

Alteration Minerals and Mineralization in the Shakanai Kuroko Deposit, Akita Prefecture*

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Abstract: The modes of occurrence, associated mineral assemblages, and chemical compositions of minerals from the No. 11 ore deposit and from the samples of bore holes in the north area of the Shakanai mine, are described on the basis of microscopic observation, X-ray diffraction analysis and electron probe microanalysis. As a first step to estimate the activity ratio of Mg^{++} to Fe^{++} in hydrothermal solution, exchange isotherm between chlorite and chloride solution has been made.

Though principal constituent ore minerals of the No. 11 ore deposit are similar to those of other kuroko deposits, they have wide varieties in mode of occurrence, texture and chemical compositions. Complex mixtures of black ore and tuff breccia, and a paragenesis of various sphalerites support that the No. 11 ore deposit has formed at various stages.

Chlorite minerals and interstratified sericite/montmorillonite are extensively distributed around the ore deposits. Contribution of magnesium-rich hydrothermal solution is primary factor for the formation of Mg-chlorite. It is possible that the mixed layer clay zone closely associated with the ore has formed in a different process from the formation of the mixed layer clay zone regarded as a transitional zone. This zone associated with the ore is considered to be influenced by the deposition of sulfide minerals with decreasing of temperature.

Introduction

The Shakanai mine is one of the leading Kuroko mines in Japan. Various alterations surrounding a number of ore bodies of this kuroko-type deposits have been investigated in detail by many researchers. The distribution of the alteration zones suggests some genetical relationships with kuroko-type mineralization (OHTAGAKI et al., 1969; IJIMA, 1974; NISHIYAMA et al., 1973). Reports on the geology and ore deposits of the Shakanai mine have been made by SAKAZAKI et al. (1965), OHTAGAKI (1966), OHTAGAKI et al. (1969,

1974) and MIYAZAKI et al. (1978). Biostratigraphical study has been made by KUMITA et al. (1980). Studies on the modes of occurrence and physicochemical considerations on deposition of the No. 1 ore deposit have been made by KAJIWARA (1970). The mineralogy of the ores has been studied by NISHIYAMA (1974), SATO (1974) and MATSUKUMA and YUI (1979).

The purpose of this paper is to describe the mode of occurrence of ore and clay minerals in the No. 11 ore deposit and to consider the mechanism of hydrothermal alterations related to kuroko mineralization.

Outline of Geology and Ore Deposits

The Shakanai mine is located in the so-called Green Tuff Region in Northeast Japan which was the site of intense submarine volcanic activity during the Miocene. The volcano-sedimentary rocks around the area are generally divided into the Oya formation of the Monzen stage, the Hotakizawa and Shakanai formations of the Nishikurosawa stage and the Sainokami formation of the Onnagawa stage in ascending order. In the Shakanai area, pre-Tertiary rocks, the Oya and

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Keywords: Shakanai mine (釈迦内鉱山), Kuroko deposit (黒鉱鉱床), Mg-chlorite (Mg-緑泥石). Interstratified sericite/montmorillonite (絹雲母/モンモリロナイト混合層鉱物)

the Hotakizawa formations have not yet been recognized (MIYAZAKI et al., 1978). Tertiary rocks of Shakanai area is mainly composed of dacitic pyroclastic rocks and lava flows. These rocks are widely overlain by Quaternary alluvium.

The Shakanai formation consists of dacitic tuff breccia, lava flow, pumice tuff and mudstone. Ore deposits are often embedded in the upper members of this formation. The formation is overlain conformably by the Sainokami formation which is composed mainly of mudstone, dacite lava flow and pumice tuff. The intrusive rocks of dacite, dolerite and breccia dike are frequently found in the north area of the Shakanai mine. In the vicinity of the No. 11 ore deposit, the upper members in the Shakanai formation are characterized by the cyclic piles, which are made up of tuff breccia, ore body, mudstone, tuff, tuff breccia, ore body, mudstone, tuff and tuff breccia in ascending order. The ore bodies in the lower pile are stratigraphically correlated with the main ore body in the No. 11 ore deposit.

The ore deposit are composed of several metallic ore bodies which are underlain by anhydrite-gypsum ores. The metallic ore bodies show a characteristic mineral zonation like in many other kuroko-type deposits. Stratigraphically highest is the black ores which change

downwards into the yellow ores and then into the pyrite ores. Tuff breccia is distributed between the black ore bodies (Fig. 1).

Ores and Clay Minerals from the No. 11 Ore Deposit

Principal constituent minerals of the No. 11 ore deposit are similar to those of other kuroko deposits. They have varieties in mode of occurrence, texture and chemical compositions.

Gypsum and anhydrite are extensively distributed in dacitic tuff breccia under the sulfide ore bodies (Fig. 1). Anhydrite occurs in more abundance to the sulfide ore bodies. Satinspar, which occurs with gypsum may be a recrystallized mineral from gypsum or anhydrite. Disseminated tuff breccia is distributed between the black ore bodies. This is composed mainly of fragments of dacite, andesite, mudstone, chert, black ore and yellow ore. Constituents and grain sizes of the fragments in the disseminated tuff breccia are generally variable. Complex mixtures of black ore and tuff breccia are partly visible near the boundary between the black ore body and the disseminated tuff breccia. The erupted tuff breccia might have been accumulated with the pre-existent unconsolidated sulfide ores. The texture of mixtures show reworked process in consequence above.

Mineral composition and relative abundance of the minerals from samples on the -365 m level of the No. 11 ore deposit are shown in Figs. 2 and 3. Polished thin sections of rock samples were observed under the microscope in order to study the mode of occurrence of authigenic minerals and textural varieties of sphalerite. Non-orientated, orientated and glycolated samples of clay minerals were studied by using X-ray diffractometer.

Chalcopyrite and tennantite are more common in the black ore of the No. 11 ore deposit than other kuroko deposits. Galena, tennantite and barite increase in the upper horizon (Fig. 3). The bornite-bearing black ore occurs as lenses or veins in the middle and upper part of black ore. In addition to bornite, electrum and silver-bearing minerals of Ag_2S-Cu_2S

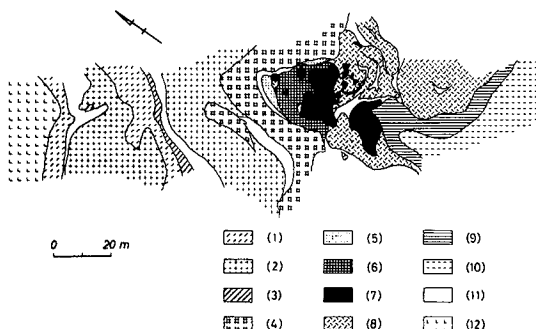


Fig. 1 Underground geologic map on -365 m level of the No. 11 ore deposit in the Shakanai mine.

(1): dacitic tuff breccia, (2): gypsum zone, (3): dacitic tuff, (4): anhydrite zone, (5): pyrite ore, (6): yellow ore, (7): black ore, (8): disseminated tuff breccia, (9): mudstone, (10): andesitic tuff, (11): clay zone, (12): dacite (intrusive).

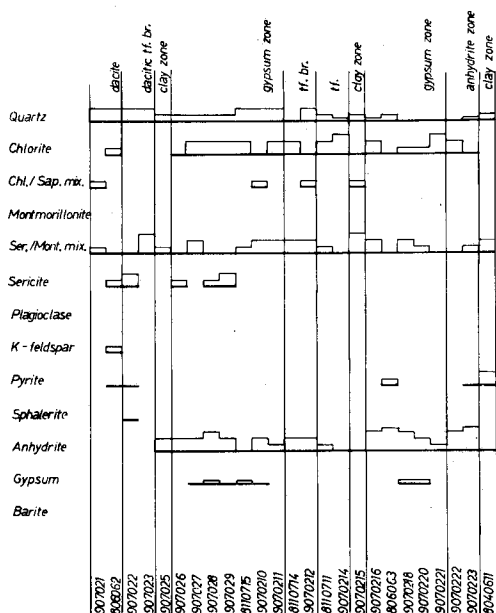


Fig. 2

Fig. 2 Mineral composition and relative abundance of the minerals from samples under the sulfide ore body, Sam- ples are collected along the main gallery on the -365 m level of the No. 11 ore deposit in the Shakanai mine. chl./sap. mix.: interstratified chlorite/saponite, ser./mont. mix.: interstratified sericite/montmorillonite.

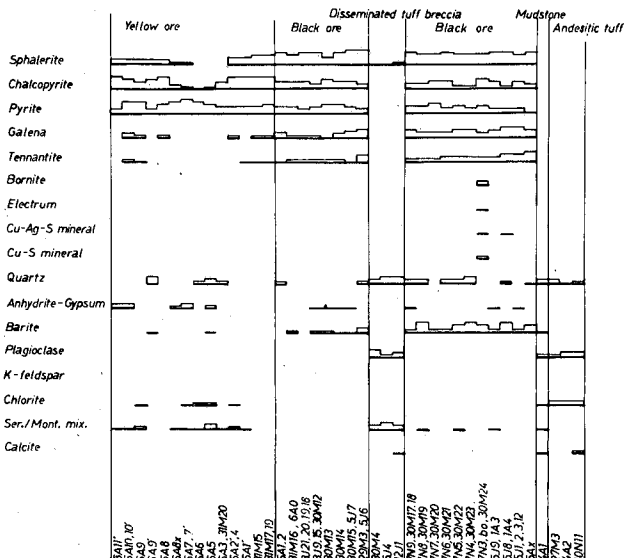


Fig. 3

Fig. 3 Mineral composition and relative abundance of the minerals from samples of the ore body. Samples are collected along the main gallery on the -365m level of the No. 11 ore deposit in the Shakanai mine.

series are frequently found in the ore. Some rare minerals have been reported from here by MATSUKUMA and YUI (1979).

The mineral assemblage of sphalerite, pyrite, bornite and chalcocopyrite gives us an information on fs_2 -temperature range at the time of formation. Iso-activity curves of FeS in sphalerite coexisting with pyrite, drawn with the function of temperature, fs_2 and content of FeS in sphalerite, intersect the equilibrium curve for the assemblage of chalcocopyrite, pyrite and bornite on the temperature- fs_2 diagram, and physical condition of the ore formation can be estimated. When we use a mean value, 0.17 FeS mole% in sphalerite (Table 1), it is calculated that bornite-bearing black ore has been formed at about 250°C and under $10^{-8.2}$ atom- fs_2 .

Sphalerite and tetrahedrite-tennantite group minerals are commonly found in the black ore. The texture of sphalerite ores observed in polished thin sections shows a great complex paragenesis in the middle to the upper part

of the black ore. The mode of occurrence of sphalerites as broken fragments, later fillings, showing growth banding and exhibiting fine dots of chalcocopyrite supports that there are various stages in the deposition of sphalerite.

Table 1 EPMA analytical data of sphalerite coexisting with bornite, chalcocopyrite and pyrite.

Weight %							
Zn	Fe	Cu	Mn	Cd	S	Total	FeS (mole%)
65.84	0.027	0.23	0.19	0.37	32.91	99.6	0.024
66.08	0.038	0.39	0.04	0.31	32.55	99.4	0.033
66.07	0.091	0.09	0.15	0.31	31.74	98.4	0.082
66.58	0.097	0.46	0.07	0.19	32.76	100.2	0.085
65.93	0.111	0.35	0.17	0.40	31.70	98.7	0.099
66.58	0.117	0.67	0.00	0.40	33.69	101.5	0.100
66.87	0.128	0.36	0.07	0.24	32.88	100.5	0.111
66.32	0.139	0.64	0.00	0.31	33.18	100.6	0.121
66.35	0.141	0.18	0.19	0.46	32.62	99.9	0.124
65.92	0.148	0.39	0.16	0.34	33.09	100.0	0.126
65.77	0.156	0.89	0.05	0.55	32.59	100.0	0.137
66.63	0.231	0.40	0.05	0.31	32.86	100.5	0.201
66.36	0.234	0.28	0.04	0.25	32.86	100.0	0.204
66.52	0.243	0.19	0.04	0.44	32.91	100.3	0.211
66.50	0.278	0.19	0.05	0.31	32.88	100.2	0.242
64.08	0.372	0.57	0.05	0.32	33.04	98.4	0.328
65.09	0.814	0.32	0.00	0.42	32.20	98.8	0.720

mean value = 0.17

Table 2 EPMA analytical data of coexisting sphalerite and tetrahedrite-tennantite group minerals in the black ore body of the No. 11 ore deposit in the Shakanai mine. Upper paragraph corresponds to sphalerite and tetrahedrite-tennantite group minerals found in the upper ore body, the lower to the lower black ore body. tet: tetrahedrite-tennantite group minerals, sph: sphalerite.

		Atomic %											
		Cu	Ag	Zn	Fe	As	Sb	Mn	Cd	S	Total (wt%)	As/As+Sb	Fe/Fe+Zn
Bon	tet:	35.3	0.0	7.0	0.6	12.7	0.4	0.0	0.1	44.1	98.4	1.0	0.08
	sph:	0.7	0.0	49.2	0.1	0.0	0.0	0.1	0.3	49.7	100.0		
31M04	tet:	33.4	0.8	5.8	0.8	7.0	9.0	0.1	0.1	43.0	101.7	0.4	0.12
	sph:	0.2	0.0	48.7	0.2	0.0	0.0	0.1	0.2	50.7	100.1		
31M05	tet:	33.7	0.4	5.4	1.3	10.7	3.8	0.1	0.0	44.7	98.8	0.7	0.19
	sph:	1.3	0.0	46.6	0.9	0.0	0.0	0.0	0.1	51.2	99.8		
30M19	tet:	33.5	0.0	6.3	1.5	13.7	0.1	0.1	0.0	44.9	97.7	1.0	0.19
	sph:	1.1	0.0	47.9	0.8	0.0	0.0	0.1	0.3	49.9	100.1		
30M17	tet:	34.5	0.0	5.9	1.3	11.2	2.7	0.2	0.0	44.3	101.8	0.8	0.18
	sph:	2.6	0.0	47.1	0.8	0.0	0.0	0.2	0.0	49.5	99.6		
31M25	tet:	33.8	0.5	5.7	1.5	11.7	2.7	0.0	0.0	44.2	99.5	0.8	0.21
	sph:	0.0	0.0	48.3	0.8	0.0	0.0	0.1	0.0	50.9	98.8		
30M15	tet:	33.7	0.3	5.9	1.4	12.6	1.5	0.1	0.1	44.4	99.4	0.9	0.19
	sph:	0.7	0.0	48.1	0.7	0.0	0.0	0.2	0.0	50.4	100.0		
31M22	tet:	33.4	0.4	5.7	1.1	11.4	3.0	0.1	0.1	44.9	99.5	0.8	0.16
	sph:	1.0	0.0	47.6	1.0	0.0	0.0	0.1	0.2	50.1	99.4		
30M12	tet:	33.5	0.3	5.9	1.5	11.8	2.0	0.1	0.1	44.8	99.7	0.9	0.20
	sph:	1.5	0.0	46.4	1.2	0.0	0.0	0.1	0.2	50.7	99.7		
6Ab	tet:	33.3	0.5	6.1	1.0	10.1	3.7	0.2	0.2	45.2	100.7	0.7	0.13
	sph:	0.1	0.0	48.8	0.1	0.0	0.1	0.2	0.2	50.6	99.9		
31M16	tet:	34.0	0.3	7.2	0.7	10.1	3.6	0.1	0.0	44.1	98.6	0.7	0.09
	sph:	0.4	0.1	49.0	0.1	0.0	0.0	0.0	0.1	50.5	98.0		

Table 3 EPMA analytical data of coexisting sphalerite and tetrahedrite-tennantite group minerals in the yellow ore.

		Atomic %											
		Cu	Ag	Zn	Fe	As	Sb	Mn	Cd	S	Total (wt%)	As/As+Sb	Fe/Fe+Zn
31M19	tet:	36.2	0.1	6.3	1.1	12.3	2.4	0.1	0.0	41.6	96.7	0.8	0.14
	sph:	0.7	0.0	50.7	0.6	0.0	0.0	0.2	0.2	47.7	97.0		
31M17	tet:	34.3	0.0	7.1	1.1	11.2	2.7	0.0	0.0	43.6	101.0	0.8	0.13
	sph:	0.6	0.0	50.5	0.4	0.0	0.0	0.0	0.1	49.3	98.6		
31M17	tet:	34.4	0.0	7.0	0.7	13.4	0.2	0.0	0.0	44.2	99.0	1.0	0.09
	sph:	0.3	0.0	50.3	0.0	0.0	0.0	0.0	0.1	49.3	99.0		
6A11'	tet:	33.9	0.1	6.0	1.1	12.9	0.5	0.2	0.2	45.2	100.0	1.0	0.16
	sph:	0.2	0.0	49.2	0.3	0.0	0.1	0.2	0.2	49.9	100.0		

High molar ratios of As/As+Sb shown in Tables 2 and 3 indicate that tetrahedrite-tennantite group minerals found in the No. 11 ore deposit of the Shakanai mine should be identified as tennantite. Tennantite as listed in Tables 2 and 3 is poor in silver, while some tennantites rich in antimony have higher content of silver. There is, however, no frequent compositional zoning in a single grain of tennantite. Furthermore, there is no gradual

variation in chemical compositions of sphalerite and tennantite between different horizons in ores. Zinc and iron contents of tennantite is proportional to those of sphalerite coexisting with tennantite (Tables 2 and 3).

The commonest clay mineral in the altered host rocks of the No. 11 ore deposit in the Shakanai mine is interstratified spicrite/montmorillonite, which contains small amounts of expandable layers. The characteristic 10-

Table 4 X-ray fluorescence analytical data of altered rocks in the north area of the Shakanai mine.

	K-feldspar zone		Chlorite-sericite zone		Mixed layer clay zone under the ore		Mixed layer clay zone as a transitional zone		Montmorillonite zone		Mordenite zone	
	700-345	699-276	637-430	693-303	693-333	693-335	607-435	638-359	607-275	638-49	607-335	638-110
SiO ₂	61.0	68.8	59.8	68.8	71.0	52.9	56.9	71.8	63.3	55.0	65.2	63.4
TiO ₂	0.2	0.3	0.4	0.3	0.3	0.5	0.4	0.3	0.2	0.2	0.3	0.2
Al ₂ O ₃	13.4	13.5	20.3	15.2	13.7	19.6	21.7	13.7	11.0	13.5	12.9	13.3
Fe ₂ O ₃	8.8	3.8	3.8	3.1	4.5	5.7	2.0	2.3	2.1	4.0	2.3	2.0
MnO	0.1	0.2	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1
MgO	3.1	3.3	4.5	3.1	1.3	4.3	6.5	3.2	3.2	4.0	0.9	0.9
CaO	0.2	0.2	0.3	0.2	0.2	0.4	0.3	0.2	1.3	4.2	1.6	0.9
Na ₂ O	1.9	1.1	1.5	2.0	1.1	0.4	0.3	3.8	1.5	2.7	2.3	3.0
K ₂ O	4.6	4.2	4.1	3.0	3.2	4.1	5.0	1.5	0.2	0.6	2.4	3.2
P ₂ O ₅	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ig. loss	5.5	3.5	4.7	3.5	5.0	10.5	6.7	2.9	17.9	15.7	12.7	13.1
Total	98.7	99.0	99.3	99.3	100.3	98.4	99.7	99.7	100.6	99.9	100.5	100.0

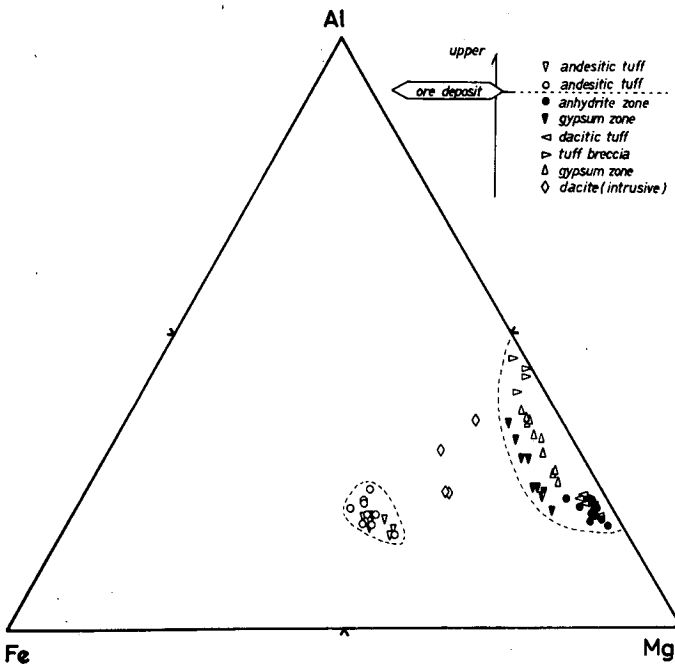


Fig. 4

Fig. 4 Al-Fe-Mg mole proportional diagram for chlorite from the No. 11 ore deposit in the Shakanai mine, analyzed by EPMA.

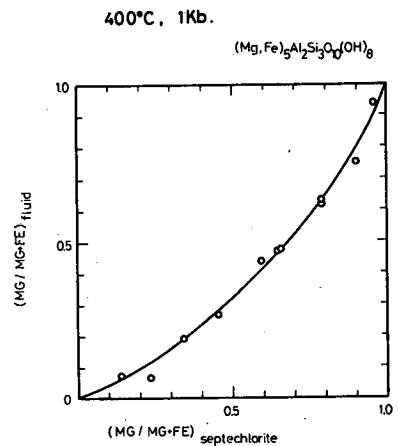


Fig. 5

Fig. 5 Experimental result on the distribution of Mg and Fe between septechlorite and chloride solution (total $m_{cl^-} = 1.0$ mole/l) at 400°C and under 1 Kb.

11 Å reflections for these interstratified types are somewhat broadened and variable due to an interference of the first (10.0 Å) order reflection of mica layer with the first (15.0 Å)

and/or second (7.5 Å) orders of montmorillonite layer.

Chlorite minerals are the next most widespread after interstratified sericite/montmoril-

lonite in the deposits. Chemical compositions of chlorite from the No. 11 ore deposit are plotted in Fig. 4. These data were obtained by electron probe X-ray microanalyzer. As shown in Fig. 4, they are grouped into three varieties. Based on the classification of chlorites by HEY (1954), chlorites under the ore horizon are corundophilite — sheridanite — clinochlore — penninite and those on the ore horizon are diabantite and those in the intrusive dacite are equivalent to pycnochlorite. Molar ratios of Mg/Fe are distinctly different between chlorites in the foot-wall rocks and those in the hanging-wall rocks. Chlorites under the ore deposit are very rich in Mg.

Alteration Zone around the Ore Deposit

Alteration minerals from the samples of bore holes, including the bore hole No. 693 which bored 9 meters black ore body, in the north area of the Shakanai mine, have been investigated. All rock samples studied were collected from six bore holes as follows: No. 607, No. 621, No. 693, No. 641, and No. 638 drillings of the Shakanai mine; and HO-37 drilling promoted by MMAJ (1977). The drilling sites are shown in Fig. 6. Samples were assembled from each bore hole at intervals of 5 to 10 meters in average, 0.5 meter near the ore horizon. X-ray diffraction of the un-separated bulk clay samples and of the clay fractions separated by sedimentation method was mainly used for identification. In some cases air-dried orientated aggregates and unorientated aggregates on slides were examined, and some of them were treated with ethylene glycol. Although a great number of authigenic minerals were produced by hydrothermal activities, their assemblages, which were formed at approximate thermodynamic equilibrium, can be grouped according to temperature and the ratio of alkali and alkali earth activity to hydrogen activity in solution (UTADA, 1980). Based on the classification of alteration mineral assemblages by UTADA (1980), the alteration zones appearing in the north area of the Shakanai mine can be defined as follows: mordenite zone, montmorillonite zone, mixed layer clay mineral zone, chlorite-

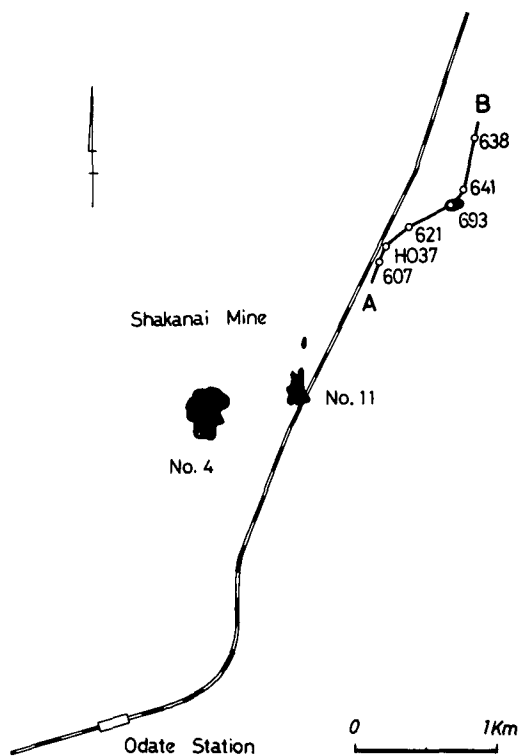


Fig. 6 Location map of investigated drill holes and ore deposits.

	K-feldspar zone	chl.-ser. zone	mix. layer clay zone	mont. zone	mordenite zone
quartz					
opal					
K-feldspar					
albite					
clinoptil.					
mordenite					
mont.					
ser./mont.					
chl./smec.					
chlorite					
sericite					
gypsum			---		
anhydrite			--		
barite			--		
pyrite			-----		

Fig. 7 Mineral assemblages of the alteration zones found in the north area of the Shakanai mine. mont: montmorillonite, clinoptil:clinoptilolite, ser./mont: interstratified sericite/montmorillonite, chl./smec: interstratified chlorite/smectite.

sericite zone and K-feldspar zone. They are shown in Fig. 7. Many mixed layer clay minerals are identified as interstratified sericite/montmorillonite, but interstratified chlorite/smectite occurs rarely. Expandable layer is not identified in detail. Distinction between sericite and interstratified sericite/montmorillonite is admitted to be

$$d(001)_{\text{natural}} - d(001)_{\text{E.G.}} = 0.2 \text{ \AA}$$

This indicates that percentage of montmorillonite layer in interstratified sericite/montmorillonite reaches to 4 to 5 percent, based on data summarized by SHIMODA (1977).

Mineral assemblage in drill hole No. 693 is characterized by the presence of mixed layer clay minerals under the ore and K-feldspar zone found above the ore. The rest is classified into chlorite-sericite zone (Fig. 8). A series of alteration zones in this area is found in drill hole No. 638. In comparison with diagenetic

alteration in the upper pile, hydrothermal alteration zones develops in the lower part (Fig. 9). Alteration zones determined in this way from each bore hole sample are summarized in Fig. 10.

Mixed layer clay mineral zone occurs closely related to the ore deposit. The chlorite-sericite zone is extensively distributed, enclosing and surrounding them. On either side of them,

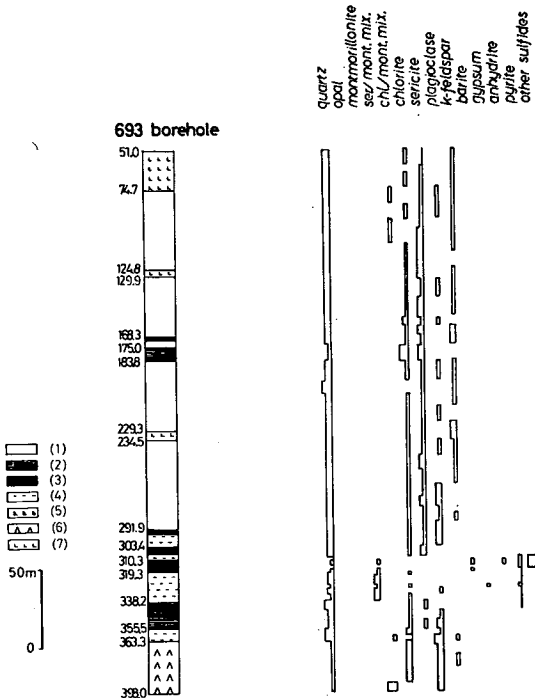


Fig. 8 Mineral assemblages in drill hole No. 693. (1): acidic pyroclastic rocks and lava flows (Sainokami formation), (2): mudstone, (3): ore deposit, (4): acidic pyroclastic rocks and lava flows (Shakanai formation), (5): dacite (intrusive), (6): dolerite (intrusive), (7): dacite (intrusive).

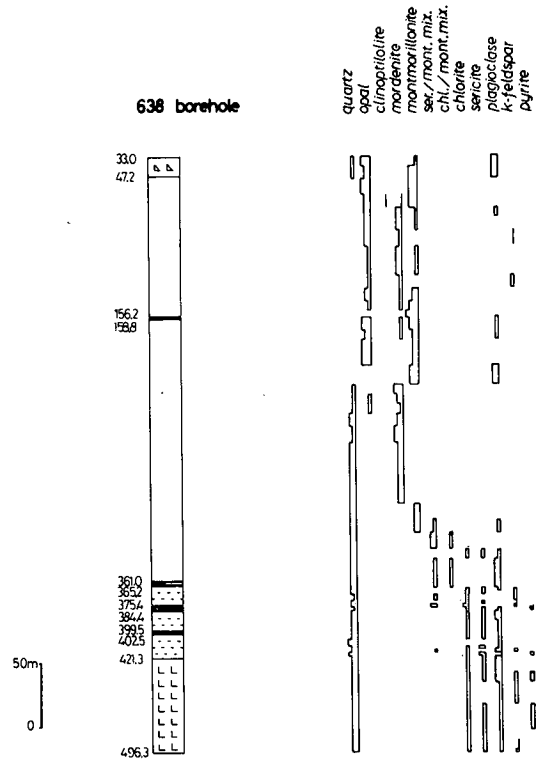


Fig. 9 Mineral assemblages in drill hole No. 638.

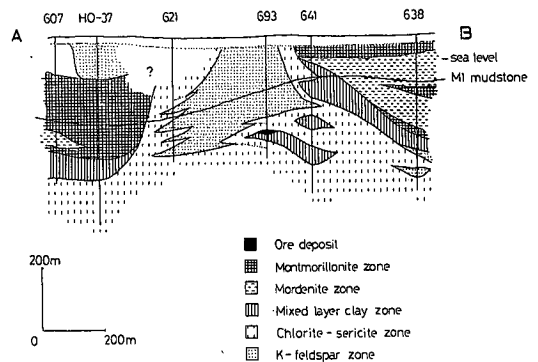


Fig. 10 Cross section showing the alteration zones, along the A-B line.

another mixed layer clay mineral zone and montmorillonite zone are distributed. These hydrothermal alteration zones and diagenetic alteration zones were subjected later to peculiar hydrothermal alteration characterized by K-feldspar zone. When hydrothermal activity in the Shakanai area took place only at the time of kuroko mineralization in Nishikurosawa stage, the volcano-sedimentary rocks lying on the ore should be characterized by diagenetic alteration zones. However, Fig. 10 indicates that the rocks were subjected to hydrothermal alteration characterized by K-feldspar zone and chlorite-sericite zone after Onnagawa stage.

Chlorites from bore samples are classified as Mg-chlorite, but they are poorer in Mg and Si than chlorites found under the No. 11 ore deposit. As already mentioned, in the No. 11 ore deposit of the Shakanai mine, chlorite quite rich in Mg occurs under the ore body, chlorite found above the ore is Mg-Fe chlorite. Similar phenomena can also be observed in drill hole No. 693, but this is less remarkable than that in the No. 11 ore deposit. In some drill holes which were bored at a short distance from the No. 693 ore body, chemical composition of chlorite under the ore horizon is not any more different from that above the ore horizon. Most of chlorites might have been subjected to later hydrothermal alterations in the north area of the Shakanai mine. The difference in the chemical compositions of chlorite might have been remained only near the ore deposit.

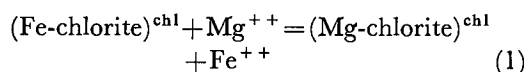
Mixed layer clay zones can be divided into two types. One is closely associated with the ores and the other is regarded as transitional zone far from the ores. Alteration minerals in the mixed layer clay zones are both composed mainly of chlorite, quartz and interstratified sericite/montmorillonite whose expandable layer has below 10 percent in the mineral. Also in the No. 11 ore deposit, interstratified sericite/montmorillonite occurs widely (Figs. 2 and 3). In the ground, hydrothermal alteration zones surrounding ore deposits are distributed in a definite order of the zones as follows: chlorite-sericite zone, mixed layer clay

zone and montmorillonite zone, according to temperature and ion activity ratio of a_{K^+}/a_{H^+} and $a_{Mg^{++}}/a_{H^+}^2$ in solution. Nevertheless, the presence of the mixed layer clay zone closely associated with the ore is inconsistent with the trend above mentioned.

Experimental and Theoretical Considerations on Some Clay Minerals

Chlorite

It should be here taken into consideration on the genesis of Mg-chlorite. From the following reaction:



activity ratio of Mg-chlorite component in chlorites to Fe-chlorite component in chlorites is given by

$$a_{Mg}^{\text{chl}}/a_{Fe}^{\text{chl}} = K_1 (a_{Mg^{++}}/a_{Fe^{++}})$$

where K_1 is an equilibrium constant for the reaction (1). $(\text{Fe-chlorite})^{\text{chl}}$ and $(\text{Mg-chlorite})^{\text{chl}}$ are Fe-chlorite component and Mg-chlorite component in chlorites, respectively. Because K_1 value is unknown, $(a_{Mg^{++}}/a_{Fe^{++}})$ in aqueous solution in equilibrium with minerals is difficult to estimate. As a first step to estimate the activity ratio of Mg^{++} to Fe^{++} in hydrothermal solution, the following experiment for the reaction (1) has been made.

All interactions were carried out in about 250 micro liter gold tube in a cold seal type autoclave. Prepared gel deversed to clinocllore $(\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8)$ -daphnite $(\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8)$ placed in contact with 0.5 m MgCl_2 - FeCl_2 solution has reacted under the condition at 400 °C and under 1 Kbar for seven days. To maintain iron in ferric state during experiments, a mixture of Al_2O_3 -3 SiO_2 gel and equivalent metal-iron powder was used with 0.006-0.01 gram oxalic acid $\text{C}_2\text{H}_2\text{O}_4$ as a reducing agent. After the completion of each run, liquid phase and solid phase were separated by suction filtration. After that the solid and liquid phases have been analysed for iron and magnesium with atomic absorption. Solid phase was identified by X-ray powder diffractometer as chlorite minerals.

Products were identified as 7 Å-septechlorite of clinochlore-daphnite solid solution. Exchange isotherm shown in Fig. 5 has tendency to nearly ideal solution of 7 Å-septechlorite and enrichment of Mg into the chlorites. From these results, excess Gibbs free energy of mixing of septechlorite at 400°C and under 1 Kbar was calculated as low as 0.06 Kcal/mole.

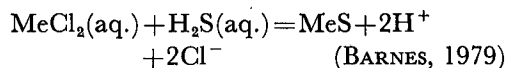
The relative stability of clinochlore has revealed considerable attention in recent years (FAWCETT and YODER, 1966; SEIFERT, 1970; BIRD and FAWCETT, 1973; BIRD and ANDERSON, 1973; ZEN, 1973; HELGESON et al., 1978). It has been observed repeatedly in previous experimental phase equilibrium studies that 7 Å-septechlorite commonly forms initially as a reaction product in the vicinity of 500°C, but it later inverts to its 14 Å counterpart. At high temperatures, 14 Å-chlorite forms immediately, but at low temperatures, only 7 Å-septechlorite forms. Conversion of 7 Å-clinochlore to the 14 Å variety probably requires a relatively high activation energy, which could account for the persistence of 7 Å-clinochlore in weathering profiles, sedimentary environments, hydrothermal alteration zones and laboratory experiments at temperatures from 400°C to 500°C. When there is little significant difference in Mg-Fe distribution between chlorite and chloride solution through this conversion, it can be stated that chlorite quite rich in magnesium has participated with magnesium-rich hydrothermal solution. As a matter of fact, Mg-metasomatism is evident in hydrothermal alteration zones surrounding Kuroko deposits (IIJIMA, 1974; IZAWA et al., 1978). Accordingly, contribution of magnesium-rich hydrothermal solution is primary factor for the formation of Mg-chlorite. Under the high total sulfur concentration condition, activity of Fe^{++} in solution might be restricted lower, due to deposition of pyrite with decreasing of temperature. In contrast with it, interaction between magnesium rich hydrothermal solution and rocks has taken place strongly near the place of ore deposition. As the result of this, $a_{Mg^{++}}/a_{Fe^{++}}$ in solution has increased relatively. Chlorites in equilibrium with high $a_{Mg^{++}}/a_{Fe^{++}}$ solution form Mg-chlorite.

Mg^{++} in chloride solution has tendency to be fixed into chlorite than Fe^{++} (Fig. 4). This may be accelerated with decreasing of temperature.

It is interesting to note that the chlorite closely associated with sulfide minerals is absent. It seems that solubility of chlorite is related to deposition of sulfide minerals. It is well known that the chlorite is unstable under the low pH condition. As a result of large quantity of deposition of sulfide minerals, H^+ has been probably brought into solution and increased solubility of chlorite.

Mixed layer clay mineral

It is possible that the mixed layer clay zone found under the ore has formed in a different process from the formation of the mixed layer clay zone regarded as a transitional zone. The mixed layer clay zone closely associated with the ore is considered to be influenced by the deposition of sulfide minerals. As recognized from the reaction:



activity of H^+ in solution will increase after the deposition of large quantity of sulfide minerals. Because of this, ratio of ion activities in solution, a_{K^+}/a_{H^+} , becomes lower. In lower a_{K^+}/a_{H^+} condition and at lower temperatures, interstratified sericite/montmorillonite might become more stable than sericite. Higher activity of H^+ may cause to increase the solubility of chlorite associated with sulfide minerals, as mentioned before.

In this connection, Mg^{++} and Ba^{++} in ore-forming solution may also play an important role to form the interstratification of the minerals. From the experiment in which Li^+ has caused to form the interstratified structure, Mg^{++} with most similar ion-radius (0.65 Å) to Li^+ (0.60 Å) may accelerate the interstratification in the same manner. For instance, TOMITA and SUDO (1971) and SHIMODA et al. (1974) have synthesized the mixed layer minerals from sericite reacted with $LiNO_3$ solution. Li^+ gets into unoccupied site in octahedral layer of dioctahedral muscovite (sericite). To keep electro neutrality

in muscovite structure, interlayer K^+ is easy to release. Potassium is held strongly adjacent to interlayer regions where the potassium is replaced, i.e. the two regions will alternate. This is interstratification. With respect to Ba^{++} , the experiment by REICHENBACH and RICH (1968) has revealed that interlayer-K could be removed almost completely from muscovite by using 0.1 N $BaCl_2$ solution at 120°C. This K-exchange may induce to form the interstratification.

Mixed layer clay mineral can not be disposed as an intermediate metastable alteration product. This should be reconsidered from the viewpoint as a characteristic reflection of kuroko mineralization.

Conclusion

1. Complex mixtures of black ore and tuff breccia and a paragenesis of various sphalerites support that the No. 11 ore deposit in the Shakanai mine has formed at various stages.

2. Electrum and silver minerals are frequently found in the bornite-bearing black ore. It is calculated that this ore has been formed at about 250°C and under $10^{-8.2}$ atom-fs₂.

3. Tetrahedrite-tennantite group minerals are rich in arsenic and poor in silver. Their zinc and iron contents are proportional to those of sphalerite coexisting with them.

4. The commonest clay mineral in the altered host rocks of the Shakanai ore deposit is interstratified sericite/montmorillonite, which contains small amounts of expandable layers. Chlorite minerals are the next most widespread around the deposits.

5. Chlorite rich in Mg occurs widely under the ore deposits. Contribution of magnesium-rich hydrothermal solution is primary factor for the formation of Mg-chlorite.

6. The mixed layer clay zone closely associated with the ore deposits has formed in a different process from the formation of the mixed layer clay zone far from the ore deposits. The rocks have been altered to the sericite-chlorite zone by the ore-forming solution at first. As the result of the deposition of large quantity of sulfide minerals, H^+ was released

to the host rocks and to the sea water. At lower temperatures and in lower a_{K^+}/a_{H^+} and $a_{Mg^{++}}/a_{H^+}^2$ conditions, it came easy to form interstratified minerals from sericite or chlorite.

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秋田県釈迦内黒鉱鉱床における変質鉱物と鉱化作用

田村元紀

要旨 釈迦内鉱山第11鉱体と、釈迦内北部のポーリングコアにみられる鉱物の産状・鉱物種とその化学組成の記載を顕微鏡観察、X線粉末回折データ、EPMA分析値などをもとに行なった。鉱液中の $a_{Mg^{++}}/a_{Fe^{++}}$ を推定する第一歩として、緑泥石と塩水溶液間のイオン交換平衡実験を行なった。

釈迦内鉱山第11鉱体でみられる鉱石鉱物は他の黒鉱鉱床のものとは基本的に変わりはないが、その組織や化学組成は非常に変化に富んでいる。黒鉱鉱石と酸性火砕岩が密雑に混合したものや多種の閃亜鉛鉱が同じ鉱石にみ

れることなどは、第11鉱体がさまざまな形成過程を経ていることを暗示している。

絹雲母/モンモリロナイトの混合層粘土鉱物と緑泥石は鉱床付近に広くみられる。Mgに富む緑泥石は鉱床下にしばしばみられ、その生成には、Mgに富む溶液の関与が基本的な要因である。鉱体に密接に伴ってみられる混合層粘土鉱物帯は、変質帯間の遷移帯とは成因的に区別され、温度の降下に伴って、硫化鉱物の沈澱に影響を受けて生成したと考えられる。