

Role of Halogen Elements on the Panguna Porphyry Copper Mineralization, Bougainville, Papua New Guinea

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Abstract

Chemical compositions were measured on the apatite and biotite of magmatic and hydrothermal origin from the Panguna porphyry copper deposit, Papua New Guinea.

The magmatic apatite and biotite in the intrusives which predated the mineralization were characterized by a high Cl/OH ratio. The Cl/OH ratios of the earlier hydrothermal minerals (biotitization and early veining stages) were almost as high as in the magmatic stage. The F/Cl/FH₂O ratios of the magmatic and early hydrothermal stages were rather high, compared with other mining areas in the island arcs. The apatites showed the effect of chemical exchange during the mineralization and/or later hydrothermal stage. There were two exchanging processes; Cl leaching in the surrounding potassic alteration zone (high Cu precipitation zone), and F additional process in the central chlorite-sericite-clay alteration zone (low Cu zone). The apatite and biotite in the Biuro Granodiorite which postdated mineralization were relatively poor in Cl and F.

The chemical compositions and paragenesis of the hydrous minerals suggest the following process of mineralization. A Cl rich fluid emanating from Cl rich magma and carrying base metals precipitated Cl rich hydrous minerals. The meteoric water mixed with this magmatic fluid in the surrounding potassic zone, and precipitated ore minerals from magmatic fluid. The meteoric water which entered into the central zone lost the ability to precipitate ore minerals by mixing with the magmatic fluid in the surrounding potassic zone. The central chlorite-sericite-clay zone was enriched in F by the fluid from a more differentiated magma.

Key words: Chlorine, Fluorine, Panguna deposit, Mineralization, Papua New Guinea.

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Introduction

The chemical role of felsic magma for mineralization has been discussed by many investigators. HOLLAND (1972) estimated the partitioning coefficient of some metals between melt and fluid under saline condition, and simulated the emanation process of metals during differentiation of magma. URABE (1987) showed the dependency of the partition coefficient of base metals between the melt and aqueous phases on the pressure of emplacement. CANDELA and HOLLAND (1986) proposed a mass transfer model to interpret the origin of porphyry copper mineralization. Those laboratory works have emphasized the important role of halogen elements for metal transportation from residual magma.

On the other hand, there are some methods to estimate the natural behavior of halogen elements from geological evidence (e.g. salinity in fluid inclusions and halogen contents in whole rocks). Some common hydrous minerals contain Cl and F substituting OH. The halogen behavior in magmatism and mineralization of the Panguna porphyry copper system was discussed using the chemical compositions of hydrous minerals in this paper.

The Panguna ore deposit is known as a typical porphyry copper deposit. Cu, Mo, Au and other metals are precipitated in or near the Panguna igneous complex, and it is believed that the mineralization was closely related to the felsic magmatism.

Outline of Geology

The general geology has already been described by many workers (e.g. MACNAMARA, 1968; FOUNTAIN 1972; BAUMER and FRASTER, 1975; BALDWIN *et al.*, 1978). A simplified geological map is shown in Fig. 1. The sampling sites are also shown on the map.

The southern part of Bougainville Island is essentially composed of volcanics of the upper Oligocene to the lower Miocene, intrusive complexes of Pliocene, and recent volcanics. The Panguna porphyry copper deposit is situated at the southwestern end of the intrusive complex.

The earliest intrusive body, the Kaverong Quartz Diorite, intrudes the Panguna Andesite of the upper Oligocene to lower Miocene. The southwestern margin of the Kaverong Quartz Diorite is enriched in biotite, and is called the Biotite Diorite. Some porphyritic stocks, named the Biotite Granodiorite, the Leucocratic Quartz Diorite, the Feldspar Porphyry, and the Biuro Granodiorite are found in or near the southwestern end of the Kaverong Quartz Diorite. MASON and McDONALD (1978) grouped the intrusive complex into the earlier high K₂O and the later low K₂O suites, and pointed out that the later intrusive was genetically related to mineralization. BALDWIN *et al.* (1978) recognized three different mineralization stages, and thought that the Biotite Granodiorite had assimilated and remobilized copper from its roof into the surrounding Biotite Diorite. NEDACHI *et al.* (1985) confirmed the temporal relationship between intrusives and mineralization by rock magnetism, as summarized in Table 1. The first weak Cu-Fe mineralization was associated with the Kaverong Quartz Diorite/Biotite Diorite; the second strong Cu mineralization accompanied with the Biotite Granodiorite and the third

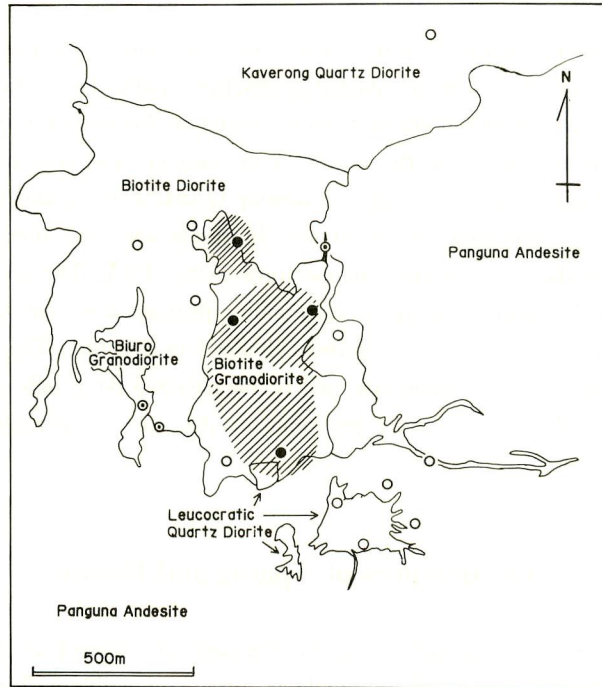


Fig. 1. Simplified geological map of the Panguna porphyry copper ore deposit and the locality of samples examined in the present work. Solid, open and open circles with dot represent the samples of chlorite-sericite-clay alteration, potassic alteration, and fresh rock, respectively. The area of oblique lines represents the chlorite-sericite-clay zone.

Table 1. The geological sequence of intrusion and mineralization of the Panguna porphyry copper deposit (NEDACHI *et al.*, 1985).

IGNEOUS EVENTS	HYDROTHERMAL and/or PNEUMATRITIC EVENTS	MAGNETIC POLARITY
	Pebble dyke	
Biuro Granodiorite	(Pyrite-clay veining)	Reversed
Feldspar Porphyry		Reversed
Brecciation (?)	Quartz-Cu,Fe,Mo sulfide veining	Reversed
Leucocratic Quartz Diorite	Amphibole-magnetite-quartz veining	?
	Argillization	
	Pyrite-clay veining	
	Quartz-Cu,Fe,Mo sulfide veining	
Brecciation (?)	Magnetite-biotite dissemination (Biotite Diorite)	Normal
Biotite Granodiorite		Normal
	(Quartz-Cu,Fe sulfide veining)	
Kaverong Quartz Diorite (Biotite Diorite ?)		Reversed
Panguna Andesite		Reversed (?)

one with the Leucocratic Quartz Diorite. The postdated intrusion is the Biuro Granodiorite.

The alteration aureole can be recognized as chlorite-sericite-clay, potassic (biotite and K-feldspar), and propylitic alteration zones, from the center to the margin in the mining area. The Biotite Granodiorite is situated in the center of the aureole, and was altered to a chlorite-sericite-clay assemblage. Panguna Andesite, Kaverong Quartz Diorite, and Biotite Diorite were altered to a potassic assemblage. Much of the chlorite-sericite-clay alteration postdated the potassic alteration in the center at lower temperature (FORD, 1978). The ore grade is rather low ($\text{Cu} < 0.3\text{wt}\%$) in the center than in the surrounding potassic alteration zone, where the distribution of high Cu concentrated zone forms cylinder like structure. The Leucocratic Quartz Diorite intruded after Biotite Granodiorite, and is characterized by a high concentration of Cu, and the K-feldspar alteration is more predominant than the biotitization. (EASTOE, 1978; NEDACHI *et al.*, 1985).

Occurrences of Apatite and Biotite

The main halogen bearing minerals in the Panguna ore deposit are biotite, apatite, and amphibole. The halogen contents of amphibole are often compatible with those of biotite, but the physico-chemical data is not available for discussion in detail. Hence, apatite and biotite were analyzed in this study.

Apatite occurs in two modes. Magmatic apatite occurs as an euhedral to subhedral form, mainly in the phenocrysts of hornblende, primary biotite and their pseudomorphs. Hydrothermal apatite is not so common in the mining area. In some places, apatite occurs in hydrothermal veins. The wall rock alteration along the vein is a magnetite-amphibole assemblage, which has been recognized as an early alteration product (FORD, 1978). The apatite grows from the vein wall followed by chalcopyrite and quartz. The apatite settled in the early stage of the hydrothermal veining.

Biotite occurs as a magmatic mineral and also as a hydrothermal mineral. In the mining area, the many magmatic biotites are decomposed, and almost all biotites are hydrothermal products. Magmatic biotites are observed only in three samples of Biotite Diorite, Biotite Granodiorite, and Biuro Granodiorite, as shown in Fig 1. Hydrothermal biotites are disseminated predominantly in the Kaverong Quartz Diorite, Biotite Diorite, Panguna Andesite. The biotites occur as aggregates after the phenocrysts of pyroxene and amphibole, occur along micro veinlets, and also scatter individually in the rocks. They are reddish brown to pale brown. In the central chlorite-sericite-clay zone, however, hydrothermal biotite of pale greenish brown color coexists with chlorite and other alteration products.

In this study, these two biotites are distinguished as disseminated biotite and biotite in the chlorite-sericite-clay zone.

Chemical Composition of the Apatite

Representative chemical compositions of apatite obtained from electron probe microanalyses are shown in Table 2. Although apatite contains many trace cations, there is no large correlation with their occurrences. It is only recognized that the apatite in the Biotite Granodiorite is rich in Fe, Mn and Mg, compared to those in the other intrusives and hydrothermal veins.

The Cl and F contents vary widely, especially Cl variation in the hydrothermal apatite. As shown in Fig. 2, the heterogeneity is recognized in the photographs of the characteristic X-ray

Table 2. Representative chemical compositions of igneous and hydrothermal apatites of the Panguna ore deposit.

SAMPLE	1	2	3	4	5	6	7	8
Al ₂ O ₃	0.04	0.07	0.02	0.00	0.00	0.00	0.00	0.00
Y ₂ O ₃	0.20	0.17	0.00	0.16	0.14	0.09	0.11	0.11
La ₂ O ₃	0.03	0.04	0.02	0.04	0.06	0.06	0.03	0.01
Ce ₂ O ₃	0.17	0.10	0.09	0.13	0.08	0.14	0.10	0.01
Nd ₂ O ₃	0.13	0.09	0.00	0.06	0.12	0.04	0.06	0.04
Sm ₂ O ₃	0.03	0.03	0.00	0.01	0.02	0.02	0.01	0.00
Gd ₂ O ₃	0.07	0.03	0.00	0.03	0.05	0.03	0.03	0.01
FeO	0.05	0.09	0.56	0.62	0.07	0.08	0.02	0.01
MnO	0.12	0.10	0.54	0.51	0.12	0.13	0.05	0.04
MgO	0.00	0.01	0.18	0.24	0.03	0.02	0.01	0.01
CaO	54.81	54.08	53.46	53.95	54.48	55.19	55.46	55.64
SrO	0.03	0.02	0.06	0.07	0.01	0.03	0.02	0.02
Na ₂ O	0.16	0.11	0.13	0.18	0.08	0.11	0.03	0.03
P ₂ O ₅	41.39	41.64	42.18	41.43	41.62	42.14	41.50	42.40
SiO ₂	0.12	0.11	0.17	0.06	0.10	0.10	0.11	0.08
SO ₃	0.04	0.04	0.05	0.16	0.02	0.03	0.02	0.05
Cl	0.77	1.45	0.99	1.18	1.06	1.31	0.06	0.15
F	2.24	1.94	2.68	2.22	2.08	1.54	1.87	2.14
H ₂ O	0.51	0.47	0.26	0.42	0.51	0.72	0.87	0.75
-O	-1.11	-1.14	-1.35	-1.20	-1.12	-0.94	-0.80	-0.93
Total	99.77	99.45	100.03	100.27	99.55	100.84	99.55	100.56
Al	0.008	0.013	0.003	0.000	0.000	0.000	0.000	0.000
Y	0.018	0.015	0.000	0.014	0.013	0.008	0.009	0.010
La	0.002	0.002	0.001	0.003	0.004	0.004	0.002	0.000
Ce	0.011	0.006	0.006	0.008	0.005	0.009	0.006	0.000
Nd	0.008	0.005	0.000	0.004	0.007	0.003	0.004	0.002
Sm	0.002	0.002	0.000	0.001	0.001	0.001	0.000	0.000
Gd	0.004	0.002	0.000	0.002	0.003	0.002	0.002	0.001
Fe	0.007	0.013	0.079	0.088	0.011	0.011	0.003	0.002
Mn	0.017	0.015	0.077	0.073	0.017	0.019	0.007	0.005
Mg	0.000	0.002	0.046	0.061	0.008	0.004	0.002	0.001
Ca	9.964	9.853	9.650	9.785	9.910	9.917	10.049	9.947
Sr	0.003	0.002	0.006	0.007	0.001	0.003	0.002	0.002
Na	0.027	0.018	0.021	0.030	0.013	0.017	0.005	0.005
P	5.945	5.994	6.016	5.938	5.982	5.982	5.942	5.989
Si	0.021	0.019	0.029	0.010	0.017	0.016	0.018	0.013
S	0.004	0.004	0.007	0.020	0.003	0.003	0.003	0.007
Cl	0.221	0.417	0.282	0.337	0.305	0.373	0.017	0.043
F	1.199	1.045	1.426	1.188	1.119	0.817	1.000	1.127
OH	0.579	0.538	0.292	0.475	0.576	0.810	0.983	0.830

Total Fe is represented as FeO. The chemical formulae are calculated assuming the total cation charge of 50, the OH-site charge of -4. H₂O is estimated from the calculated OH. -O represents the excess oxygen corresponding to Cl+F. 1~7 are apatites from Kaverong Quartz Diorite (1), Biotite Diorite (2), Biotite Granodiorite (3, 4), relic hydrothermal apatite (5, 6), and replaced hydrothermal apatite (7, 8).

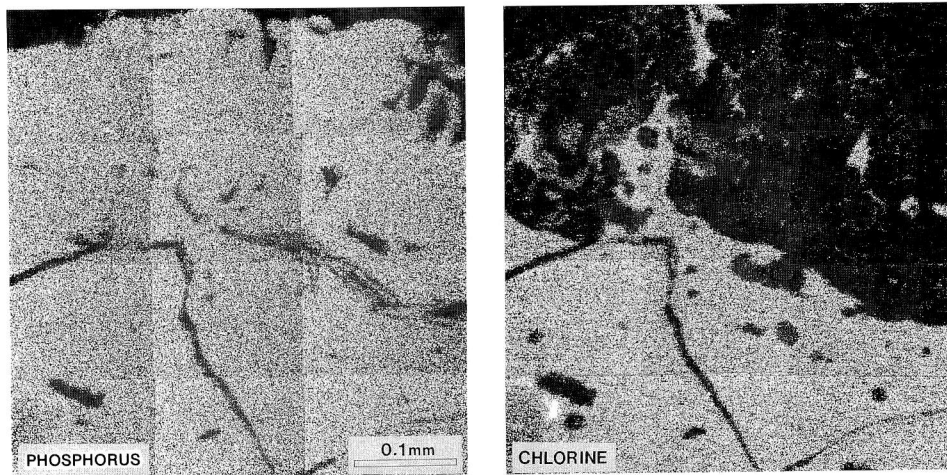


Fig. 2. Characteristic X-ray images of P (left) and Cl (right) of apatite in the hydrothermal vein of the Panguna ore deposit (NEDACHI, 1988).

images of single crystal. The upper limit of P distribution corresponds to the crystal surface of apatite. The Cl distribution indicates the relic texture, that is, primary apatite was rich in Cl, and changed into a Cl poor composition at a later stage. Fig. 3 shows the Cl and F contents of hydrothermal apatite. The primary relic apatites are represented by a solid triangle, and the changed compositions represent by an open triangle. Cl decreases greatly. F seems to be slightly enriched. In other words, F/OH might have been constant during the chemical exchange. This apatite occurs growing from the magnetite-amphibole alteration wall and chalcopyrite overlain by quartz.

Fig. 4 shows the Cl and F contents of the apatite in the igneous rocks. The compositions are also widely dispersed, and it is not clear if the dispersion was affected either by the change of magmatic conditions during crystallization or by the alteration. NEDACHI and UENO (1981) reported similar phenomena in the Orikabe granitic rocks in Japan. Their rocks were fresh, and they interpreted that the compositions were affected by changing magmatic conditions. In this study, however, there was no significant correlation between the compositions of the apatite and the whole rock (e.g., differentiation index). The compositional heterogeneity in apatite is observed in some grains; Cl rich in the center, and poor in the margin. The boundary is often irregular, which might be thought not to be a growth texture, but a relic texture. Defining "fresh rock" by the existence of primary magmatic biotite, the apatites classified according to the petrography of the host rock are shown in Fig. 4. The apatite in the fresh rock is illustrated as a solid symbol, and that in the altered rock as an open symbol. The former is rich in Cl and poor in F. Therefore, it is thought that the dispersion of compositions depends upon the chemical exchange during the later hydrothermal alteration, as the phenomena of the apatite in the hydrothermal vein.

In Fig. 4 two chemical exchanges can be recognized. Apatites in the central chlorite-sericite-clay zone, of which the original rocks are mainly Biotite Granodiorite, are rather rich

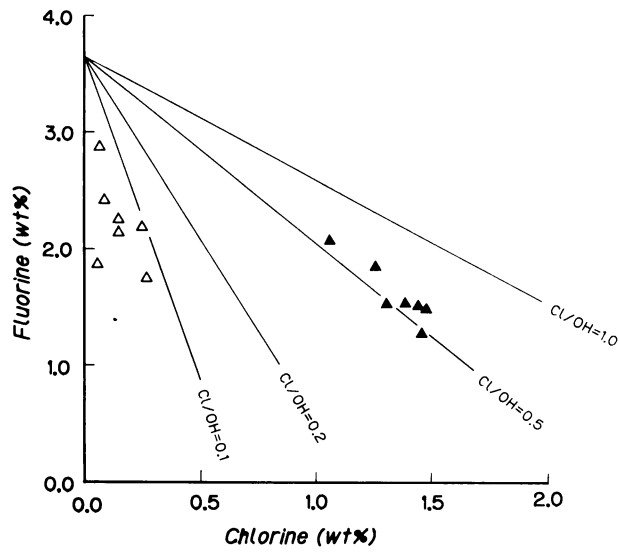


Fig. 3. Cl and F contents of apatite in the hydrothermal vein. Solid and open triangles represent the primary apatite (relic) and replaced apatite, respectively.

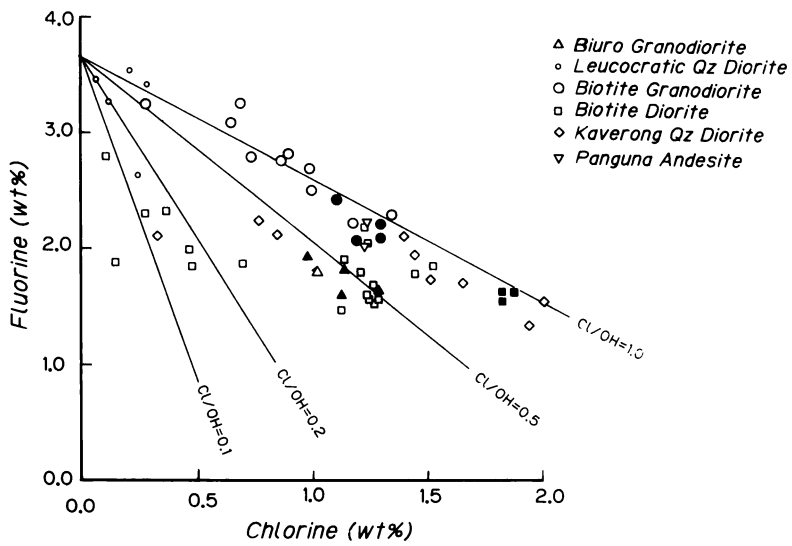


Fig. 4. Cl and F contents of apatite in the intrusive rocks. Solid and open symbols represent the apatites in the fresh rocks and in the altered rocks, respectively.

in F, and it increases along the constant line of Cl/OH ratio (= 1.0) during the chemical exchange (F additional process). On the other hand, Cl/OH decreases steeply in the surrounding Biotite Diorite, Kaverong Diorite and Panguna Andesite (Cl leaching process).

The apatites in the potassic altered Leucocratic Quartz Diorite are near fluorapatite end member.

The apatites in the fresh Biuro Granodiorite are slightly poor in Cl + F, compared to other magmatic apatites. As mentioned previously, the Biuro Granodiorite postdated the major mineralization, and is neither strongly altered nor mineralized. It is thought that the low halogen content is correlated with the barren intrusion.

Biotite Chemistry

Representative chemical compositions of biotite are shown in Table 3, and all the data are plotted in Figs. 5 and 6. In contrast with the apatite, the biotite grains are almost homogeneous, and the distinguishing compositional heterogeneity is not observed.

As shown, biotite compositions are similar to one another with a few exceptions; that is, the biotite in the Panguna Andesite is rich in Si (Fig. 5), and the octahedral Al is calculated on the biotite in the chlorite-sericite-clay zone (Table 3). As shown in Fig. 5, mg values (= Mg/Mg + Fe + Mn) of biotite are from 0.6 to 0.8. Generally, the biotite from porphyry copper type changes into a phlogopitic composition with advancing the alteration. In fact, the disseminated biotite in the Biotite Diorite is rich in Mg, compared to magmatic biotite. However, some biotites in the chlorite-sericite-clay alteration zone are rich in Fe as in sample PG81 in Table 3. This biotite is pale green, associates closely with chlorite, and the octahedral Al is calculated. The biotite in this zone has formed under different conditions.

The halogen contents of biotite are dependent on the composition of the octahedral site (LUDINGTON, 1978; MUNOZ and SWENSON, 1981). Fig. 6 shows the halogens/OH ratios of the biotite against the mg value, and the constant lines of the fugacity ratio of HCl and HF to H₂O of the liquid equilibrated with biotite are also drafted. The temperature is assumed to be 600°C, because the geothermometer of F-OH exchange between biotite and apatite proposed by LUDINGTON (1978) supplies the temperature from 380°C to 800°C with an average of about 600°C.

Almost all biotites are plotted along the constant line of the $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ ratio ($10^{-1.4} \sim 10^{-1.8}$) of the coexisting fluid, which is rather high compared to those of the other mining fields in island arc systems (e.g., NEDACHI, 1988).

In spite of the ambiguity, the following features might be suggested. The magmatic $f_{\text{HF}}/f_{\text{H}_2\text{O}}$ ratios of the later intrusives, the Biotite Granodiorite and the Biuro Granodiorite, are slightly higher than those of the earlier intrusive; the Biotite Diorite. The magmatic $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ ratios of the Biotite Granodiorite are almost same as those of the Biotite Diorite, but higher than those of the Biuro Granodiorite.

The $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ and $f_{\text{HF}}/f_{\text{H}_2\text{O}}$ of the hydrothermal fluid, equilibrated with biotite in the potassic zone, are almost same or slightly higher than those of the magmatic ones. The

Table 3. Representative chemical compositions of biotites of the Panguna ore deposit.

SAMPLE HOST ROCK OCCURRENCE	PG19 PA DIS	PG76 KD DIS	PG44 BD MAG	PG61 BD DIS	PG136 GD MAG	PG81 GD CSC	PG96 GD CSC	PG28 LQD CSC
SiO ₂	38.27	36.34	36.69	37.02	36.65	36.08	36.90	36.85
TiO ₂	3.56	3.81	3.39	4.26	3.98	3.14	2.81	3.21
Al ₂ O ₃	13.23	14.44	14.42	13.79	14.25	17.10	15.54	14.45
FeO	13.37	16.47	15.45	13.58	15.75	16.71	9.32	13.36
MnO	0.16	0.09	0.12	0.20	0.15	0.12	0.07	0.09
MgO	18.35	16.31	16.39	18.02	16.75	13.33	20.30	18.74
CaO	0.07	0.01	0.01	0.01	0.03	0.02	0.04	0.07
Na ₂ O	0.13	0.14	0.15	0.20	0.17	0.20	0.22	0.17
K ₂ O	9.21	9.29	9.61	9.84	9.51	9.65	9.35	8.84
Cl	0.17	0.24	0.20	0.17	0.17	0.20	0.07	0.18
F	0.43	0.24	0.27	0.49	0.37	0.44	1.01	0.86
H ₂ O	3.85	3.86	3.85	3.80	3.84	3.76	3.59	3.61
-O	-0.22	-0.16	-0.16	-0.25	-0.20	-0.23	-0.44	-0.40
Total	100.58	101.10	100.40	101.13	101.44	100.50	98.78	100.05
Si	5.611	5.396	5.465	5.441	5.411	5.384	5.418	5.436
Al (4)	2.287	2.526	2.532	2.389	2.480	2.616	2.582	2.512
Al (6)	0.000	0.000	0.000	0.000	0.000	0.393	0.108	0.000
Ti	0.393	0.425	0.379	0.471	0.442	0.352	0.310	0.356
Fe	1.639	2.045	1.924	1.669	1.945	2.085	1.145	1.648
Mn	0.020	0.012	0.015	0.024	0.018	0.015	0.008	0.012
Mg	4.012	3.610	3.638	3.948	3.687	2.965	4.443	4.122
Ca	0.012	0.002	0.002	0.001	0.005	0.002	0.006	0.011
Na	0.037	0.039	0.044	0.057	0.049	0.057	0.063	0.050
K	1.722	1.760	1.826	1.846	1.791	1.837	1.751	1.663
Cl	0.042	0.061	0.052	0.044	0.042	0.051	0.017	0.046
F	0.197	0.115	0.127	0.230	0.174	0.209	0.470	0.401
OH	3.761	3.824	3.822	3.727	3.784	3.740	3.512	3.553
Z	7.898	7.922	7.996	7.829	7.890	8.000	8.000	7.948
Y	5.650	5.655	5.562	5.617	5.632	5.443	5.696	5.770
X	1.771	1.801	1.873	1.904	1.844	1.897	1.820	1.724
OH	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000

Total Fe is represented as FeO, and H₂O was calculated assuming that total charge of cations is 44 and that charge of OH site is -4. -O represents the excess oxygen correspond to Cl+F. PA: Panguna Andesite, KD: Kaverong Diorite, BD: Biotite Diorite, GD: Biotite Granodiorite, LQD: Leucocratic Quartz Diorite, DIS: Disseminated biotite, MAG: Magmatic biotite, CSC: Biotite in chlorite-sericite-clay zone.

fHF/fH₂O of the hydrothermal fluid in the chlorite-sericite-clay zone are distinctly higher than those of the magmatic ones and in the potassic zone. Both the fHCl/fH₂O and fHF/fH₂O of the hydrothermal fluid in or near the Leucocratic Quartz Diorite are higher than in the others.

Behavior of Halogen in Mineralization

Based on the halogen contents of the apatite and biotite in the Panguna ore deposit, the behavior of halogen elements in the mineralization is discussed below.

Magmatic stage: The F content of the apatite in the fresh Biotite Diorite is slightly lower than that of the fresh Biotite Granodiorite. However, both have high Cl/OH ratios from 0.7 to 1.0, which suggest a high fHCl/fH₂O ratio of those magmas (KORZHINSKIY, 1981). The same suggestion is derived from the compositions of the primary magmatic biotite. Those ratios of the magmas of Biotite Diorite and Biotite Granodiorite are higher than those of the Biuro

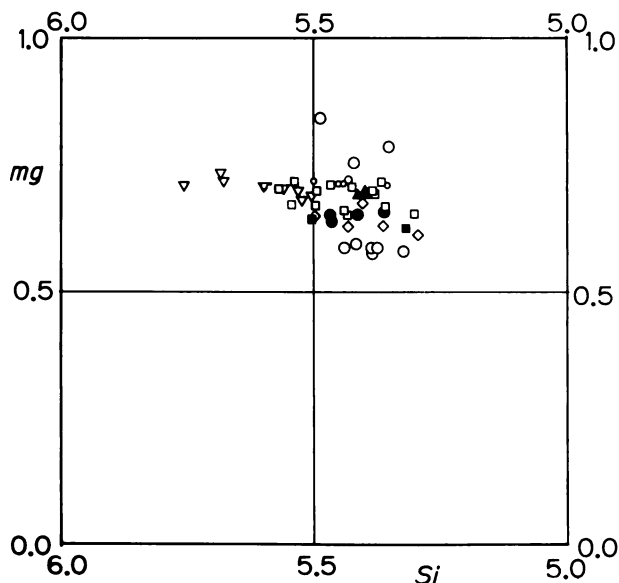


Fig. 5. Si versus mg ($Mg/Mg + Fe + Mn$) of biotites from the Panguna ore deposit. Symbols are same as those in Fig. 4.

Granodiorite postdating the Panguna mineralization, and also rather higher than those of the other island arc intrusives. On the other hand, the magmatic $fHCl/fH_2O$ of the Biotite Granodiorite is slightly higher than that of the Biotite Diorite.

Early hydrothermal stage: The $fHCl/fH_2O$ ratio of the hydrothermal fluid of the potassic alteration stage can be obtained from the chemical composition of the hydrothermal biotite, which is approximately the same as the magmatic one. The hydrothermal apatite is thought to be precipitated at a rather earlier stage of veining, and the Cl/OH ratio of the relic part is almost the same as that of the magmatic apatite in the fresh Biotite Diorite and the Biotite Granodiorite. Hence, the $fHCl/fH_2O$ of the earlier hydrothermal fluid predating the mineralization might be as high as that of magma. Although the halogen contents of the apatite in the altered intrusives vary widely, the data does not contradict the suggestion described above. That is, if the apatites high in Cl and low in F in the altered rock could be thought to be the compositions of early hydrothermal stage, the compositions are similar to magmatic ones.

The chemical compositions of hydrous minerals suggest that the magmatic fluid high in $fHCl/fH_2O$ might have emanated from the magma of the Biotite Granodiorite (and/or Biotite Diorite), and that the fluid precipitated the hydrothermal biotite and apatite of high Cl/OH ratios mainly in the potassic zone of the Biotite Diorite, Kaverong Diorite and Panguna Andesite. EASTOE (1983) suggested that the salt-rich liquid was of magmatic origin based on the hydrogen and oxygen isotope reported by FORD and GREEN (1977).

Late hydrothermal stage: The wide variation of the halogen contents of the apatite in the altered igneous rocks and the hydrothermal apatite can be explained by the chemical exchange that took place during the later hydrothermal stage. There are two processes of chemical exchanges.

The chemical exchange in the potassic zone is characterized by a Cl leaching process. This

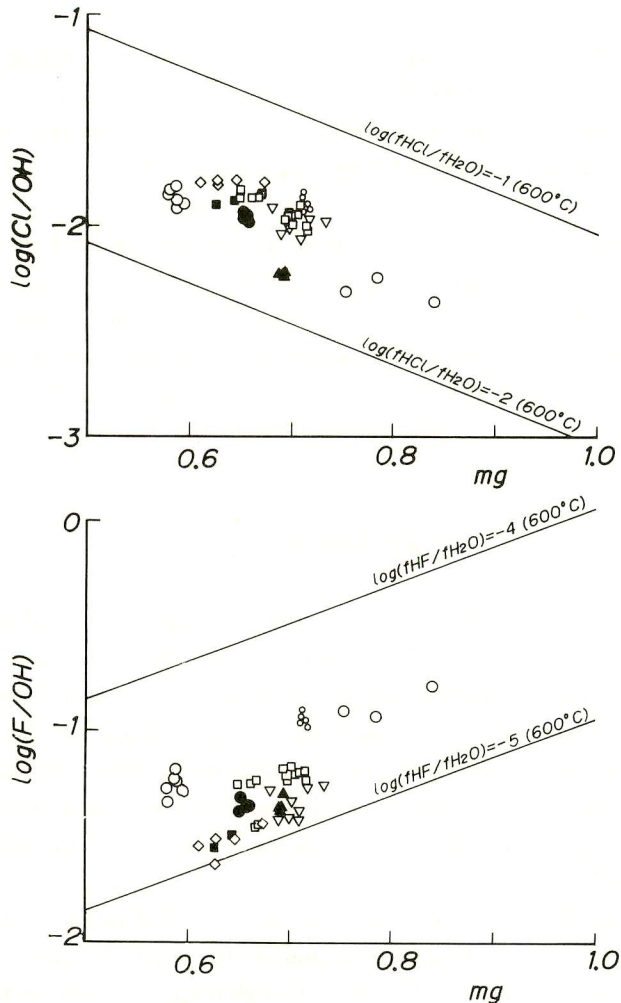


Fig. 6. Log (Cl/OH)-mg (above) and log (F/OH)-mg (below) of biotites from the Panguna ore deposit. Symbols are same as those in Fig. 4.

potassic zone surrounds the chlorite-sericite-clay zone. The evidence suggests that the Cl leaching in the potassic zone might occur with the addition of the meteoric water convecting around the magma. Cl is partitioned into a vapor phase more easily than F and H₂O. The Cl leaching zone also corresponds with the strongly Cu concentrated cylinder. Hence the meteoric water has played an important role for the precipitation of Cu and other ore minerals in the magmatic fluid by mixing. The occurrence of chalcopyrite on the surface of the hydrothermal apatite support this process.

In the central chlorite-sericite-clay zone, the apatite in the Biotite Granodiorite, shows evidence of a F additional process. The Cl/OH ratio is almost constant during the process. Even if the meteoric water passed through the outer potassic zone into the central zone, the infiltrated meteoric water might be enriched in Cl by mixing with the primary magmatic fluid, and by the reaction with the earlier Cl rich minerals in the outer potassic zone. The altered meteoric water in the chlorite-sericite-clay zone might lose the ability to dilute the magmatic water to precipi-

tate ore minerals. This altered meteoric water played a role only for transportation of base metals to the outer zone as mentioned by BALDWIN *et al.* (1978). Hence, the cylinder-like distribution of high Cu concentration might have been furthered. Fluorine might be enriched in the later magmatic fluid from the more differentiated magma and have been fixed in the chlorite-sericite-clay zone.

The apatite and biotite in the Leucocratic Quartz Diorite suggest that both $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ and $f_{\text{HF}}/f_{\text{H}_2\text{O}}$ was high in or near this intrusive. EASTOE (1978) and NEDACHI *et al.* (1985) pointed out that the mineralization around the Leucocratic Quartz Diorite has postdated the mineralization around the Biotite Granodiorite. It might be interpreted that the magma of the Leucocratic Quartz Diorite emanated the well differentiated and refreshed ore fluid of high f_{HCl} and f_{HF} .

Conclusions

The chemical compositions of the apatite and biotite of magmatic and hydrothermal origin of the Panguna porphyry copper deposit, Papua New Guinea, were measured.

The apatite and biotite of magmatic and earlier hydrothermal origin show a high $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$. In the later hydrothermal stage two different chemical exchanges of halogen elements occurred in the surrounding potassic zone and the other in the central chlorite-sericite-clay zone. The former exchange is characterized by a Cl decreasing process, and the later by a F increasing process. The hydrothermal fluid in and near the Leucocratic Quartz Diorite might be high $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ and also high $f_{\text{HF}}/f_{\text{H}_2\text{O}}$.

The evolution of ore fluid might be drawn as follows; 1) Fluid rich in Cl emanated from the Cl rich felsic magma of Biotite Granodiorite (and/or Biotite Diorite) and Cl rich hydrous minerals precipitated from the fluid. 2) Dilution of Cl rich magmatic water by meteoric water took place in the outer potassic zone and decomposed the chloride complex and induced the precipitation of the ore minerals. Hence, the cylinder-like distributions of high Cu concentration formed. 3) With decreasing temperature, the meteoric water might have infiltrated into the roof of the residual magma. However the meteoric water lost the ability to precipitate base metals, because of mixing with the magmatic fluid and of the reaction with the Cl rich hydrous minerals in the outer potassic zone. The role of the altered meteoric water in the central zone might be the same as that of the magmatic fluid which transported the base metals to the outer potassic zone. 4) Fluorine increased in the later magmatic fluid and fixed in the biotite and apatite in the central chlorite-sericite-clay zone. 5) The later magmatism of the Leucocratic Quartz Diorite might emanated the other fluid of high $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ and $f_{\text{HF}}/f_{\text{H}_2\text{O}}$.

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