ANOMALOUS CHLORINE CONTENTS OF MIOCENE GRANITOIDS FROM TSUSHIMA, JAPAN

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Miocene granite and granodiorite of Tsushima islands contain 700 to 1,400 ppm Cl in general, which are higher in one order of magnitude than chlorine contents of common granitoids in Japan. The Miocene granitoids belong to so-called calc-alkaline series but slightly potassic, and contain no Cl-minerals. The main cause for the anomalous values seems to be chlorine trapped in fluid inclusions contained in various rock-forming minerals. Ratios of chlorine contained in fluid inclusions and rock-forming minerals appear to increase with increasing silica contents. This Cl-enrichment in aqueous phase during the magmatic fractionation as well as original high content may have played an important role for lead-zinc mineralization of the Taishu mine.

INTRODUCTION

Japanese granitoids contain generally 100 to 200 ppm Cl. The average contents for those from non-metamorphic terrains for example, vary from 137 ppm ($n=60$) of the San'in belt to 187 ppm ($n=48$) of the Kitakami and Abukuma belts (Ishihara and Terashima, 1977). However the reconnaissance study has shown that Miocene granites from Tsushima islands are very rich in chlorine, ranging from 600 to 960 ppm. The samples used for that study are obtained from satellitic small masses around the main granitic stock. Thus additional sampling was made on the main, central mass, and the samples collected were analyzed for Cl and F and major elements in order to clarify petrochemical character of the Miocene granitoids.

The samples are so-called fresh rocks available on surface. They were washed by

water and crushed under 130 mesh. Chlorine and fluorine were analyzed by a spectrophotometric method (Terashima, 1974). The other elements were analyzed by the ways described in Terashima (1978, 1979).

GENERAL REMARKS

Tsushima consists of North and South islands. The granitoids occur in the South island as small stocks, less than 5 km in diameter (Fig. 1), but a large hidden mass is assumed for presence of satellitic masses around the main mass and thermal aureole recorded in the roof sedimentary rocks. The hidden mass may even be present in the North island according to drill core study (Metallic Mining Agency of Japan, 1974).

The granitoids have Miocene age (12 Ma, Kawano and Ueda, 1966), low Sr initial ratio (0.7037, Shibata and Ishihara, 1979) and high $\delta^{34}\text{S}$ rock sulfur +2.5%, Sasaki and Ishihara, 1979). They intrude into Taishu formation of Oligocene-Miocene-age, which consists of sandstone, shale and inter-

Fig. 1 Distribution of the Miocene granitoids and locality of the analyzed samples in the South island, Tsushima. Geological information is taken from data provided by the Taishu mine. Solid circle, the magnetite-series and open circle, the ilmenite-series of Ishihara (1977).

calated silicic volcanic rocks. This formation is tightly folded; the granitoids occur in one of the anticlinal axes. Lead-zinc veins of the Taishu mine are distributed in the north-northwestern flank of the granitic masses.

The granitoids are generally fine-grained monzogranite and granodiorite. Biotite is universal mafic silicate; hornblende is common in the granodiorite. Magnetite is present in general, but absent in the satalitic masses where interaction of the gra-

nitoids with country rocks is evident. pyrrhotite and graphite-like mineral are seen in some of the magnetite-free granitoids.

Pyrite is abundant locally. Thus, the Miocene granitoids belong essentially to the magnetite-series of Ishihara (1977) (see also Fig. 1).

ANALYTICAL RESULTS

All the rocks collected were analyzed for Cl and F, and also P_2O_5 . The results are

Table 1 List of the analyzed samples and results of P_2O_5 , Cl and F analyses

Sample No	Sample description	$P_2O_5(\%)$	Cl(ppm)	F(ppm)	$\chi(\times 10^{-6}, \text{emu/g})$
Central mass					
<u>TI-10</u>	Fine-grained, biotite-amphibole granodiorite	0.28	1385	580	1056
<u>TI-20A</u>	Fine-grained, amphibole-biotite granodiorite	0.22	1220	400	309
<u>TI-20B</u>	Medium-grained, amphibole-biotite granodiorite	0.22	1420	520	679
TI-21A	ditto	0.15	1400	420	521
<u>TI-11</u>	Medium-grained, amphibole-bearing biotite granodiorite	0.14	1160	680	870
TI-15	Medium-grained, (amphibole-bearing) biotite granodiorite	0.14	1340	550	35
TI-18A	Fine-grained, biotite granodiorite	0.14	1190	350	68
<u>TI-19</u>	Fine-grained, (amphibole-bearing) biotite monzogranite	0.07	890	190	602
<u>TI-12</u>	Medium-grained, biotite monzogranite	0.02	1130	280	77
TI-13	ditto	0.03	715	600	23
<u>TI-14A</u>	ditto	0.04	845	460	279
TI-2	Fine-grained biotite monzogranite	0.03	710	310	34
TI-14B	ditto*	0.04	915	300	19
Southeastern mass					
TI-17	Medium-grained, biotite granodiorite	0.25	4400	1010	44
TI-16A	Coarse-grained, biotite granodiorite*	0.04	1125	480	23
TI-16B	Fine-grained, biotite monzogranite	0.05	920	440	27
TI-1	ditto	0.05	930	540	12
Northern mass					
TI-4	Coarse-grained, biotite granodiorite	0.12	960	830	21
TI-3	Medium-grained, biotite monzogranite	0.06	608	670	269

* Feldspars slightly argillized

X, Magnetic susceptibility measured by H. KAWAYA

Underlined sample numbers are those listed in Table 2

Table 2 Major chemistry of selected samples from the central mass and southeastern mass (TI-17). Analytical methods for major components are described in Terashima (1979). Sulfur and total carbon by infrared absorption spectroscopy (Terashima, 1978).

	TI-17	TI-10	TI-20B	TI-20A	TI-11	TI-18	TI-19	TI-14A	TI-12
SiO ₂	61.61	61.91	64.16	66.41	68.29	68.58	73.23	75.02	75.94
TiO ₂	0.90	1.21	0.76	0.63	0.57	0.59	0.28	0.22	0.16
Al ₂ O ₃	15.30	15.23	15.88	15.86	14.92	14.38	13.31	13.02	12.71
Fe ₂ O ₃	1.52	2.36	1.88	1.43	1.97	1.07	1.45	1.19	0.70
FeO	6.87	4.83	4.03	3.24	2.69	3.31	1.45	0.91	0.84
MnO	0.041	0.104	0.036	0.027	0.043	0.015	0.015	0.023	0.015
MgO	2.71	2.12	1.52	1.20	0.98	1.10	0.47	0.32	0.26
CaO	3.20	5.75	4.20	3.61	3.10	2.56	2.00	1.34	1.32
Na ₂ O	3.48	3.40	3.44	3.95	3.65	2.96	2.98	3.18	3.06
K ₂ O	3.03	2.16	3.07	2.93	3.25	4.09	4.30	4.31	4.47
P ₂ O ₅	0.25	0.28	0.22	0.22	0.14	0.14	0.07	0.04	0.02
S	0.066	0.034	0.032	0.045	0.004	0.636	0.025	0.003	0.003
C	0.005	0.012	0.006	0.005	0.007	0.002	0.003	0.003	0.004
H ₂ O(+)	0.80	0.46	0.58	0.45	0.34	0.48	0.38	0.36	0.39
H ₂ O(-)	0.11	0.03	0.07	0.05	0.02	0.07	0.03	0.08	0.09
Total	99.89	99.89	99.88	100.06	99.98	99.94	99.97	100.02	99.98

C: carbon from mostly carbon dioxide

listed in Table 1. Chlorine varies generally from 1400 ppm to 600 ppm, which confirms the results of the previous reconnaissance study. Unusually high value, 4400 ppm, was found in granodiorite from the southeastern satellitic mass. Content of chlorine is more than that of fluorine, which is also unusual as compared with the other granitoids in Japan (see Ishihara and Terashima, 1977).

In Table 1, the samples are listed in the order of their color index obtained in the field work. In the main mass, content of chlorine decreases slightly, from 1400 ppm to 700 ppm, with decreasing the color index. However, the phosphorus content decreases in the order of magnitude from granodiorite to monzogranite.

Chlorine minerals are known to occur in alkaline granites, so that nine samples were selected for major chemical analysis, in order to identify the rock-series of these granitoids. The results are given in Table 2.

The analyzed samples have silica contents from 62 to 76 percent and normative feldspar ratios of granodiorite and monzogranite. As compared with the average composition of the Japanese granitoids (Aramaki et al., 1972), the Miocene granitoids are about 1 percent rich in K_2O , but the silica and sodium are close to the averages (Fig. 2). Thus the granitoids are so different from rocks to be called alkaline-series, but belong to normal calc-alkaline series granitoids slightly potassic.

As to the femic components, the Miocene granitoids are characterized by abundance of the total iron. Contents of both Fe_2O_3 and FeO are higher than those of the Japanese average (Fig. 3). Titanium is also higher than the average. The unusually high chlorine rock of TI-17 is unique in its

Fig. 2 Salic components plotted against the differentiation index. Solid circle, samples from the central mass; open circle, those from the southeastern mass; straight line, the Japanese average.

high contents of FeO and MgO but low contents of Al_2O_3 and CaO .

DISCUSSION

Among common rock-forming minerals of calc-alkaline series rocks, apatite and biotite may be a major carrier of chlorine. As compared with a wide variation in content of phosphorous and ferromagnesian components, however, change of chlorine contents is small indicating some other source for chlorine. Nedachi (1980), indeed,

Fig. 3 Femic components plotted against the differentiation index. Circle and line designation, see Fig. 2. In P_2O_5 and Cl section, Cl is shown by triangle. Broken lines are general trend of P_2O_5 and Cl of the Miocene granitoids.

studied these minerals and found that chlorine contents of apatite and biotite are around 0.3 and 0.06 percent, respectively.

Poly-phase inclusions have been found in quartz of the Miocene granitoids of the northern satellitic group (Imai et al., 1971). Preliminary study by S. Takenouchi on our samples indicate that the poly-phase inclusions are abundant in rocks having high chlorine contents of the main mass (person-

al communication, 1978). Thus, the highly saline inclusions (up to ca. 60 wt. %, NaCl Imai et al., 1971), either in quartz or other rock-forming minerals, could be a major cause for the anomalous chlorine values of the Miocene granitoids. The poly-phase inclusions are seen even in granodiorite. The Miocene granitoids seem to have had originally high chlorine content.

As is shown in Figure 3, ratios of Cl/ P_2O_5 and Cl/ferromagnesian components are higher in the rocks of high DI range than those of low DI range. This observation may indicate that aqueous phase of the well differentiated granites, as compared that of granodiorite, is very enriched in chlorine, which agrees with the general understanding on behaviour of chlorine in magmatic differentiation (Kilinc and Burnham, 1972; Fuge, 1977; Burnham and Ohmoto, 1980). This highly saline fluid may have been attributed to lead-zinc mineralization at Taishu, as concluded by Imai et al. (1971).

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対馬産花崗岩類中の異常な塩素含有量

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対馬の新第三紀花崗岩類中の塩素含有量は 700~1400 ppm で他の地域に比べておよそ一桁高い値を示す。これら花崗岩類は SiO_2 62~76% の変化を示し、わずかにカリウムに富むがいわゆるカルクアルカリ岩に分類されるものであり、塩素鉱物は含まれていない。塩素量は苦鉄質な岩石ほど多い傾向を示す。

SiO_2 に対する P_2O_5 , $\text{FeO}+\text{MgO}$, Cl の相関性、鏡下にみられる流体包有物などから、岩石中の塩素は主として各種造岩鉱物に含まれる流体包有物に起因すると考えられる。流体包有物中の塩素/燐灰石+黒雲母中の塩素比は SiO_2 の増加と共に上昇し、このことは対州鉱山の鉛・亜鉛鉱化作用と密接であったと思われる。