyo islands in Ehime Prefecture consists chiefly of upper-Cretaceous granitic rocks in a series of the Ryoke granite divided into three types of hornblende-biotite granite, fine-grained biotite granite and coarse-grained biotite granite, which locally intruded into the Ryoke metamorphic rocks accompanying schistose hornfels on the central summit and in the southwest coast (Murakami and Matsunaga, 1966). Petrological studies of the granitic rocks have revealed that the metasomatism by hydrothermal alkali solution altered coarse-grained biotite granite into the syenite with aegirine as a phenocryst, albite, wollastonite, pectolite and minor accessory minerals (e.g., Murakami and Matsunaga, 1966). Furthermore, rare Li-bearing minerals of sugilite [KNa₂(Fe,Mn,Al)₂Li₃Si₁₂O₃₀] and katayamalite [KCa₇(Ti,Zr)₂Li₃Ca₇Si₁₂O₃₆(OH,F)₂] were found out in the syenite (Murakami et al., 1976 ; Kato and Murakami, 1985). The distribution of the aegirine syenite is confined to a specific area as a small stock-like mass (0.20 x 0.15 km) at the northeastern part (Funakoshi) of Iwagijima Island (Murakami et al., 1976).

Metasomatic reaction of the granitic rocks with hydrothermal alkali solution is characterized by the alkalization in the process from plagioclase and K-feldspar in granitic rocks to albitic plagioclase in syenite (e.g., Murakami and Matsunaga, 1966). Such alkalization accompanying albitization of the feldspar has been reported in type B syenite proposed by Murakami (1958), and investigated in detail on the syenite from the Cerro Balmaceda pluton in the Patagonian Andes (Nakano et al., 2005). Kayama et al. (2010) pointed out that cathodoluminescence (CL) of the feldspar in the Balmaceda syenite reflects trace impurities and structural defects in the feldspar closely related to the process of metasomatic reactions among constituent feldspar.

CL microscopy and spectroscopy provide useful information on existence and distribution of impurity elements related to crystal chemistry and lattice defects produced by destruction or distortion of atomic linkages with a high-spatial resolution, which should be more informative to characterize the crystal-chemical features of feldspar. Therefore, the present study has been conducted to clarify the feldspar with a variety of metasomatic alteration in the granite-syenite

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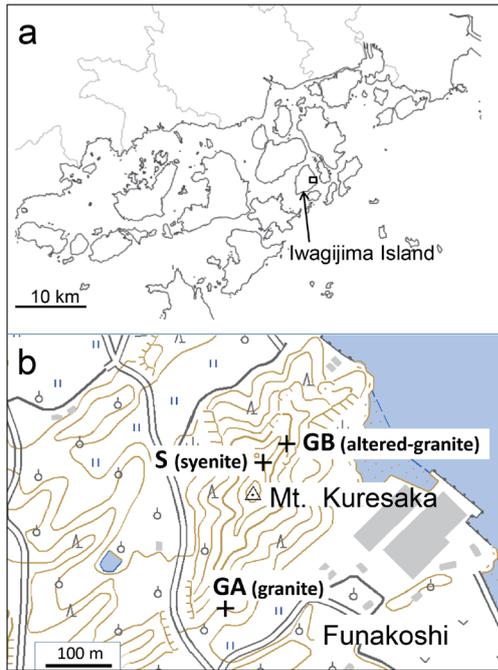


Fig. 1. a: location map of Iwajijima Island; b: sampling localities of granite (GA), altered granite (GB) and syenite (S) around Mt. Kuresaka in the eastern part of Iwajijima Island referred to a 1/25,000 topographical map (Iwagi) published by the Geographical Survey Institute.

from Iwajijima Island by using color CL imaging and CL spectral analysis.

Samples and methods

Three samples of granite, partly metasomatic granite and syenite rocks from Mt. Kuresaka were selected for CL measurements (Fig. 1). The granite (GA) shows a granular texture with quartz, biotite, plagioclase (oligoclase to albite), K-feldspar (predominant microcline), zircon and apatite under a polarized microscope (Fig. 2). The syenite (S) from Mt. Kuresaka in Funakoshi area has a hypidiomorphic texture with coarse-grained albitic feldspar ($Ab > 95$) and aegirine accompanying minor pectolite, sugilite and apatite by a polarized-microscope examination (Fig. 3). The partly altered granite (GB) intermediate between GA and S was collected from Mt. Kuresaka in the vicinity of the locality of the S. It exhibits a similar texture of the GA, and contains quartz, altered biotite and plagioclase, and partly altered K-feldspar, which maintains its external shape with a turbid core of survived K-feldspar surrounded by albite in a polarized-microscope image (Fig. 4).

The sliced samples adhered on a slide glass with epoxy resin (I.T.W. industry: Devcon ET), which shows almost no luminescence. They were fixed in thickness of $\sim 30 \mu\text{m}$ with a diamond abrasive, which were coated with $\sim 2 \text{ nm}$ carbon thin-film to prevent a charging up on the surface after a microscopic observation.

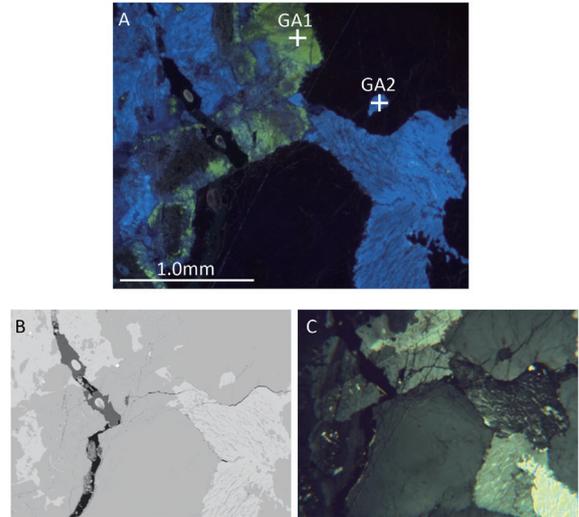


Fig. 2. Color CL image (A), BSE image (B) and polarized-microscope image with cross PL (C) of feldspar minerals in granite GA from Iwajijima Island.

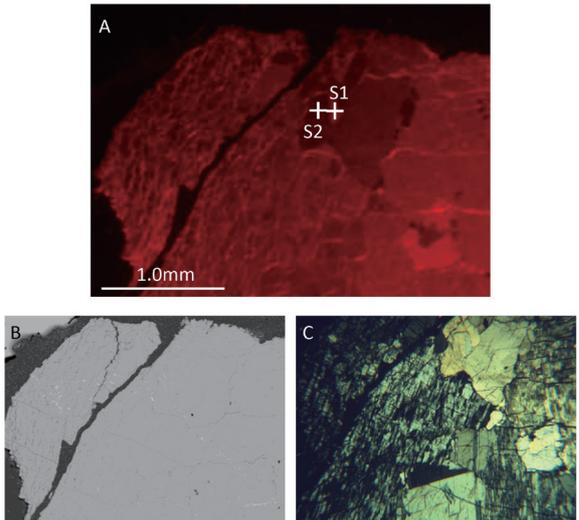


Fig. 3. Color CL image (A), BSE image (B) and polarized-microscope image with cross PL (C) of feldspar minerals in syenite S from Iwajijima Island.

CL color images were obtained using the Luminoscope (ELM-3), attached with a cooled charge-coupled device (CCD) camera, which is consisted of a cold cathode discharge tube and a vacuum chamber placed inside by the sample. It was operated stably with electron beams generated by an excitation voltage of 10 kV and a beam current of 0.5 mA. CL spectroscopy was conducted by SEM-CL system, which consists of an SEM (JEOL, JSM-5410LV) combined with a grating monochromator (Oxford, Mono CL2) with operating conditions of 15 kV and 0.2-1.0 nA in a scanning mode. The CL emitted from the samples was collected by use of a retractable parabolic mirror. The CL signals dispersed by a grating monochromator were recorded with a photomultiplier tube by a photon counting meth-

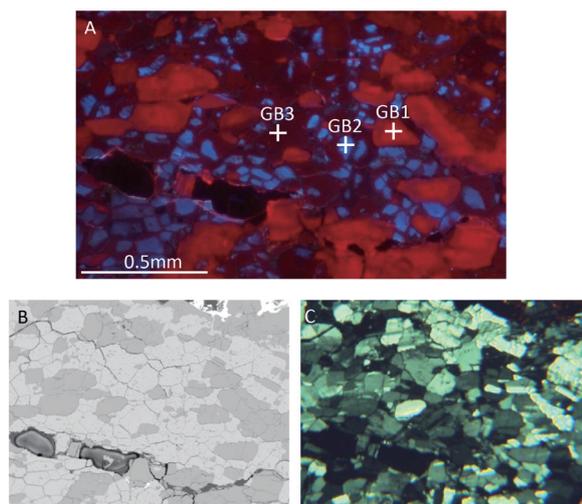


Fig. 4. Color CL image (A), BSE image (B) and polarized-microscope image with cross PL (C) of feldspar minerals in partly altered granite GB from Iwagijima Island.

od. All CL spectra were corrected for total instrumental response, which was measured using of a calibrated standard lamp. Detailed construction of the equipment and the analytical procedure can be found in Ikenaga et al. (2000).

Results and discussion

Color CL microscopy

Color CL imaging of the granite GA shows blue to deep blue for K-feldspar (microcline) and green to apple green for plagioclase (oligoclase-albite), and occasionally cream to yellow for minute zircon and apatite (Fig. 2). Under a polarizing microscope, plagioclase grains are almost homogeneous with same optical features corresponding to CL. K-feldspar grains show turbid features well-known in plutonic K-feldspar, whereas the CL exhibits modestly homogeneous over the grain.

The partly-altered granite GB exhibits a complicated color CL features in K-feldspar grains, where the mantle albite along the relic of K-feldspar shows a bright red CL with a dark blue CL of survived K-feldspar at a core part accompanying dull red to ochre CL of alkali feldspar as a transition zone of albitization (Fig. 4). Also most plagioclase is altered by albitization to a greater or less extent, which can be distinguished by the color CL of red corresponding to albitic feldspar. These petrographic features are not so obvious by the conventional optical methods.

The syenite is characterized by a predominant red CL of albite, which occupies almost all feldspar minerals as a result of severe albitization (Fig. 3). Occasionally, the relics of the K-feldspar grain are recognized due to the irregular inclusions of survive K-bearing alkali feldspar, of which CL indicates dull red to dark ochre without

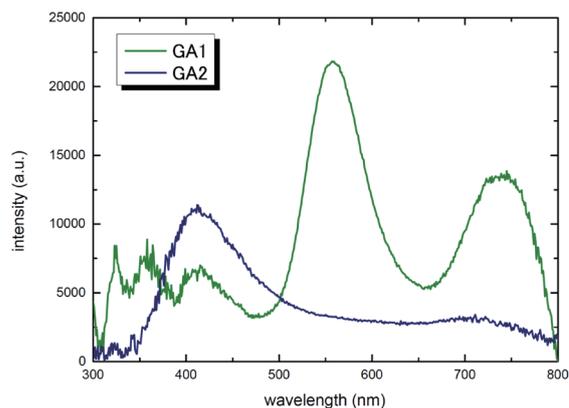


Fig. 5. CL spectra of plagioclase (GA1) and K-feldspar (GA2) in granite GA from Iwagijima Island.

any blue CL detected in the K-feldspar. Accessory mineral of katayamalite emit a blue CL as a small spot scattered over all the red albite, whereas the pectolite shows a similar bright-blue CL as a lath shape attached with the red albite grains.

CL spectroscopy

In the granite GA, the plagioclase with an apple green CL gives a broad band at 730-740 nm in a red region, an enhanced emission peak at around 560 nm in a green region and weak broad bands from 330 nm up to 430 nm in a blue region (Fig. 5), which well corresponds to the optical CL. A red CL emission might be attributed from an impurity center of Fe^{3+} , which replaces Al^{3+} in tetrahedron site judging from the previous studies (e.g., White et al., 1986). Götze et al. (2000) demonstrated that a ratio of Ab/An in the solid solution closely relates to a wavelength centered at an emission peak caused by Fe^{3+} activator, suggesting a higher Ab content a longer wavelength of emission peak position. This fact is consistent with the value obtained from this feldspar ($\text{Ab}_{80}\text{An}_{20}$). A green CL can be assigned to an impurity center of Mn^{2+} ion as an activator, where the Mn^{2+} substituted for Ca^{2+} activates as an electron transition of ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ by referring to the results previously reported (e.g., Götze et al., 2000). A blue CL is complicated emission bands overlapped with more than one emission components such as impurity centers and defect center. Most plagioclase has a blue CL emission at 400-480 nm derived from the Al-O-Al center, which is formed as an oxygen defect associated with Al-O-Al bridge (Löwenstein bridge) (e.g., Finch and Klein, 1999; Götze et al., 2000). On the other hand, Ti^{4+} ion in feldspar structure emits a blue CL at 450-460 nm whereas it is not clear that Ti^{4+} ion acts as an activator or creates a radiative emission center related to the structural defect caused by an intrusion of Ti^{4+} ion into the lattice. Further impurity centers such as Ce^{3+} (~320 and

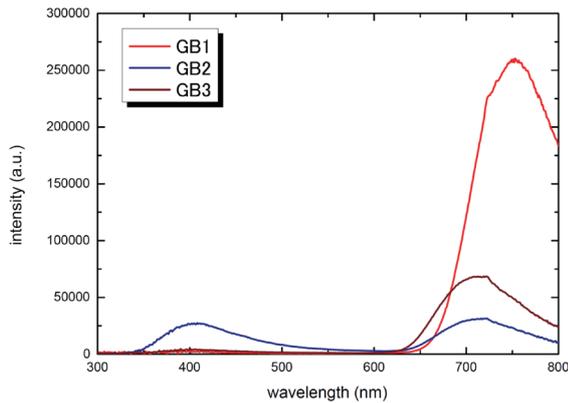


Fig. 6. CL spectra of plagioclase (GB1), K-feldspar (GB2) and altered K-feldspar (GB3) in partly altered granite GB from Iwagijima Island.

~ 350 nm) and Eu^{2+} (380-420 nm) should be considered for the assignments of emission components in a blue region (Kayama and Nishido, 2008). Therefore, a weak blue CL observed in the plagioclase is not specified from the spectral data. The alkali feldspar in the granite GA shows a broad emission band at around 420 nm in a blue region with a tailing to a longer-wavelength side and a weak broad band around 720 nm in a red region (Fig. 5). The former indicates a similar manner of the plagioclase, suggesting a same emission center related to Al-O-Al defect and/or Ti^{4+} ion impurity as mentioned above. The latter might be assigned to an impurity center of Fe^{3+} .

In the partly-altered granite GB, relatively large grains of albite show an enhanced emission band at around 750 nm in a red region without any emissions in blue and green regions (Fig. 6). The red CL is derived from Fe^{3+} activator in a feldspar structure as previously mentioned. However, the wavelength of the emission peak is somewhat longer than that of 730-740 nm for the plagioclase observed in the granite GA. It is concordant with the albitic components of the plagioclase ($\text{Ab}_{80}\text{An}_{20}$) in the GA and the plagioclase ($\text{Ab}_{90}\text{An}_{10}$) in the GB due to a longer wavelength of emission peak position for a higher component of Ab, whereas the difference in the Ab content for the plagioclase is difficult to be recognize in their BSE images. K-feldspar with a blue CL gives a broad emission band at around 720 nm with a tailing toward a longer wavelength in a red-IR region and a broad emission band at around 420 nm in a blue region (Fig. 6). The spectral features are in fairly similar to those obtained in the K-feldspar from the GA. Furthermore, survived K-feldspar with dull red CL has a broad emission band at around 720 nm with a higher intensity rather than original K-feldspar and a slight emission band at around 400 nm, suggesting an obvious alteration of the K-feldspar by albitization. However, this fact cannot be detected by any other methods

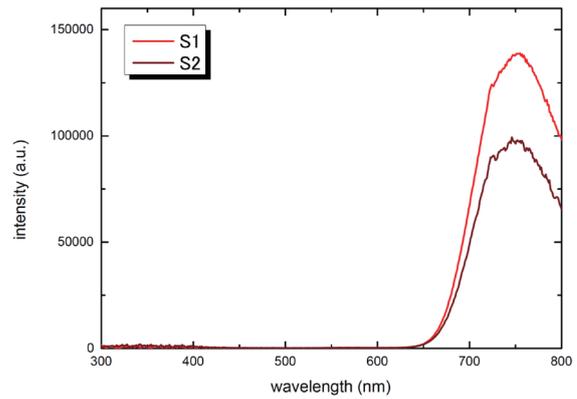


Fig. 7. CL spectra of albite (S1 and S2) in syenite S from Iwagijima Island.

such as optical examination and EPMA element mapping.

In the syenite S, most albite shows a bright red CL with an enhanced emission peak centered at around 750 nm in a red-IR region assigned to an impurity center of Fe^{3+} ion without any emissions in green and blue regions (Fig. 7). It is the almost same as the CL spectrum of the albite in the GB (Fig. 6), but with an extremely high intensity. Dull-red CL looked like the survived K-feldspar in the GB is studded in the bright red albite (Fig. 6), but corresponding to pure albite by the reason of EPMA analysis. This spectrum has an enhanced emission peak at around 750 nm (Fig. 7), which is different from the peak position of ~ 720 nm in that of the survived K-feldspar. It implies that the albite with a bright red CL might have a well-crystallized phase rather than that with a dull red emission due to an effect of crystal field on the CL emission.

CL spectral analysis

The CL of feldspar minerals is composed of many types of emission centers such as activated impurity elements and structural defects, of which component cannot be identified by the information of measured spectral data. In general, a spectral peak fitted by one Gaussian curve in energy units can be assigned to one specific type of emission center (Yacobi and Holt, 1990; Blasse and Grabmaier, 1994; Stevens-Kalceff, 2009). Kayama et al. (2010) demonstrated that a spectral deconvolution method of CL in alkali feldspar using a Gaussian curve successfully provides the emission components assigned to specific emission centers. Therefore, all spectral data were converted to the data in energy units for a spectral deconvolution. The emission components were derived by a Gaussian fitting with the peak-fitting software (Peak Analyzer) implemented in OriginPro9, where a number of the component was determined using a statistical test of χ^2 factor

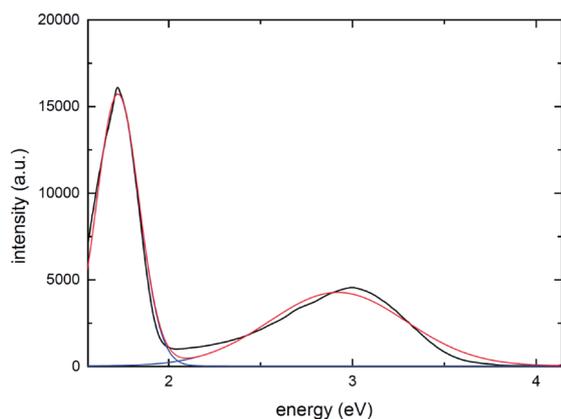


Fig. 8. Emission components derived from CL spectrum of plagioclase (GA1) in granite GA using a Gaussian curve fitting.

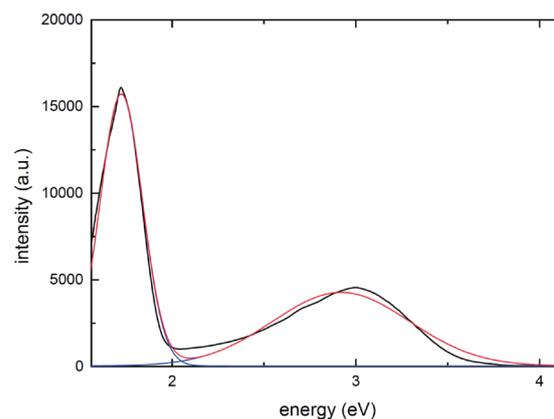


Fig. 9. Emission components derived from CL spectrum of K-feldspar (GB2) in granite GB using a Gaussian curve fitting.

proposed by Stevens-Kalceff (2009). In analytical procedures, the center and full width at half maximum (FWHM) were optimized through the samples on the basis of r^2 coefficient value.

The result of the deconvolution of CL spectrum for the plagioclase in the granite GA shows many emission components at 1.68 eV in a red region, 2.19 eV in a green region, and 2.90, 3.45 and 3.83 eV in a blue region (Fig. 8). A green emission at 2.19 eV is identified to the Mn^{2+} activation caused by an electron transition of ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$. As previously mentioned, the blue CL in feldspar minerals is involved with many kinds of emission centers. Al-O-Al defect center has been reported as a broad emission peak at 400-480 nm in a number of plagioclase, and also at the same energy of 450-460 nm an emission related to Ti^{4+} impurity has been recognized (e.g., Kayama and Nishido, 2008). In the case of this sample, Al-O-Al defect center possibly corresponds to the component at 2.90 eV (427 nm), whereas the presence of Ti^{4+} impurity center cannot be detected. Judging from the results previously reported (Kayama and Nishido, 2008), the emission components at 3.45 and 3.83 eV might be impurity centers of Eu^{2+} and Ce^{3+} activators, respectively. The deconvolution of CL spectrum for the K-feldspar in the granite GB results in two emission components at 1.72 eV corresponding to Fe^{3+} impurity center and at 2.92 eV to Al-O-Al defect center (Fig. 9). The Fe^{3+} ion should occupy a specific site in K-feldspar structure because the emission caused by Fe^{3+} activation in plagioclase structure has a lower energy of 1.68 eV as compared with the peak wavelengths of both emissions (Fig. 5 and Fig. 6), whereas the content of Fe in the feldspar exceeds the detection limits by EPMA analysis. The CL of albite in the syenite gives one emission component at 1.63 eV, which is assigned to an impurity center of Fe^{3+} with different crystal field from that in the K-feldspar (Fig. 10). The content

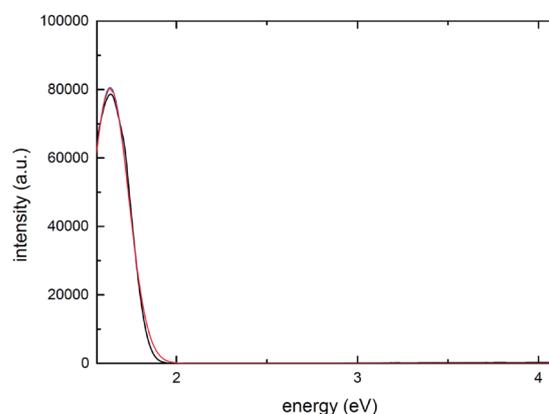


Fig. 10. Emission components derived from CL spectrum of albite (S1) in syenite S using a Gaussian curve fitting.

of Fe in the albite is too low to be determined precisely, suggesting an appreciably high efficiency of Fe^{3+} activator in albite structure.

Kayama et al. (2010) investigated the peak changes of a blue emission peak at 420 nm in alkali feldspar, and they found that the luminescence of Al-O-Al defect center was affected by hydrothermal metasomatism possibly at 250 °C. Therefore, the disappearance of a blue emission in alkali feldspar in syenite implies that alkali-rich (sodium-rich) hydrothermal metasomatism for the formation of syenite could act at relatively high temperature above 250 °C successively after granitic magmatism.

A hydrothermal metasomatism with a high alkaline solution in Iwagijima Island altered the feldspar mineral including plagioclase and K-feldspar in granitic rocks eventually into albite, of which process promotes a formation of syenitic rocks. CL microscopy of the feldspar minerals with various degrees of alteration reveals albitization of plagioclase with red emission and hydrothermal alteration of K-feldspar with a blue CL accompanying the deletion of structural defect related to Al-O-Al bridge and intercalation of

Fe³⁺ ion related to a red CL into the structure, and finally completed albitization of feldspar minerals with a bright red CL in the syenite. The detailed process during metasomatic albitization in the Iwagijima granitic rocks has been clarified using CL microscopy and spectroscopy in the present study, although the other optical and analytical methods do not enable to find out clear evidence on this matter.

Acknowledgement

We are deeply indebted to M. Kayama (Kobe University) for valuable advice on the CL of feldspar, and to H. Mori (Education division, Ueshima-cho) for helpful information on the occurrence of the syenite in Iwagijima Island.

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眞木誠也・大郷周平・西戸裕嗣：愛媛県岩城島に産する花崗岩-閃長岩を構成する長石のカソードルミネッセンス特性

要旨

愛媛県芸予諸島にある岩城島は主に領家花崗岩からなるが、一部にアルカリ岩化を伴う交代作用によりエジリン閃長岩が生成している。この交代作用の過程は、母岩を構成する長石鉱物の曹長石化により把握できる。長石薄片のカソードルミネッセンス(CL)観察により、曹長石化過程を直接視認できた。初期に斜長石が曹長石へ変わり、同時にカリ長石の一部が曹長石へ置き換わり、最終的に全ての長石が曹長石になった。長石鉱物から得られたCLスペクトルから、曹長石化に伴いFe³⁺イオンが長石構造へ付加され、カリ長石の構造欠陥は解消することが明らかになった。これらの長石の変化はチリ・バルマセーダの閃長岩に布存する長石の曹長石化過程に類似し、両者の比較から岩城島における交代作用は250℃を越す比較的高温のNa成分に富む熱水によることが推定された。この様な活動は花崗岩生成後すぐの熱水によるものであろう。

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