LETTER

Partial replacement of plagioclase by smectite within the Takakumayama Granite, Kagoshima, Japan

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Plagioclase crystals up to 5 mm long partially replaced by pink-colored smectite, from the Takakumayama Granite, Kagoshima, Japan, were examined using optical microscopy, X-ray diffraction, electron probe microanalysis, and X-ray analytical microscopy. A map of Ca concentration reveals distinct zoning that is probably due to abrupt changes in growth conditions. In terms of zoning, there are three distinct regions within the plagioclase crystal: (1) an unzoned core, (2) an intermediate region between the core and the rim that corresponds to the pink alteration mineral visible in hand specimens, and (3) oscillatory zoning in the rim. The pink alteration mineral was identified as smectite, with a characteristic basal spacing of 1.58 nm under air-dried and untreated conditions. The alteration is associated with defects and dendritic textures that are abundant in the intermediate regions of the crystals. It is postulated that the alteration resulted from the action of externally derived hydrothermal fluids that accessed the defects and dendritic texture in the plagioclase crystals via microfractures that subsequently sealed during cooling of the granite.

Keywords: Replacement, Smectite, Plagioclase, Hydrothermal alteration, Takakumayama Granite

INTRODUCTION

A number of studies have reported that the alteration of plagioclase is mainly related to the activity of hydrothermal fluid (e.g., Fournier, 1965; Page and Wenk, 1979; Peters and Hofmann, 1984; Kamineni et al., 1993; Que and Allen, 1996). During fieldwork examining granitic rocks and their constituent minerals within the Takakumayama district, Kagoshima Prefecture, Japan, pink altered plagioclases up to 5 mm long were observed within the Honjo River in the Sarugajo Valley. As the altered plagioclases are relatively euhedral and are easily removed from the host rock, they appear as pseudomorphs after plagioclase in hand specimens. Most studies on the petrogenesis of granitic rocks in the Takakumayama district have involved heating experiments on alkali feldspar (Yamamoto, 1975) and hydrothermal experiments on whole-rock samples (Yamamoto, 1976, 1977). Although Hibbard (1981) discussed dendritic texture within plagioclase within these rocks in relation to magma mixing, the descriptive mineralogy of these plagioclase crystals has not been described. The purpose of the present work is to describe the occurrence and origin of the pink altered plagioclase crystals within granitic rocks of the Takakuma-

yama district.

OCCURRENCE

Takakumayama is located on the west of the Osumi Peninsula, approximately 25 km southeast of Kagoshima City. The Takakumayama granitic stock is one of a number of Middle Miocene granitoids that intrude the Late Mesozoic Takakumayama Formation: an accretionary complex within the Shimanto Belt of the Outer Zone of Kyushu. The granitic rocks are divided into two types, Shinkoji type (granodiorite) and Sarugajo type (aplitic adamellite), on the basis of contrasting petrological characteristics (Kawachi, 1961). The detailed geology and petrology of the Takakumayama granitic stock have been described previously (e.g., Oba, 1958, 1963, 1967; Ishihara and Kawachi, 1961; Ota, 1963; Ota and Kawachi, 1965; Kawachi, 1969; Tsusue, 1973). To investigate the formation of the Takakumayama Granite, Yamamoto (1975) carried out chemical and X-ray powder diffraction studies on alkali feldspar from the granite and conducted heating experiments in air. Crystallization temperatures were estimated to have been above 700 and 800 °C for the granodiorite and aplitic adamellite, respectively. Hydrothermal experiments by Yamamoto (1976, 1977) revealed that the granite formed in water-saturated condi-

Figure 1. Photograph of a hand specimen of Shinkoji-type granodiorite from Takakumayama. Pink altered plagioclase is marked by the arrow. Bt, biotite; Kfs, alkali feldspar; Pl, plagioclase; Qtz, quartz; Tur, tourmaline.

Figure 2. Photomicrograph of the plagioclase crystal with pink alteration zoning (crossed polars) that is evident in the upper right of Figure 1. Boundaries between different regions of zoning are marked by dotted lines. See Figure 1 for abbreviations.

Figure 3. X-ray powder diffraction pattern for pink alteration mineral within Shinkoji-type granodiorite from Takakumayama (40 kV, 20 mA, step, 0.01°; speed, 2°/min). The peaks for smectite and plagioclase were identified. Sm, smectite.

Figure 4. Compositional maps of plagioclase containing pink altered zones sampled from Shinkoji-type granodiorite from Takakumayama. Warm colors correspond to high concentrations. Boundaries of the different regions of zoning are marked by dotted lines.

tions at pressures below 1 kbar and at a temperature of approximately 720 °C. Miyachi (1985) determined a zircon fission-track age of 12.7 ± 1.2 Ma for granitic rocks in this area.

The Shinkoji-type granodiorite is composed mainly of quartz, alkali feldspar, plagioclase, biotite, and accessory minerals such as muscovite, zircon, apatite, magnetite, garnet, and tourmaline. Pink, altered, euhedral plagioclase crystals up to 5 mm long are mantled by white plagioclase and in some cases have a black core; these are found only in the Shinkoji-type granodiorite (Fig. 1). Alkali feldspar shows no evidence of alteration or red pigmentation due to the presence of iron oxide. The plagioclase occurs as two types of contrasting size: euhedral crystals up to 5 mm long with remarkable optical zoning, albite-carlsbad twins, and dusty zoning; and subhedral

crystals approximately 1 mm long with optical zoning and albite–carlsbad twins (Ishihara and Kawachi, 1961). The pink altered plagioclase studied here occurs as the former type.

ANALYTICAL METHODS

Thin sections were made from rock fragments of Shinkoji-type granodiorite from Takakumayama and observed under a polarizing microscope. For mineral identification, X-ray powder diffraction patterns were obtained using a Rigaku Geigerflex CN4037A1 X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation (40 kV, 20 mA). Chemical analyses were carried out using a JEOL JXA-8621 EPMA (20 kV, 1.0×10^{-7} A for qualitative analyses; 20 kV, 1.0×10^{-8} A for quantitative analyses; 10 μm spot size). ZAF online full matrix corrections were used for quantitative analyses (Reed, 1996). Compositional maps were obtained using a HORIBA XGT-5000 X-ray analytical microscope (50 kV, 1.00 mA; 10 μm spot size).

RESULTS

Microscopic observations

A photomicrograph (crossed polars) of the pink altered plagioclase is shown in Figure 2. In thin section, three zones can be recognized within plagioclase crystals: (1) an unzoned core, (2) an intermediate region between the core and the rim that corresponds to the pink altered mineral visible in hand specimens, and (3) oscillatory zoning in the rim. In Figure 2, the boundaries between these zones are indicated by dotted lines. The pink altered mineral appears a dusty pale brown color in thin section. Alteration is generally restricted to the intermediate region. It appears that alteration began in the intermediate zone before spreading to the cores and rims along defects such as cleavage planes. Remarkable albite–carlsbad twins and inclusions of biotite are present within the cores. The zones of oscillatory zoning in crystal rims are free of inclusions and represent an aggregation of multiple plagioclase grains. Macroscopically, the cores and rims are colorless and transparent.

Table 1. Representative microprobe analyses of plagioclase crystals containing pink altered zones and unaltered plagioclase from the same sample of Shinkoji-type granodiorite from Takakumayama

	PIP (Core)		PIP		PIP (Rim)	PI
	An-rich	Ab-rich	(Intermediate)			
SiO ₂	55.31	57.75	57.39		61.09	62.05
Al ₂ O ₃	28.48	26.55	26.92		23.87	24.13
CaO	10.77	8.82	8.79		5.60	5.47
Na ₂ O	5.14	6.46	6.33		8.21	8.52
K ₂ O	0.16	0.17	0.18		0.34	0.32
Total	99.86	99.75	99.61		99.11	100.49
Cations per 8 oxygens						
	Obs.	Calc.*	Obs.	Calc.*	Obs.	Calc.*
Si	2.490	2.490	2.590	2.592	2.578	2.581
Al	1.511	1.510	1.404	1.408	1.425	1.419
Ca	0.520	0.524	0.424	0.420	0.423	0.429
Na	0.449	0.453	0.562	0.558	0.551	0.551
K	0.009	0.009	0.010	0.010	0.010	0.010
Total	4.979	4.986	4.990	4.988	4.987	4.990
Designation by feldspar end members						
CaAl ₂ Si ₂ O ₈	52.4		42.0		42.9	26.5
NaAlSi ₃ O ₈	45.3		55.8		55.1	71.5
KAlSi ₃ O ₈	0.9		1.0		1.0	2.0
□Si ₄ O ₈ **	1.4		1.2		1.0	-
Total	100.0		100.0		100.0	100.0

Abbreviations: PIP, plagioclase crystal containing pink altered zone; PI, unaltered plagioclase.

* Calculated on the basis of end-member.

** Excess silica component; $\square$ stands for a defect at M site.

X-ray diffraction analyses

The mineral that forms the pink altered zone within plagioclase crystals has a basal spacing of 1.58 nm under air-dried and untreated conditions (Fig. 3). This implies the presence of the clay mineral smectite. The 0.149 nm peak indicates the (060) reflection of smectite and confirms its dioctahedral character. Plagioclase was also identified within the intermediate region, but iron oxides and other minerals that can contribute to pink coloration were not observed. Precise identification of the clay mineral requires further treatment with ethylene glycol, glycerol, cation exchange, and heating.

Chemistry

Representative microprobe analyses of crystals of plagioclase from the granodiorite are provided in Table 1. Five elements were detected: Si, Al, Ca, K, and Na, but Fe and Mn were absent. The calculated end members are $\text{CaAl}_2\text{Si}_2\text{O}_8$ (An), $\text{NaAlSi}_3\text{O}_8$ (Ab), KAlSi_3O_8 (Or), and $\square\text{Si}_4\text{O}_8$. $\square\text{Si}_4\text{O}_8$, which is an excess silica component in feldspar, was calculated for the core and the intermediate regions of samples. Exsolution is evident in the core region. The An contents of the core are 52.4 and 42.0 (mol%) in the An- and Ab-rich regions, respectively. Both the rim of altered plagioclase and plagioclase crystal without alteration zoning have an An content of approximately 25 (mol%).

Quantitative variations in chemistry were determined using an X-ray analytical microscope (Fig. 4). The map of Ca concentration shows distinct zoning that probably reflects abrupt changes in growth conditions. The boundaries between growth stages evident in Figure 4 are indicated by dotted lines. K, Mn, and Fe are concentrated within the altered zone and vary in concentration independently of Ca content. The cause of the pink color observed within the intermediate region of the plagioclase crystals may be the occurrence of Fe- and/or Mn-bearing smectite. The compositional maps reveal that the pink altered plagioclase is composed of a Ca-rich core, a Ca-rich intermediate region that is partially replaced by smectite, and a Ca-poor rim.

SUMMARY

Hibbard (1981) presented data on the relationship between zoning and dendritic texture within plagioclase from the Takakumayama Granite. Dendritic texture is commonly developed within the intermediate region of plagioclase crystals, but is absent from the cores and rims. The replacement of plagioclase by smectite is therefore

associated with the occurrence of dendritic texture. It is postulated that the alteration resulted from the action of externally derived hydrothermal fluids that gained access to defects or dendritic texture within plagioclase crystals via microfractures that subsequently sealed during cooling of the granite. The petrogenetic environment estimated on the basis of this descriptive mineralogy is in accordance with the water-saturated conditions of crystallization proposed by Yamamoto (1976, 1977).

The results of the present study lead to the following conclusion: the pink altered plagioclase formed hydrothermally via the partial replacement of plagioclase by smectite within the intermediate regions of crystals. Further investigation is required to completely understand the formation of the Takakumayama Granite, but the new findings of the present study on pink altered plagioclase crystals provide fundamental information on the cooling history and, in particular, hydrothermal events of the Takakumayama Granite.

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