

Microprobe analyses of halogen contents in apatite of quartz diorite of the Koyama calc-alkaline intrusive, Susa, southwest Japan

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In quartz diorite of the Koyama calc-alkaline intrusive, Susa, southwest Japan, small columnar crystals and needles of apatite are included in interstitial amphibole, biotite and quartz which have formed under late-magmatic oxidizing condition of interstitial magma. Microprobe analyses of apatite show that the columnar apatite has comparatively large Cl content ranging from 0.27 to 0.60 per formula unit based on (O, OH, F, Cl)=26, relative to the needles of apatite (0.08-0.26). There is no significant difference in (F/OH) ratio between the two types of apatite. The columnar apatite with the large Cl content can not be considered to have crystallized from Cl-depleted liquid after degassing. It is suggested that diffusive loss of H₂, promoting oxidation of interstitial magma, have preceded the vapor saturation and the resulting degassing process.

Introduction

Quartz diorite of the Koyama intrusive contains interstitial, hydrous silicate and Fe-Ti oxide minerals, which have formed under progressively oxidizing condition in late- and post-magmatic process of interstitial residuum. Mineral chemistries and textural relations suggest that the late-magmatic oxidation is related to increasing vapor pressure of interstitial liquid and the related diffusive loss of H₂ (Yamaguchi, 1987A, 1987B, 1987C). Halogen contents in apatite is known to be a useful indicator of vapor saturation (Tsuchiya, 1986). The quartz diorite contains small crystals of apatite, which are included in these interstitial phases. I will preliminarily report the occurrence and halogen contents of apatite, and will discuss the compositional change of apatite, responsible for vapor saturation and the resulting degassing process.

Geological setting

The Koyama calc-alkaline intrusive (2.0×2.4 km) intrudes the Susa groups of Miocene Age, converting them to pyroxene hornfels facies in the contact aureole (Yamazaki, 1967; Yamaguchi *et al.*, 1974; Suzuki and Nishimura, 1983; Okamoto, 1983). The intrusive body is considered to have solidified at approximately 14 Ma, from the data of biotite K-Ar age (Matsumoto and Itaya, 1986). The body consists of olivine gabbro, anorthositic gabbro, quartz gabbro and quartz diorite, with gradational con-

tacts. The quartz diorite occurs in the upper border of the body.

In the quartz diorite, amphibole, Fe-Ti oxides, biotite, potassium-feldspar and Quartz are interstitial to early-crystallized plagioclase and pyroxenes. Plagioclase, ortho- and clinopyroxene show strong zoning. Plagioclase generally has calcic core (An_{85}). Clinopyroxene is zoned with Fe-increase trend in core ($Ca_{40}Mg_{50}Fe_{10} \rightarrow Ca_{38}Mg_{35}Fe_{27}$), however, shows contrasting reverse trend in rim, with Fe-decreasing and Ca-increasing ($\rightarrow Ca_{45}Mg_{35}Fe_{20}$). The clinopyroxene crystallization is estimated to have terminated at approximately 600°C, using the pyroxene thermometry proposed by Lindsley (1983).

Magnetite mostly intergrows with ilmenite. The magnetite-ilmenite composite grains are texturally associated with amphibole and biotite, around pyroxene and plagioclase, but are not included in these early-formed phases. Equilibrium temperature, obtained using the Fe-Ti oxide thermometer (Spencer and Lindsley, 1981), is about 600°C at fO_2 of 10^{-19} – 10^{-21} , similar to that for rim of clinopyroxene (Yamaguchi, 1987B). This provides an evidence, in consistence with the textural relationship between pyroxene and Fe-Ti oxide, strongly suggesting that the reverse trend of the last pyroxene crystallization was resulted from fractionation of Fe by the Fe-Ti oxide precipitation.

Small potassium-feldspar (20–100 μm) occurs, occasionally intergrown with the reequilibrated outermost rim of plagioclase. Equilibrium temperature derived from the two feldspar thermometry (Whitney and Stormer, 1977) is within 490–590°C (Yamaguchi, 1987). Two feldspar compositions in the immediately adjacent contact zone yield lower equilibrium temperature of 450–500°C.

Occurrence and microprobe analyses of apatite

Apatite in the quartz diorite occurs with two different shapes, 1) hexagonal columnar crystal of apatite (0.02×0.04 – 0.04×0.15 mm), and 2) needle of apatite (0.01–0.1 mm long). All of apatites are, however, not necessarily distinctive, rather gradually differ between the two types. The columnar apatites are in many cases included in amphibole, biotite and often quartz. The needles of apatite are mostly included in quartz, having no preferred orientation, and occasionally in amphibole and biotite.

Microprobe analyses of apatite were made using a JXA-733 microanalyser. The analytical conditions were previously described (Kawakatsu and Yamaguchi, 1987). NaCl, natural fluorapatite and chlorapatite were used as reference standard, respectively, for Cl, F, and P. Apatite structural formulae were calculated on the basis of 26 (O, OH, F, Cl), and OH content is calculated on the assumption of $Cl + F + OH = 2.0$ in the structural formula. The resultant analyses of apatite are listed in Table 1, and Cl, F, and OH contents are plotted in Fig. 1.

In the structural formulae, shown in Table 1, (P+Si) and total cation numbers are

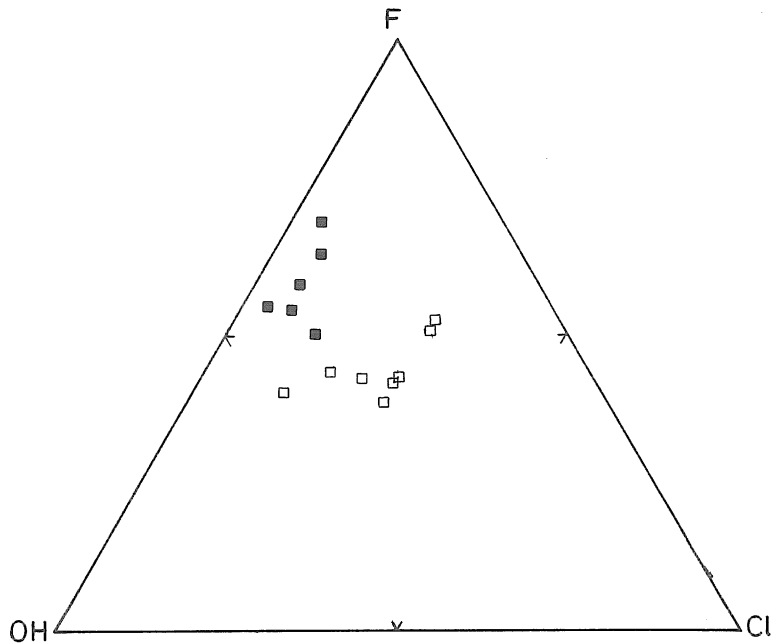


Fig. 1. Molecular proportions of F, OH, and Cl of apatite. Open square, hexagonal columnar apatite; solid square, needle of apatite.

clustered, respectively, near 6.0 and 16.0. There is no significant variation in apatite composition, except for halogen content. The columnar apatite has comparatively large Cl content ranging from 0.27 to 0.60 per formula unit. The needles of apatites are poor in Cl, ranging from 0.08 to 0.26, relative to the columnar apatites. There is no significant difference in (F/OH) ratio between the two types of apatite.

Discussion

Cl and F contents of apatite provide potentially useful information about water saturation of magma (Tsuchiya, 1986). Kilinc and Burnham (1972) have shown that Cl has a strong affinity for aqueous phase exsolved from crystallizing magma. Therefore, magma decreases in Cl content during degassing process (Anderson, 1974). On the other hand, F is not so affected by vapor separation and tends to remain in magma (Munoz and Eugster, 1969; Fuge, 1977).

Halogen contents of apatite have been studied in plutonic intrusions (Nash, 1972, 1976; Roegge *et al.* 1974; Nedachi and Ueno, 1981; Tsuchiya, 1986). Tsuchiya (1986) made detailed study on halogen contents of apatite in the Matsumae plutonic rocks. In these rocks, Cl content of apatite crystallized from primarily water-rich magma (Am series) is generally low, whereas that in water-undersaturated magma (Pl series) is rather

Table 1. Representative analyses of apatite.

	1	2	3	4
P ₂ O ₅	41.72	41.32	42.12	42.20
SiO ₂	0.21	0.27	0.01	0.05
TiO ₂	0.00	0.00	0.02	0.01
Al ₂ O ₃	0.00	0.00	0.00	0.00
FeO*	0.31	0.26	0.00	0.00
MnO	0.09	0.08	0.12	0.13
MgO	0.01	0.01	0.00	0.00
CaO	54.69	54.54	55.47	55.75
Na ₂ O	0.20	0.07	0.01	0.03
K ₂ O	0.01	0.04	0.00	0.00
F	1.59	1.94	2.20	2.59
Cl	1.67	2.06	0.46	0.33
Sum	100.50	100.59	100.42	101.10
-O=F, Cl	1.05	1.28	1.03	1.17
Total				
Structure formulae on the bases of 26 (O, OH, F, Cl)				
P	5.971	5.957	5.993	5.982
Si	0.035	0.046	0.002	0.008
Ti	0.000	0.000	0.003	0.002
Al	0.000	0.000	0.000	0.001
Fe	0.044	0.037	0.000	0.000
Mn	0.013	0.012	0.017	0.018
Mg	0.003	0.003	0.000	0.000
Ca	9.906	9.950	9.989	10.002
Na	0.066	0.022	0.004	0.010
K	0.003	0.008	0.000	0.001
F	0.848	1.045	1.171	1.374
Cl	0.479	0.595	0.132	0.094
OH*	0.673	0.360	0.697	0.532

1 and 2, hexagonal columnar apatite; 3 and 4, needle of apatite.

* Total Fe as FeO.

** Calculated on the basis of F+Cl+OH=2.0 in the structural formula.

high in less differentiated rocks and abruptly decreases without decrease in F in the course of differentiation. He explained these behaviors of Cl and F in apatite in terms of the degassing process (Tsuchiya, 1986).

In the Koyama intrusive, the solidification process was principally controlled by incomplete settling of crystalline phases in the magma chamber (Yamazaki, 1967; Yamaguchi *et al.*, 1974). The various rock types in the intrusive were evolved in

response to different degree of accumulation of early-formed pyroxene and plagioclase. Amphibole and biotite in all of the rock types formed at the latest stage of solidification of interstitial magma and at the subsequent post-magmatic process. In the quartz diorite, mineralogic data and textural relation, described above, show that amphibole began to form when pyroxene crystallization terminated at about 600°C under oxidizing condition responsible for abundant Fe-Ti oxide precipitation (Yamaguchi, 1985). This suggests that increasing vapor pressure of interstitial liquid and the related diffusive loss of H₂ (Czamanske *et al.*, 1981) play a potential role on the abrupt start of progressive oxidation in the latest magmatic stage.

Textural evidence indicates that apatite in the quartz diorite began to form in the latest stage of solidification of interstitial liquid, at which pyroxene crystallization was replaced by the formation of amphibole, biotite and Fe-Ti oxides. The compositional change of apatite, with decrease in Cl content without decrease in F, is essentially similar to that of apatite in the Matsumae plutonic rocks (Tsuchiya, 1986). The columnar apatite, associated with amphibole and biotite, is considered to have formed earlier than the needle of apatite. The columnar apatite with significantly large Cl content can not be considered to have crystallized from strongly Cl-depleted liquid after degassing. Therefore, it is suggested that the oxidation of the interstitial magma, responsible for the reverse trend of pyroxene crystallization and for the abundant Fe-Ti oxide precipitation, is not essentially related to the degassing process involving Cl depletion of magma. Tsuchiya (1986) pointed out no correlation between oxidation state and the variation of Cl content of apatite in the Matsumae plutonic rocks, and explained that the oxidation of magma was not brought about by vapor exsolution but by diffusive loss of H₂ through the country rocks. In the Koyama intrusive, diffusive loss of H₂, promoting oxidation of interstitial magma, may have preceded the vapor saturation of magma and the resulting degassing process.

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