Geochemical Behavior of Minor Elements in the Altered Zone of Some Hydrothermal Deposits

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Introduction

During the past decade there has been considerable development in the field of geochemistry, and many investigators have discussed the behavior of minor elements in minerals and rocks. However, few geochemical studies on the hydrothermal deposits have been attempted. The geochemical studies on the altered zone around hydrothermal deposit have become important as a key for approaching the ore genesis.

The geochemical behavior of some minor elements in the altered zones around hydrothermal deposits is discussed in this paper. The deposits involved in this discussion are "Kuroko" (Hanaoka, Hanawa, Kamikita and Aomori Mines), gold (Kasuga Mine), pyrophyllite (Yonago Mine) and sulfur (Azuma Mine) deposits.

In Japan, lead, zinc and copper ores (galena, zincblende and chalcopyrite) are frequently found closely associated with Tertiary tuff, tuffaceous sediments and volcanic rocks, and are commonly called "Kuroko" deposit.

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Aspect on the geochemical behavior of minor elements in some altered zone of hydrothermal deposits

Throughout the investigation, lead is found to be one of the most ubiquitous of the rarer elements without exception in the altered zones of any kind of hydrothermal deposits. Averages of lead for the altered zone and ore bodies of "Kuroko" deposit are 216.7 p.p.m. and 229.0 p.p.m., respectively.

An average for altered zones of the other investigated hydrothermal deposits is only 51.6 p.p.m. The high value of lead in the altered zones of "Kuroko" deposits appear to be indicative of their unique character against other hydrothermal deposits. Average involved in the discussion is summarized in Table 1. All determinations of minor elements were carried out using spectrochemical methods (KURODA, 1954; HAMAGUCHI & KURODA, 1957; HAMAGUCHI, KURODA & NEGISHI 1960).

Silver and copper are detected in all specimens from the investigated altered zone of "Kuroko" deposits (ISHIKAWA & KURODA, 1958, 1960).

Tin is only detected in the pyrophyllite zone and the kaolinite-pyrophyllite transitional zone of the "Kuroko" deposits. Tin is not found in the other altered rocks consisting of sericite-, chlorite-, montmorillonite-, and silicified zones even in "Kuroko" deposit (ISHIKAWA & SUDO, 1957; ISHIKAWA 1959). IWAO et al (1955) also found the

Table 1. Averages of minor elements for altered zones

Deposit type	Mine	Deposit	Ore type	Country rock	Number of analyses
"Kuroko"	Hanaoka	Tsutsumizawa	Black	Tuff	14
		Doyashiki	Black	Tuff	11
	Hanawa	Yamabnki	Black	Tuff	8
	Kamikita	Honko	Yellow	A.Z. Lip.	26
				O.B. Lip.	13
		Tateishi	Black	A.Z. Lip.	22
				O.B. Lip.	10
		Kaminozawa	Black	Lip. Tuff	7
		Okunosawa (Honko)	Black	Tuff	17
		Okunosawa (E. 2)	Black	Tuff	6
	Aomori		Black	Tuff	16
Pyrophyllite	Yonago			Andesite	12
Gold	Kasuga			Andesite	16
Sulfur	Azuma			Andesite	6

A. Z.....Altered zone O. B.....Ore body Lip.....Liparite *.....not detected

similar behavior of tin in the Kosaka Mine. However, the presence of tin does not be restricted to the altered rocks containing pyrophyllite. Altered rocks around gold and sulfur deposits also contain appreciable amounts of tin (ISHIKAWA & SHIMODA, 1962). Average of tin for the pyrophyllite zone of Honko deposit, Kamikita Mine, is 26.1 p.p.m. An average 53.1 p.p.m. is found for the zone of pyrophyllite and transitional zones of Aomori deposit. For the investigated pyrophyllite-, gold-, and sulfur-deposits, over-all averages of tin are 202.6 p.p.m., 79.6 p.p.m. and 47.0 p.p.m., respectively. It is noticed that the pyrophyllite deposit is rich in tin (ISHIKAWA & SHIMODA, 1962). Such behavior of tin in the altered zones around hydrothermal deposits seems to be important for the interpretation of the geological condition of hydrothermal alteration.

The content of nickel and cobalt does not much differ zone by zone. The averages of nickel and cobalt for all investigated hydrothermal deposits are estimated to be 5.96 p.p.m. and 7.7 p.p.m., respectively.

Vanadium is concentrated preferably in the pyrophyllite and gold deposits as shown in Table 1. The contents are variable throughout the investigated altered zones of hydrothermal deposits.

The strong enrichment of strontium is characteristic of the Doyashiki zone of Hanaoka Mine, of which main mineralogic constituent is gypsum (ISHIKAWA& SUDO, 1957). Although altered rocks around the "Kuroko" deposit are rather poor in chromium, considerable enrichment of chromium is usually found for the altered zone of gold-, pyrophyllite- and sulfur-deposits.

Geochemical coherence among the minor elements in some altered zones of hydrothermal deposits

Many discussions have been presented for the association of minor elements in

and ore bodies of some hydrothermal deposits.

Pb	Co	Cr	Ni	V	Ga	Sn	Ba	Sr	B	Ag	Cu
192.2	*	8.9	6.2	40.2	96.3	*	68.1	9.0	25.8	0.29	n. d.
76.8	*	1.8	11.7	*	4.3	*	114.0	225.4	16.5	n. d.	n. d.
387.7	*	10.3	17.3	40.6	20.7	*	565.0	*	96.2	2.55	335.6
198.4	3.8	0.78	2.0	28.5	81.8	25.6					
103.0	13.2	*	2.8	13.0	73.8	26.6					
96.7	14.7	*	*	6.2	32.5	*					
355.0	30.5	6.0	1.4	5.2	168.5	*					
307.5	*	*	0.8	5	168.5	*					
331.8	9.9	7.8	6.3	5.3	22.1	*					
128.0	*	41.6	4.2	13.6	33.8	*					
231.5	0.9	24.3	0.43	68.3	64.3	53.1					
86	4.4	174.0	9.8	275.0	53.2	202.6					
42	13.3	63.6	4.3	517.0	96.0	79.6					
27	17.4	32.0	16.2	15.2	2.6	47.0					

rocks and minerals. It is of interest to survey the geochemical associaton among minor elements in the altered zones of hydrothermal deposits.

The geochemical association between Ag^{+} (ionic radius 1.26Å) and Pb^{2+} (ionic radius 1.20Å) is fairly close in the altered zone of Yamabuki deposit, Hanawa Mine (ISHIKAWA & KURODA, 1958). The association of lead with vanadium in minerals and rocks has not been generally recognized. However, the association is sometimes remarkable in some altered zone of "Kuroko" deposit, i. e. Hanaoka, Hanawa and Kamikita Mines.

The geochemical similarities of gallium and cobalt have been indicated by Ahrens (1953). Although there is no crystallochemical relation between Ga^{3+} and Co^{2+}, greater similarities are found between Ga^{3+} and Co^{3+} in the ionic radius, ionization potential and ionic field strength as shown in Table 2.

Table 2. The ionic radii, ionization potentials and ionic field strength for Co^{3+} and Ga^{3+}

	r	I	F
Co^{3+}	0.63	33.8	52.5
Ga^{3+}	0.62	30.7	49.7

r.....Ionic radius
I.....Ionization potential
F.....Ionic field strength

As a matter of fact their close associaton is found in the Tateishi deposit in Kamikita Mine (ISHIKAWA, 1959). Cobalt is considered to be associated with gallium as Co^{3+} ions.

It is well known that chromium, vanadium and nickel substitute for iron in minerals and rocks by reason of the similarity in their ionic properties. There are no close associations of these elements in the altered zones of hydrothermal deposits except for the ones around some "Kuroko" deposits. The high affinity of copper and silver for sulfur is the factor determining the manner of occurrence of both elements in the upper lithospher. Consequently, copper and silver belong to the group of the sulfofile elements, as pointed out by HAMAGUCHI and KURODA (1959). On the other hand, the

behavior of lead somewhat differs from those of copper and silver. The substitution of lead for potassium is the important factor determining the distribution of lead in igneous rocks, although, to a lesser extent, the precipitation of lead sulfide minerals should not be overlooked during magmatic crystallization. On the contrary, close positive correlation among silver, copper and lead should be noticed in the altered rocks around the hydrothermal deposit (ISHIKAWA & KURODA, 1958, 1960). The foregoing facts suggest that most part of the elements could have been precipitated as sulfides during the course of wall rock alteration by hydrothermal solution, although some contribution of the elements from silicate minerals may not be ignored.

A consideration on the behavior of minor elements during the wall rock alteration of hydrothermal deposits

Appreciable amounts of lead, vanadium and gallium are present in the altered zones of hydrothermal deposits. The contents of lead, silver, tin and copper are also generally much higher than those of the original rocks. It suggests that such elements are added to the original rocks from hydrothermal solution during the wall rock alteration. Original rocks are usually low in gallium. Diadochic substitution of gallium for aluminum may explain the gallium enrichment in the altered rocks.

In the gypsum zone of Doyashiki deposit, the strontium is extensively substituted for calcium of gypsum.

The contents of minor elements in the altered rocks differ by the nature of according to the types of hydrothermal deposits. Chromium, vanadium and tin in "Kuroko" deposits are especially less abundant than in the other hydrothermal deposits, whereas lead is more abundant in "Kuroko" deposit. The behavior of tin seems to be depended on pH condition of altered zone forming fluids. The existence of vanadium and chromium are also largely related to such a condition.

In addition to the chemical composition, pH and temperature of altered zone forming fluids, geological conditions appear to play important roles on the behavior of minor elements in the altered zone of hydrothermal deposits.

Summary

The geochemical behavior of minor elements in the altered zone of some hydrothermal deposits, i. e. "Kuroko" (Black Ores), gold, pyrophyllite and sulfur deposits in Japan is considered.

The minor elements involved in the discussion are barium, strontium, boron, gallium, vanadium, lead, chromium, cobalt, nickel, silver and copper.

The geochemical association among some minor elements in the altered zone of hydrothermal deposits differs remarkably from that in wall rocks and minerals. The contents of minor elements in the altered rocks varies corresponding to the nature of hydrothermal deposits. Lead, vanadium, and gallium are always present in the all altered zones of hydrothermal deposits investigated. Chromium in "Kuroko" deposits in less abundant than in the other hydrothermal deposits, whereas lead is more abundant in the "Kuroko" deposit. The altered zones of the "Kuroko" deposit lack tin, except for the pyrophyllite containing one. However, tin is always found in the altered zone around the other types of hydrothermal deposits than that of "Kuroko" deposit.

Thus, it is suggested that the difference in minor element distribution is caused primarily by a different geological condition.

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