Model for Ore–forming Solutions and Ore–forming Environments:

Kuroko vs. Veins in Miocene "Green Tuff" Region of Japan

By

Takeo Sato*

Abstract

Under the assumption that Kuroko and vein-type deposits in the Miocene Green Tuff region of Japan were similar in their formative conditions and the initial chemical composition of the ore-forming solution, the physicochemical model for Kuroko mineralization and Kuroko-forming solution (Sato, 1971; 1972) are applied to the case of vein-type deposits. The mineral parageneses, the compositional variation in ores and the vertical extents, of the simulated veins show good agreement with those of the natural veins.

1　Introduction

The Kuroko-type strata-bound sulfide-sulfate deposits and the vein-type base metal and Au–Ag deposits of Miocene age occur in a similar geologic environment, called the Green Tuff region. The sulfide mineral assemblages, the ore metals precipitated, the features of wall-rock alteration, etc. are also very similar in both groups of deposit. It may be a feasible assumption that the hydrothermal solutions which formed the two types of ore deposit were similar in chemical composition and that the formative physicochemical environments were not much different between them.

On the basis of this assumption, an attempt will be made in this article to simulate various aspects of vein-type deposits, starting from the chemical model which has been postulated for the Kuroko-type deposits (Sato, 1971; 1972). Calculated ore grade and vertical extent of the hypothetical ore vein will then be compared with those observed in the natural vein-type deposits.

2　Model for the Kuroko-type Deposits

Sato (1971; 1972) calculated the formative environments of the Kuroko deposits and the initial heavy metal concentrations of the Kuroko-forming solution, and demonstrated that a chloride complex model can satisfactorily explain the mineral assemblages and the mineral distribution observed in the Kuroko deposits.

The basic assumptions adopted in these calculations were as follows:

(1)　Ore metals in the ascending solution mainly exist in the form of chloride complexes.

(2)　Initial composition of the ascending ore-forming solution does not change during the course of mineralization.

(3)　Almost all of the initially dissolved ore metals are precipitated through the ore-forming processes and fixed into the ore deposits under consideration.

(4)　The initial copper concentration is greater than 1 ppm, and the initial sulfur concentration is sufficient to precipitate all the dissolved ore metals as sulfide minerals observed in the deposits (including Ba as barite).

(5)　pH of the solution is buffered by the sericite-kaolinite assemblage.

(6)　The initial concentration of NaCl is 3 molal.

Calculations based on these assumptions revealed that the initial chemical composition of the Kuroko-forming solution should be in a very limited range to produce the mineral assemblage and its variation pattern observed in the deposits (Table 1). Progressive changes in environmental physicochemical values for the ascending solution were also calculated as shown in Table 2. In these calculations, it

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*　Mineral Deposits Department.

Table 1 Initial concentrations of some elements in the three model solutions for Kuroko
deposits at Uchinotai, Kosaka Mine (SATO, 1971)

Model	Na/K	$\log m_t(Cu)$	$\log m_t(Fe)$	$\log m_t(Pb)$	$\log m_t(Zn)$	$\log m_t(Ag)$	$\log m_t(Ba)$	$\log m_t(S)$
I	3	−4.5	−3.6	−5.5	−4.4	−7.2	−4.5	−3.0
II	3	−4.0	−3.1	−5.0	−3.9	−6.7	−4.0	−2.5
III	3	−4.5	−3.6	−5.5	−4.4	−7.2	−4.5	−2.5

Only these three combinations are possible under the assumptions adopted (see text) and changing each of
the concentrations by 0.5 in logarithmic unit. The initial NaCl concentration is fixed at 3 molal.

Table 2 Calculated progressive changes in physicochemical conditions for the hydrothermal
solution which formed the Uchinotai Kuroko deposits. The solution is assumed to
have mixed with the contemporaneous seawater at stage-II. After SATO (1972)

	Stage	T (°C)	$\log fS_2$	pH	$\log m_t(S^=)$	$\log m_t(SO_4^=)$* seawater
Model-I	I	215	−42	3.8	−3.0	—
	II	210	−43	3.8	−3.1	—
	III	195	−44	3.9	−3.3	−2.6
	IV	180	−45	4.1	−3.5	−2.3
	V	135	−51	4.6	−3.5	−1.9
Model-II	I	235	−42	3.7	−2.5	—
	II	230	−42	3.7	−2.6	—
	III	225	−42	3.8	−2.7	−3.2
	IV	210	−43	3.9	−2.8	−2.5
	V	170	−45	4.3	−2.9	−2.0

* Denoting the total molality of sulfate coming from the mixed seawater.

was necessary to assume the disequilibrated incorporation of the contemporaneous seawater sulfate in
order to account for the observed distribution of barite (SATO, 1972). The figures tabulated in Table 2
were calculated assuming that mixing of the ascending solution and the contemporaneous seawater
took place after stage-II[*1].

These calculated physicochemical values are in good agreement with those estimated from fluid
inclusion studies (LU, 1970; WATANABE, 1970) and those from examination of the observed mineral
parageneses (SATO, 1969; KAJIWARA, 1970).

3 Model for Vein-type Deposits

The basic assumption adopted here is that the same chemical model would be applicable to both
the Kuroko and the vein-type mineralizations. With respect to the values in Table 2, however, some
modifications may be required because the mixing of ore-forming solution and seawater is thought to be
not essential in the case of vein-type ore formation.

In the previous calculations (SATO, 1971), it was shown that the Kuroko mineralization excluding
the deposition of sulfate minerals can be explained without introduction of any seawater sulfate into the
site of ore formation. As the mineral parageneses of the vein-type deposits are found to be much the same
with this sulfate-less Kuroko, the hypothetical environments for the latter (Table 3) will be used in the
following calculations.

Another important difference between the two types of ore deposits would be the thermal gradient
at the site of ore formation. Since the thickness of black ore zone (between stage-III and stage-V in

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[*1] Under the assumption that the ascending solution precipitates minerals differentially along a constant physico-
chemical gradient, five stages were set in its progressively changing environmental conditions. Stages I to V cor-
respond to the conditions assumed for the bottom of the siliceous ore zone, between the siliceous and yellow ore
zones, between the yellow and the lower black ore zones, between the lower and the upper black ore zones, and
the uppermost part of the upper black ore zone, respectively (SATO, 1971).

Fig. 1a

Solubilities of Cu, Fe, Pb, Zn, Ag and silica in the two model solutions with respect to chalcopyrite, values used in the calculation are from Table 3.

The solubilities of the metals at a given temperature are given by;

$$m_{t(Cu)} = \frac{K_1}{\dot{r}_{Cu^+}\, \dot{r}_{Fl^{++}}\, \dot{r}^2{}_{S^{--}}\, m_{t(Fe)}\, m^2{}_{(S)}\, f_{O_2}{}^{\frac{1}{4}}\, a_{H^+}} \qquad \cdots\cdots(8)$$

$$m_{t(Fe)} = \frac{K_2}{\dot{r}_{Fe^{++}}\, \dot{r}^2{}_{S^{--}}\, m^2{}_{t(S)}\, f_{O_2}{}^{\frac{1}{2}}\, a^2{}_{H^+}} \qquad \cdots\cdots(9)$$

$$m_{t(Pb)} = \frac{K_3}{\dot{r}_{Pb^{++}}\, \dot{r}_{S^{--}}\, m_{t(S)}} \qquad \cdots\cdots(10)$$

$$m_{t(Zn)} = \frac{K_4}{\dot{r}_{Zn^{++}}\, \dot{r}^{S^{--}}\, m_{t(S)}} \qquad \cdots\cdots(11)$$

Fig. 1b

pyrite and chalcopyrite, galena, sphalerite, argentite, and quartz, respectively. The physicochemical

$$m_{t(\mathrm{Ag})} = \frac{K_5^{\frac{1}{2}}}{\dot{\gamma}_{\mathrm{Ag}^+} \dot{\gamma}_{\mathrm{S}^{--}}^{-\frac{1}{2}} m_{t(\mathrm{S})}^{\frac{1}{2}}} \qquad\qquad \dots\dots(12)$$

$$m_{t(\mathrm{Ba})} = \frac{K_6}{\dot{\gamma}_{\mathrm{Ba}^{++}} \dot{\gamma}_{\mathrm{SO}_4^{--}} m_{t(\mathrm{SO}_4^{--})}} \qquad\qquad \dots\dots(13)$$

$$m_{t(\mathrm{SiO}_2)} = \frac{K_7}{\dot{\gamma}_{\mathrm{H}_4\mathrm{SiO}_4} m_{t(\mathrm{SiO}_2)}} \ , \qquad\qquad \dots\dots(14)$$

where m_t represents the total molality of the subscripted species in the aqueous phase[*2], $\dot{\gamma}$ denotes the stoichiometric activity coefficient of the subscripted species as defined by HELGESON (1969), and

[*2] Strictly speaking, $m_{t(\mathrm{Cu})}$, $m_{t(\mathrm{Fe})}$ and $m_{t(\mathrm{S})}$ in the above equations should be replaced by $m_{t(\mathrm{Cu}^+)}$, $m_{t(\mathrm{Fe}^{++})}$ and $m_{t(\mathrm{S}^{--})}$ respectively. However, under the conditions shown in Table 3, total molalities of Cu^{++}, Fe^{+++} and SO_4^{--} in the solution are negligibly small in comparison with those of Cu^+, Fe^{++} and S^{--}, respectively.

Ag (g/t)
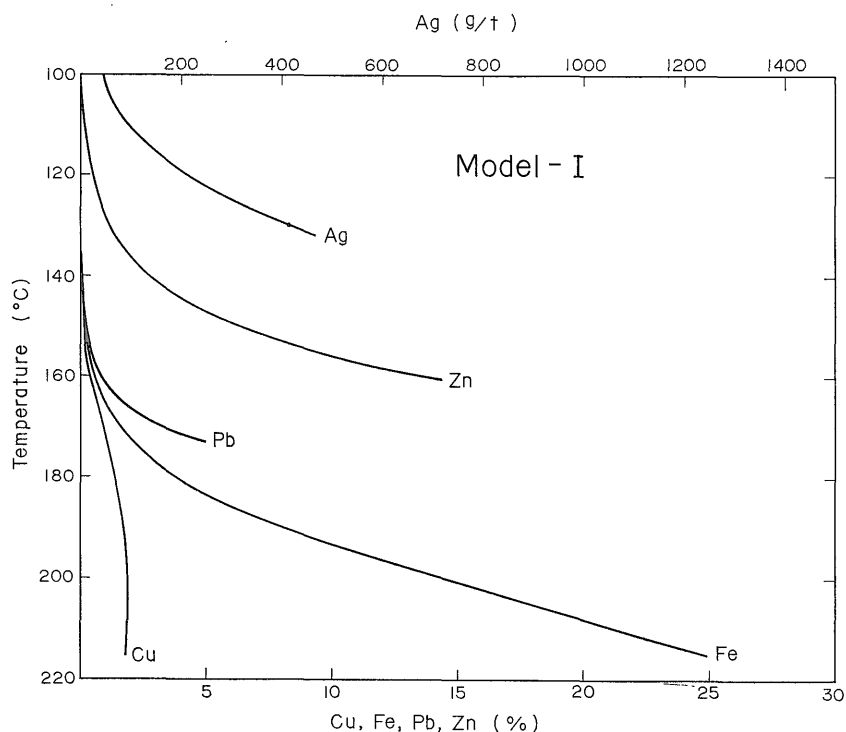
Fig. 2a

Calculated grades of Cu, Pb, Zn and Ag of the ores formed by the two model solutions. assuming

K_i represents the equilibrium constant of the i th reaction. Since K is a function of temperature only, and $\dot{\gamma}$ is that of temperature and NaCl concentration which is fixed as 3 molal, we can calculate the solubilities of the above metals from the values tabulated in Table 3 neglecting the effects of pressure. Plottings of the logarithms of these solubilities against temperature are shown in Fig. 1. The temperatures at which the individual minerals start to precipitate from the solutions of the two models are calculable from the initial concentrations of the metals given in Table 1. These temperatures are shown in Table 4.

Table 4   Temperatures in °C at which pyrite, chalcopyrite, galena, sphalerite and
argentite become saturated in the solutions estimated from their solubilities in
Fig. 1 and the initial metal concentrations in Table 1.

	Pyrite	Chalcopyrite	Galena	Sphalerite	Argentite
Model-I	215	215	173	160	132 (°C)
Model-II	235	235	194	183	150 (°C)

5   Comparison of the Calculated and the Observed Veins

From Fig. 1 and the initial metal concentrations in Table 1, we can now estimate the composition of ore formed at any given temperature assuming that the minerals precipitated from the solution are only pyrite, chalcopyrite, galena, sphalerite, argentite, barite[3] and quartz[4] (Fig. 2 and Table 5).

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[3] The model solutions are calculated to be undersaturated with respect to barite throughout the conditions considered here.

[4] The solutions are assumed to be saturated with quartz when they ascend to the site of mineralization.
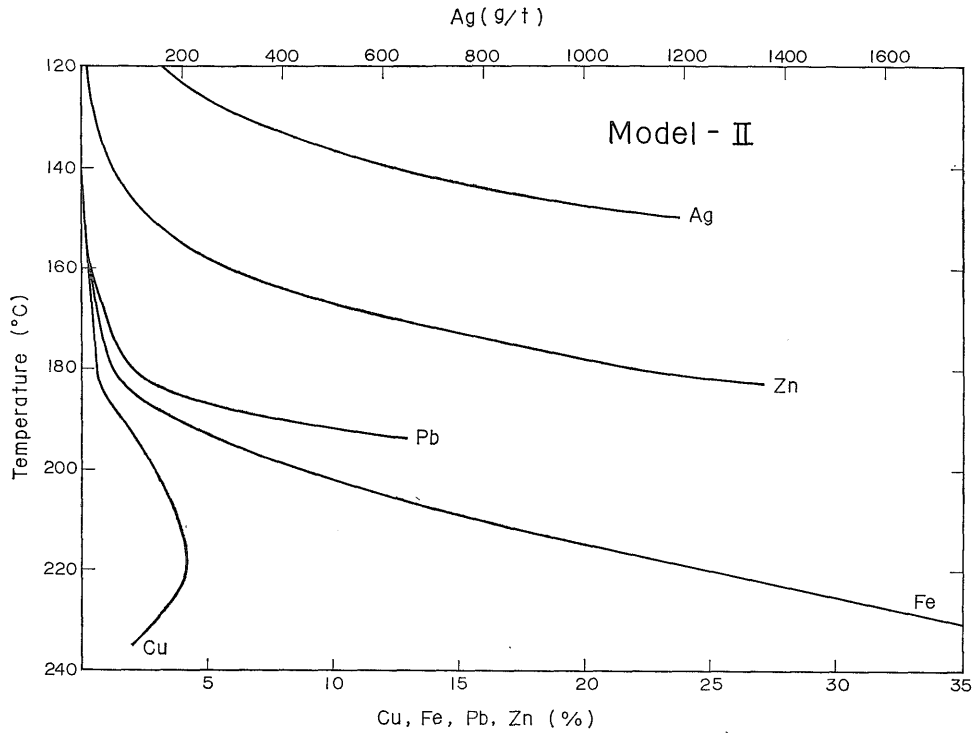
Figs. 2b

that the precipitated minerals are pyrite, chalcopyrite, galena, sphalerite, argentite and quortz.

Table 5   Calculated compositions of the ores formed from the two model solutions at
different temperatures.

Model-I

T, °C	Cu, %	Fe, %	Pb, %	Zn, %	Ag, g/t	S, %	SiO$_2$, %
100	*	*	*	*	45	*	100
110	*	*	*	0.2	90	0.1	99.7
120	*	*	*	0.5	220	0.3	99.3
130	*	*	*	1.1	430	0.6	98.3
140	0.1	0.1	0.1	2.7	–	1.5	95.4
150	0.2	0.3	0.3	6.3	–	3.6	89.3
160	0.4	0.6	0.9	13.7	–	7.9	76.6
170	0.9	1.6	3.2	–	–	1.9	92.5
180	1.3	3.7	–	–	–	4.9	90.0
190	1.7	8.1	–	–	–	8.1	82.1
200	1.9	14.7	–	–	–	15.8	67.7
210	1.9	21.7	–	–	–	23.4	53.1

Model-II

T, °C	Cu, %	Fe, %	Pb, %	Zn, %	Ag, g/t	S, %	SiO$_2$, %
120	*	*	*	0.2	160	0.1	99.7
130	*	*	*	0.5	310	0.2	99.3
140	0.1	0.1	*	1.2	620	0.8	97.8
150	0.2	0.2	0.2	2.7	1200	1.4	95.3
160	0.3	0.3	0.4	5.7	–	2.9	90.4
170	0.5	0.7	1.0	12.3	–	6.7	78.9
180	0.6	1.2	2.0	22.7	–	12.9	60.5
190	1.6	3.7	7.8	–	–	4.4	82.5
200	2.9	8.6	–	–	–	8.1	80.4
210	3.8	15.9	–	–	–	15.9	64.4
220	4.2	25.4	–	–	–	26.3	44.2
230	2.9	34.4	–	–	–	37.4	25.4

Table 6 Some data of the matural ore veins in the Green Tuff region. Vertical extents and average ore grades are from Ore Deposits of Japan, Part II (Jap. Min. Ind. Ass., 1968). Formation temperatures and temperature gradients are those estimated from fluid inclusion studies by MIYAZAWA et al. (1971) and MIYAZAWA and ENJOJI (1972).

Mine	Vein	Vert. Ext. (m)	Metal	Average Ore Grade						Form. Temp. (°C)	Temp. Grad. (°C/100 m)
				Cu, %	Pb, %	Zn, %	Au, g/t	Ag, g/t	S, %		
Tochigi	Tobu-No.4	360*	Cu	5.6	–	–	–	–	–	320–240	
Kidogasawa	Shitaban-hi	350*	Cu	1.17	–	–	–	–	–	268–180	30
Yaso	Akakura-950m	450*	Cu-(Zn)-(Pb)	3.25	–	–	–	–	–	315–182	50
	Kido-No.2	280*	Cu-(Zn)-(Pb)	2.80	–	–	–	–	–	290–168	50
Oppu	Honpi	450*	Cu-Zn-Pb	0.62	1.62	4.31	–	–	–		
Namariyama	Honpi	350*	Cu-Zn-Pb	1.75	1.01	6.65	–	–	19		
Sai	No. 1	150*	Cu-Zn-(Pb)-Ag	2.50	–	2.30	–	30	–	285–135	70
Osarizawa	Showa-No.5	585*	Cu-(Pb)-(Zn)-(Au)-(Ag)	2.2	–	–	–	–	–	266–168	30
Mikawa	Takara	300*	Cu-Zn-Pb-Au-Ag	0.62	0.29	1.78	1.9	31	–		
Toyoha	Tajima	460	Zn-Pb	–	4.46	10.44	–	–	–	220–160	30
Hosokura	Syoko	500*	Zn-Pb	–	3.13	7.86	–	–	–	240–132	
Chitose	Daikoku-No.3	500*	Au-Ag	–	–	–	18	122	–	230–145	
Seikoshi	No.2	120	Au-Ag	–	–	–	17	620	–	234–178	30–40

* Vertical extent from the outcrop.

The hypothetical veins show a distinct mineral zoning, which is very similar to that observed in the natural veins.

For the sake of comparison with the ore grades in the natural ore veins in the Green Tuff region (Table 6), average ore grades of the individual mineral zones and the whole vein are calculated assuming that the cutoff grades are Cu = 1%, Pb + Zn = 5% and Ag = 100 g/ton (Fig. 3). The vertical extents of the individual mineral zones and the whole vein are also shown in the same figure on the assumption that the thermal gradient is 10 °C/100 m or 30 °C/100 m.

6 Concluding Remarks

Agreement between the calculated and the observed values of ore grades, vertical extents of economic veins and formation temperatures are remarkable (compare Table 6 and Fig. 3). In Takara vein of Mikawa mine, for example, the average grades of Cu, Pb, Zn and Ag are 0.62%, 0.29%, 1.78% and 31 g/ton, respectively, while the calculated grades for Model-I are 1.1%, 0.3%, 1.3% and 35 g/ton, respectively. One of the major Pb-Zn veins of Toyoha mine (Tajima vein), as another example, contains 4.46% of Pb and 10.44% of Zn on the average and its formation temperatures are estimated to have been between 220° and 160 °C (MIYAZAWA et al., 1971); wheras, in the calculations for Model-II solution, a Pb-Zn vein with 2.7% Pb and 10.1% Zn is resulted between 194° and 157 °C.

These remarkable agreements suggest that the following conclusions may be drawn.

(1) The initial metal concentrations of the model ore-forming solutions adopted here appear to be most reasonable, because if we assume either higher of lower metal concentrations, the calculated ore grades show unreasonable values.

(2) The essential difference between the mineralizing processes of the Kuroko and the vein-type deposit is the incorporation of the contemporaneous seawater into the chemical system of Kuroko formation.

(3) The initial chemical composition of the ascending solution and the formative conditions such as temperature, pH and oxygen fugacity, are essentially the same between the mineralizations of the two types of ore deposit occurring in the Green Tuff region.

	Average Grade					Temp. Range (°C)	Vertcal Extent (m)	
	Cu, %	Pd, %	Zn, %	Ag, g/t	S, %		10°C/100m	30°C/100m
①	1.6	0.1	—	—	14.2	215—171	440	113
②	0.5	1.4	4.5	—	3.4	173—147	260	87
③	*	*	0.6	360	0.5	132—111	210	70
④	1.3	0.4	1.3	—	11.5	215—147	680	227
⑤	1.3	0.3	1.3	35	9.5	215—111	1,040	347
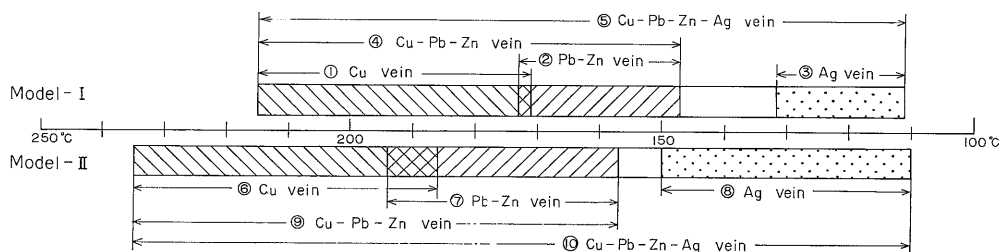
	Average Grade					Temp. Range (°C)	Vertical Extent (m)	
	Cu, %	Pb, %	Zn, %	Ag, g/t	S, %		10°C/100 m	30°C/100 m
⑥	3.1	0.6	—	—	25.8	235—186	490	126
⑦	0.6	2.7	10.1	—	7.1	194—157	370	123
⑧	*	*	1.0	520	0.5	150—110	400	133
⑨	2.8	0.9	3.4	—	14.8	235—157	780	260
⑩	2.3	0.7	3.0	74	12.2	235—110	1,250	417

Fig. 3. Average ore grades, ranges of formation temperatures and vertical extents of the calculated hypothetical ore veins. The cutoff grades are Cu = 1%, Pb + Zn = 5% and Ag = 100 g/ton. Vertical extents are calculated assuming that the thermal gradient is 10 °C/100 m or 30 °C/100 m.

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鉱化溶液と鉱床生成環境のモデル：グリーンタフ地域における黒鉱と鉱脈の比較

佐 藤 壮 郎

要　　旨

　黒鉱鉱床と鉱脈型鉱床の物理化学的な生成条件や鉱化溶液の初生的な性質には大きな違いはなかったものと仮定して，黒鉱鉱化作用および黒鉱鉱床をもたらした鉱化熱水溶液のモデル（SATO, 1971）により，仮想的な鉱脈鉱床を計算で作った．計算された鉱石品位や鉱脈の垂直的な拡がりなどは，実際にグリーンタフ地域で見られる鉱脈型鉱床の特徴によく一致し，上述の仮定が妥当なものであることを示唆している．