Calcium distribution in alkali feldspar of a quartz syenite from Cape Ashizuri, Shikoku, southwest Japan

Satoshi NAKANO*, Eiko HOSOKAWA**and Junji AKAI***

* *Department of Natural Science, Faculty of Education, Shiga University, Hiratsu 2-5-1, Otsu, Shiga 520, Japan*

** *Shiga Surveying and Planning Company, Sagami, Koka, Shiga 520-34, Japan*

****Department of Earth Sciences, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21, Japan*

Abstract

Alkali feldspar grains in a quartz syenite from Cape Ashizuri, southwest Japan, consist of two parts: clear and turbid. The rims of grains are turbid and show lamellar textures of microperthites. Both clear and turbid parts are scattered irregularly inside grains. The clear parts are optically featureless and cryptoperthitic. The inner turbid parts are mosaic and lamellar microperthites. In some sections, only lamellar microperthites are developed throughout a grain. Calcium distribution maps were obtained for feldspar grains showing the above textures. The rims are always poor in calcium (nearly 0 mol% An). The inner clear parts are generally rich in calcium (5 mol% An at the maximum) around the composition of about $\text{Or}_{33}\text{Ab}_{64}\text{An}_3$, but in some cases poor in calcium (-0.1mol% An). The sodium-rich phase of the microperthite of the inner turbid parts are variable in calcium content from 7 to nearly 0 mol% An. On the other hand, the potassium-rich phase of the microperthite is always poor in calcium both in the rims and inside the grains. The total calcium distribution patterns suggest a possible calcium transfer from the inside to the outside of grains under hydrothermal conditions with microperthite formation.

Introduction

A persuasive model has been proposed to explain the subsolidus behavior of plutonic alkali feldspars from the studies of feldspar textures in the Klokken syenites, Greenland (*e.g.*, Parsons, 1978; Parsons and Brown, 1984; Smith and Brown, 1988; Brown and Parsons, 1994). The alkali feldspars consist of two parts, clear and turbid, under an optical microscope. The clear parts are optically featureless and cryptoperthitic, and the turbid parts are optically microperthitic. The proposed formation model is as follows. In the course of subsolidus cooling of primary featureless feldspars, exsolution took place, resulting in cryptoperthite formation. At the later hydrothermal stage, coarsening of strain-controlled cryptoperthite occurred (Brown and Parsons, 1993), resulting in turbid microperthite associated with the formation of myriads of micropores (turbidity). The coarsening may have occurred not only through solid-state diffusion but also through solution-redeposition (Waldron *et al.*, 1993). No detail of microperthite

formation and subsequent reactions, however, has been elucidated yet (Nakano, 1992).

Syenitic rocks rarely occur in the Japanese Islands, and their occurrences are classified into two types. The rocks occur, in one type, as a small dyke or vein of metasomatic origin in granitic masses from the Seto-inlet Sea (Murakami, 1976), and, in another type, as a small discrete body in Oki-Dozen (Tiba, 1975) and Cape Ashizuri (Murakami and Matsuo, 1963).

The feldspar textures in the latter type of Japanese syenites are similar to the Klokken ones (Nakano, 1994a, b; Nakano and Hosokawa, 1995). Complicated calcium distribution patterns have been found in the alkali feldspar grains from the both syenites (Nakano and Hosokawa, 1995; Nakano, in submission). The behavior of calcium in alkali feldspar has not accepted proper attention hitherto. Calcium diffusion in feldspar is very slow in contrast to the diffusion of sodium and potassium. Calcium distribution in alkali feldspar should be noted from this point. This paper describes calcium distribution patterns in the Ashizuri alkali feldspar, and mentions their origin.

Geological setting, rock sample and analytical techniques

A Miocene plutonic complex occurs at Cape Ashizuri, located in the southwesternmost part of Shikoku, southwest Japan (Shibata and Nozawa, 1968) (Fig. 1). The complex shows a semi-circular structure, about 7 km in diameter, whose central segment consists of syenitic rocks (Murakami *et al.*, 1989). A rock sample for this study was collected from the second-stage quartz syenite (Murakami *et al.*, 1989), which belongs to the A-type granite with high-Ga and F contents (Murakami *et al.*, 1983; Imaoka *et al.*, 1991). The bulk composition of the rock

FIG. 1. Location of Cape Ashizuri and sampling point (cross).

TABLE 1. Bulk rock chemical composition of the Ashizuri quartz syenite sample by XRF analysis.

SiO ₂	65.76
TiO ₂	0.42
Al ₂ O ₃	15.97
Fe ₂ O ₃	4.00*
FeO	-
MnO	0.11
MgO	0.23
CaO	1.06
Na ₂ O	5.57
K ₂ O	5.82
P ₂ O ₅	0.07
H ₂ O ⁺	-
H ₂ O ⁻	-
Total	99.01%

*) Total iron as Fe₂O₃

sample was obtained by an X-ray fluorescence spectrometer (Table 1), using Rigaku RIX2000 of Shimane University, under the conditions of 50kV and 50mA (Sawada *et al.*, in press).

The rock consists essentially of alkali feldspar, interstitial albite, hornblende, biotite, interstitial quartz and tiny opaque minerals (ilmenite and magnetite). Chevkinite, a REE-Ti-Fe mineral, is documented from the syenite (Imaoka, 1994). The chemical compositions of the minerals are available in Murakami and Imaoka (1989).

Chemical compositions of feldspar were obtained by an electron probe microanalyzer (EPMA), JEOL JXA8800M of Shiga University, under the conditions where accelerating voltage is 15kV, probe current 2×10^{-8} A and an incident beam 5 μ m in diameter. Textural observations and X-ray mapping of alkali feldspar were also made by the same EPMA. The operating conditions for X-ray mapping are as follows: accelerating voltage, 15kV; probe current, 2×10^{-8} A; focused beam; pixels, 500 $\times$ 500; dwell time, 50sec/pixel; scanning method, by stage scan.

Observations of fine textures of alkali feldspar were carried out under a transmission electron microscope (TEM), JEOL CX200 of Niigata University.

Feldspar textures

Alkali feldspar grains in the rock sample have the length from about one to several mm, and consist of two distinct parts under an optical microscope: clear and featureless parts (CFF in Fig. 2), and turbid and microperthitic parts (FMP and MMP in Fig. 2). Clear parts have various sizes, and appear not in the rims but inside grains. Only lamellar microperthites are observed in some sections (see, later Fig. 8).

The rims of alkali feldspar grains consist of turbid parts where the lamellar texture of microperthite are well developed. Lamellae in the rims are generally thick and their shape is like film or vein (FMP in Fig. 2), which may be assigned to “pleated rims” (Parsons, 1978). Film- or vein-shape lamellae extend inward from the rims. Their width is variable and attain 100 μ m or more. The turbid parts inside feldspar grains consist of microperthite, which is generally mosaic (MMP in Fig. 2). Albite occurs interstitially along the boundaries between grains (IAB in Fig. 2). Albite lamellae in the rims are linked to the interstitial albite.

Micropores, about 1 μ m in size, are abundant in turbid parts, whereas generally scarce in clear parts. The turbidity is attributed to the presence of micropores as in the Klokken syenite feldspars (Worden *et al.*, 1990) and in the Oki-Dozen syenite feldspars (Nakano, 1994a, b).

Clear parts are cryptoperthitic under TEM (Fig. 3) and the width of lamellae in cryptoperthites varies from 6 to 35nm.

Chemical compositions and calcium distribution in alkali feldspar

Distribution maps of Ca, Na and K and back-scattered electron images (BEI) were obtained for a selected feldspar grain exhibiting typical microtextures (Fig. 5), where lamellae of microperthites are developed in the rims and in the mosaic parts around the cores, and

FIG. 2. Back-scattered electron image (BEI) showing alkali feldspar textures. Nearly on the (001) section. The central feldspar grain shows a typical texture. Light (white) parts correspond to potassium-rich parts, dark (black) to sodium-rich parts, and gray to clear feldspar parts. The rim consists of lamellar microperthites of film or vein type. Clear-featureless and mosaic-microperthitic parts coexist in the core. CFF: clear feldspar, FMP: lamellar microperthite of film or vein type, MMP: mosaic microperthite, IAB: interstitial albite, Q: quartz. The abbreviations are common to other photographs.

FIG. 3. Cryptoperthitic texture in a clear (001) feldspar grain. Wavy appearance is seen with albite twin.

TABLE 2. Selected chemical compositions of alkali feldspar in the rock

	1	2	3	4	5	6	7	8
SiO ₂	66.85	66.86	66.71	67.19	69.37	65.34	67.36	64.57
Al ₂ O ₃	19.04	19.12	19.33	18.54	18.95	17.55	19.80	17.80
FeO*	0.13	0.06	-	0.29	0.04	0.36	0.03	0.06
CaO	0.66	0.75	0.78	0.04	0.06	0.00	0.95	0.01
Na ₂ O	8.19	7.51	6.54	5.39	11.56	0.89	11.15	0.59
K ₂ O	4.40	6.03	7.33	9.44	0.17	15.80	0.24	15.19
BaO	0.15	0.13	0.06	0.00	0.01	0.00	0.01	0.26
Total	99.42	100.46	100.75	100.89	100.16	99.94	99.54	98.48
atomic numbers (O=8)								
Si	2.988	2.979	2.974	3.008	3.022	3.022	2.965	3.020
Al	1.003	1.004	1.016	0.978	0.973	0.957	1.028	0.907
Fe	0.005	0.003	-	0.011	0.001	0.014	0.001	0.003
Ca	0.032	0.036	0.037	0.002	0.003	0.000	0.045	0.001
Na	0.710	0.649	0.565	0.468	0.977	0.080	0.952	0.054
K	0.251	0.343	0.417	0.539	0.010	0.932	0.013	0.907
An	3.2	3.5	3.7	0.2	0.3	0.0	4.4	0.1
Ab	71.5	63.2	55.5	46.4	98.8	7.9	94.2	5.5
Or	25.3	33.3	40.9	53.4	1.0	92.1	1.3	94.4

* Total iron as FeO.

Nos.1-4: clear feldspar, Nos. 5 and 6: rim micropertthite, Nos. 7 and 8: inner micropertthite.

No.4: poor in calcium in spite of its clearness.

FIG. 4. Feldspar compositions on an Or-Ab-An diagram; f stands for feldspar, and mp for micropertthite. The potassium-rich compositions of the inner micropertthite overlap those of the rim micropertthite. The sodium-rich compositions of the rim micropertthite concentrate near the Ab apex. A broken line shows a tie line of a pair of a potassium phase and a sodium-rich phase having the maximum An content (7 mol%) in the inner micropertthite. The distribution area of the clear feldspar compositions is enclosed by thin solid lines.

clear parts are scattered around the cores. All the rims are poor in calcium. Most of two kinds of lamellae phases of the rim micropertthite have chemical compositions close to the end-members of Or and Ab, respectively (Nos. 5 and 6 in Table 2 and Fig. 4). The insides of the grains consist of both clear-featureless and turbid-micropertthitic parts. Chemical compositions of clear-featureless parts are around about Or₃₃Ab₆₄An₃ (Fig. 4), although they range from 25 to 50 mol% Or and from 5 to nearly 0 mol% An (Nos.1-4 in Table 2). Clear parts

FIG. 5. Distribution maps of Ca, Na and K with a BEI image for a feldspar grain. Calcium zoning, especially calcium depletion in the rim, is seen. The two squared areas (F6 and F7) were analyzed in detail, which are shown in Fig. 6 and Fig. 7. Ca-po-c: calcium-poor core. Other abbreviations are the same as those in Fig. 2.

are variable especially in An content, and some of the parts are poor in calcium (Fig. 4). Most of two kinds of inner microperthite phases show chemical compositions close to the end-members of Or and Ab, as well as the rim microperthite. Mosaic parts inside the grains are also variable in An content, and some of them are poor in calcium (Nos.7 and 8 in Table 2). The An content varies from 7 to nearly 0 mol% in the sodium-rich mosaic parts (Fig. 4). Calcium-poor mosaic parts are observed even in the cores of the grains (Ca-po-c in Fig. 5).

The detailed element distribution maps in both the rim microperthite and the inner microperthite of Fig. 5 are shown in Fig. 6 and in Fig. 7, respectively. In the rim, calcium is

FIG. 6. Distribution maps of Ca, Na and K with a BEI image for the rim area squared as F6 in Fig. 5. Calcium is very poor in the rim lamellar microperthite (film or vein type), and only cracks bear calcium. Potassium-rich phase is shown as Or, and sodium-rich phase as Ab.

poor even in the sodium-rich parts, and is poor in the whole microperthite of the rim (Fig. 6), because potassium-rich parts of microperthite are always poor in calcium. On the contrary, calcium is generally concentrated more or less into sodium-rich parts in the case of the inner mosaic microperthite, except for some calcium-poor ones. Figure 7 shows sodium-rich mosaic parts inside the grain, whose An contents are slightly higher than or nearly the same as those of the nearby clear parts.

The X-ray maps with a BEI image are shown in Fig. 8 for other feldspar grains, where only lamellar microperthites are developed throughout the grains. Clear parts are not observed in the grains. Calcium is very poor through the insides of all the grains, but calci-

FIG. 7. Distribution maps of Ca, Na and K with a BEI image for the core, mosaic microperthite area squared as F7 in Fig. 5. Calcium is poor in the Or mosaics, but relatively rich in the sodium-rich mosaics (Ab) more than the featureless feldspar. Calcium distribution is irregular. The preserved featureless part between mosaics of microperthite is exceptionally with holes, which are probably secondary, but is not turbid under a microscope.

um is concentrated only in the rim albite. Calcium distribution patterns are recognized to be different in every section or in every grain (Fig. 5 and Fig. 8).

Discussion

The present feldspar textures and calcium distribution patterns are summarized in Table 3. The cryptoperthite and microperthite formation can be interpreted by the Klokken model (Smith and Brown, 1988), based on the textural similarities between the present

TABLE 3. Summary of texture and calcium distribution in the Ashizuri alkali feldspar.

Rim	turbid	microperthitic (lamellar)	calcium-poor	An _{0-0.2} mol%
Inside	turbid	microperthitic (mosaic and lamellar)	calcium-rich └ calcium-poor	An _{~0.1-5} mol%
	clear	optically featureless (cryptoperthitic)	calcium-rich └ calcium-poor	An _{~0.1-7} mol%

FIG. 8. Distribution maps of Ca, Na and K with a BEI image for an assemblage of several feldspar grains. Only lamellar microperthites are observed throughout the grains. Calcium is wholly poor over each crystal, but richer in some of the albite parts of the rims of several grains. PM: paint marker. RAB: rim albite.

FIG. 9. Variation trends of feldspar compositions. A stippled area corresponds to the distribution area of the clear feldspar compositions shown in Fig. 4. Arrows a and b show probable calcium depletion trends in the present feldspars. Broken lines with arrows show exsolution trends connecting two constituent phases of the microperthites. Dotted lines with arrows show well-known crystallization trends, which are depicted in a much upper place in order to avoid complexity due to the overlapping of lines.

feldspar and the Klokken feldspars. The development of the rim microperthite can be interpreted to be due to hydrothermal solution-feldspar interaction at grain boundaries. The genesis of interstitial or rim albite may also be due to such reaction (Fig. 8).

In the Ashizuri syenite alkali feldspar presently studied, since calcium diffusion is very slow in feldspar, there are three plausible major processes to account for the calcium distribution patterns, especially the calcium-poor rims: magmatic crystallization (primary), high-temperature fluid-feldspar interaction (before hydrothermal microperthite formation) (Waldron *et al.*, 1993), and hydrothermal solution-feldspar interaction (Parsons and Brown, 1984).

The mosaic part in the core ("Ca-po-c" in Fig. 5) are wholly poor in calcium with a very notched outline to the irregularly surrounding parts. The core calcium-poor part is linked to the upper calcium-poor rim by an irregular vein of calcium-poor mosaics. This pattern can be interpreted to be a trace of calcium transfer from the inside to the rim. Figure 8 shows calcium concentration into the rim albite, supporting the calcium transfer from the insides to the rims of the grains.

Therefore, we present a plausible interpretation, based on the Klokken model which advocates the importance of hydrothermal (deuteric) solution-feldspar interaction. We consider that hydrothermal calcium transfer in a large scale occurred in relation to microperthite formation. During the microperthite formation, a solution-redeposition mechanism (Waldron *et al.*, 1993) worked and calcium moved strikingly into the sodium-rich phases (albite). In addition, hydrothermal calcium transfer in a large scale occurred from the insides to the rims, as seen in Fig. 8, and from the rims to the outsides, resulting in the calcium-poor rims as seen in Fig. 5. The calcium transfer is also traced as two arrows in Fig. 9.

Mass transfer has been recognized for trace elements in Klokken (Parsons *et al.*, 1988; Walker, 1990), although isochemical reactions have been estimated for major elements. The calcium distribution in the alkali feldspar should provide new attention on the behavior of plutonic alkali feldspars.

Acknowledgments—The authors thank to Prof. K. Suwa of Nihon-Fukushi University and Dr. K. Tomita of Kyoto University for their encouragements to our feldspar study. The authors are also grateful to Prof. T. Kutsukake of Aichi University for the critical reading of the manuscript, Prof. Y. Sawada for the XRF analysis at Shimane University, and two anonymous referees for contributing to the revision of the manuscript.

References

- BROWN, W.L. and PARSONS, I. (1993) Stored elastic strain energy: the driving force for low-temperature reactivity and alteration of alkali feldspar. In *Defects and processes in the solid state: Geoscience applications*, edited by J. BOLAND and J. D. FITZGERALD, *McLaren Vol.*, 267-290.
- BROWN, W.L. and PARSONS, I. (1994) Feldspars in igneous rocks. In *Feldspars and their reactions*, edited by I. PARSONS, NATO ASI Ser C421, *Kluwer Acad Publ BV*, Amsterdam, 449-499.
- IMAOKA, T. (1994) Chevkinite in syenites from Cape Ashizuri, Shikoku Island, Japan. *N. Jb. Mineral. Mh.*, 358-368.
- IMAOKA, T., NAKASHIMA, K. and MURAKAMI, N. (1991) Gallium in A-type granites from Cape Ashizuri, Kochi Prefecture, Japan. *J. Mineral. Petrol. Econ. Geol.*, **86**, 354-363 (in Japanese with English abstract).
- MURAKAMI, N. (1976) Paragenetic relations of main constituent minerals in metasomatic syenitic rocks in Japan. In *Progress in Research on Rock Forming Minerals*, edited by T. TOMISAKA, *J. Mineral. Petrol. Econ. Geol. Special Paper* 1, 261-281.
- MURAKAMI, N. and MATSUO, H. (1963) Petrological studies on the metasomatic syenites in Japan. Part 1. Syenites from the Cape of Ashizuri, Kochi Prefecture. *J. Mineral. Petrol. Econ. Geol.*, **50**, 93-109 (in Japanese with English abstract).
- MURAKAMI, N., KANISAWA, S. and ISHIKAWA, K. (1983) High fluorine content of Tertiary igneous rocks from the Cape of Ashizuri, Kochi Prefecture, Southwest Japan. *J. Mineral. Petrol. Econ. Geol.*, **78**, 497-504 (in Japanese with English abstract).
- MURAKAMI, N., UOZUMI, S. and IMAOKA, T. (1989) Ring complex of the Cape of Ashizuri, Kochi Prefecture, Japan. *Jap. Assoc. Geol. Collaboration Japan*, Monograph 36, 115-142 (in Japanese with English abstract).
- NAKANO, S. (1992) Alkali feldspar: Perthite problems. *Jour. Mineral. Soc. Japan*, **21**, 161-173 (in Japanese with English abstract).
- NAKANO, S. (1994a) Alkali feldspar in quartz syenite from Oki-Dozen island, Japan. *Geol. Rep. Shimane Univ.*, **13**, 1-8 (in Japanese with English abstract).
- NAKANO, S. (1994b) Mapping analyses of alkali feldspars in quartz syenite from Oki-Dozen with an electron probe microanalyser. *Mem. Fac. Educ. Shiga Univ.*, **44**, 39-50 (in Japanese with English abstract).
- NAKANO, S. and HOSOKAWA, E. (1995) Microtextures in syenite alkali feldspars (2): the Ashizuri syenite. Abst. Joint Meet. (Soc. Resource Geol., Assoc. Mineral. Petrol. Econ. Geol., Mineral. Soc. Japan), **25**. (in Japanese)
- PARSONS, I. (1978) Feldspars and fluids in cooling plutons. *Mineral. Mag.*, **42**, 1-17.
- PARSONS, I. and BROWN, W. L. (1984) Feldspars and the thermal history of igneous rocks. In *Feldspars and feldspathoids*, edited by W. L. BROWN, *Reidel, Dordrecht*, 317-371.
- PARSONS, I., REX, D. C., CUISE, P. and HALLIDAY, A. N. (1988) Argon-loss by alkali feldspars. *Cosmochim. Acta*, **52**, 1097-1112.

- SAWADA, Y., NAKAMURA, T., UMEDA, S., YOON, S. and TOKUOKA, T. (in press) Drifted pumice derived from Ulleung island in Holocene sediments at Oda, Shimane Prefecture, southwest Japan. *Quaternary Research*. (in Jap.)
- SHIBATA, H. and NOZAWA, T. (1968) K-Ar ages of granitic rocks of Ashizuri-misaki, Takatsuki-yama and Omogo, Shikoku, Japan. *Bull. Geol. Surv. Japan*, **19**, 11-16.
- SMITH, J. V. and BROWN, W. L. (1988) Feldspar minerals 1. *Springer-Verlag, Berlin, Heidelberg, New York* 828pp.
- TIBA, T. (1975) Geology of Dozen, Oki islands. *Bull. Natn. Sci. Mus. Ser. C*, **1**, 137-145.
- WALDRON, K., PARSONS, I. and BROWN, W. L. (1993) Solution-redeposition and the orthoclase-microcline transformation: evidence from granulites and relevance to ^{18}O exchange. *Mineral. Mag.*, **57**, 687-695.
- WALKER, F. D. L. (1990) Ion microprobe study of intragrain micropermeability in alkali feldspar. *Contrib. Mineral. Petrol.*, **106**, 124-128.
- WORDEN, R., WALKER, F. D. L., PARSONS, I. and BROWN, W. L. (1990) Development of microporosity, diffusion channels and deuteric coarsening in perthitic alkali feldspars. *Contrib. Mineral. Petrol.*, **104**, 507-514.

Received December 24, 1996; accepted April 28, 1997