Title	Geochemical Environments of the Neogene Ore Formation in the Green Tuff Region, Japan
Author(s)	WATANABE, Makoto
Citation	Journal of science of the Hiroshima University. Series C, Geology and mineralogy , 8 (1) : 67 - 94
Issue Date	1983-06-18
DOI	
Self DOI	10.15027/53099
URL	https://ir.lib.hiroshima-u.ac.jp/00053099
Right	
Relation	

Geochemical Environments of the Neogene Ore Formation in the Green Tuff Region, Japan

By

Makoto WATANABE

with 20 Tables and 8 Text-figures

(Received December 21, 1982)

ABSTRACT: According to the field and laboratory observations, mineral assemblages found, composition of sphalerite coexisting with pyrite, fluid inclusion data, and thermochemical calculations, the overall geochemical environments of the Neogene mineralization in the Green Tuff region of Japan are evaluated in the present article. The depositional environments prevailing at the time of the Neogene ore formation can be roughly classified into two types, those of high to intermediate oxygen and sulfur fugacity, and those of intermediate to low oxygen and sulfur fugacity, respectively. The former, including the Kuroko deposits, gold-silver veins, copper-lead-zinc-manganese veins, and pyrrhotite-free lead-zinc veins, is a region bounded by the following mineral assemblages: alabandite-rhodochrosite; pyrite-magnetite (or pyrite-hematite); magnetite-hematite; galena-anglesite; pyrite-bornite-chalcopyrite; oldahmite-anhydrite; and fixed iron content of sphalerite (3 mol. % FeS). On the other hand, the latter, including lead-zinc veins with or without pyrrhotite, is a region bounded by the assemblages: alabandite-rhodochrosite; graphite-carbon dioxide; pyrite-pyrrhotite; pyrite-magnetite; and oldahmite-anhydrite. Among them, the mineral assemblage, pyrite-bornite-chalcopyrite is characteristic of the Kuroko deposits. Then, assuming minerals-fluid equilibrium, the chemical features of the ore fluids responsible for the Neogene ore formation are estimated. The relative concentrations of major metal species present in the ore fluids are as follows: in the low oxygen fugacity region, generally, $Pb < Cu < Zn \lesssim Fe$ and $Pb < Fe < Cu \lesssim Zn$ at 200°C and 250°C, respectively. In the high oxygen fugacity region, generally, $Pb < Fe < Cu \lesssim Zn$ at 200°C and 250°C. The calculated concentrations, based on the molal concentrations in log scale, are compared with those of the active geothermal brines. The results are as follows: the geothermal fluids from New Zealand (e.g. Wairakei, Champagne Pool, and Broadlands) and possibly sea water have a similar composition to those of the Neogene ore fluids of high to intermediate oxidation state at 200°C, while the fluids from the Discovery Deep, Red Sea and Matupi, T. P. N. G. have a similarity in chemical composition to those of the Neogene ore fluids of low to intermediate oxidation state at 250°C.

CONTENTS

I. INTRODUCTION

Theoretical and experimental bases for genetical discussions of hydrothermal ore deposition were provided by investigators such as those of KULLERUD (1953, 1967), HOLLAND (1959, 1965), BARNES and KULLERUD (1961), and BARTON and TOULMIN (1966). Those have further been extended by HELGESON (1964, 1969, 1970), BARTON and SKINNER (1967), NRIAGU (1971a, 1971b), OHMOTO (1972), and many others. Such a concept of chemical equilibrium has been extensively applied to the Kuroko deposits (e.g. KAJIWARA, 1970, 1971, 1973a, 1973b; KAJIWARA and HONMA, 1972; SATO, 1972, 1973; URABE, 1974a, 1974b; WATANABE, 1976), to vein-type deposits of volcanic affinity (e.g. HELGESON and GARRELS, 1968; SHIKAZONO, 1973, 1974a, 1974b, 1975; ROBINSON, 1974; HATTORI, 1975; WATANABE, 1976), to the Mississippi Valley-type deposits (e.g. ANDERSON, 1975), to wall rock alteration including porphyry copper deposits (e.g. MEYER and HEMLEY, 1967; RAYAMAHASHAY and HOLLAND, 1969), and to other deposits.

As to the Neogene ore deposits in the Green Tuff region, geochemical environments of the Kuroko mineralization were first discussed by KAJIWARA (ditto), combined with sulfur isotope and fluid inclusion data. SATO (1973) proposed a chloride complex model for the Kuroko formation on the assumption that 1 ppm of copper had been dissolved in the ascending Kuroko-forming solution. ICHIKUNI (1975) and SHIKAZONO (1976a) also proposed chemical models for the Kuroko-forming solutions. URABE (1974a) carried out analyses of sphalerite in the Kuroko deposits and emphasized upward decrease in iron content in each Kuroko deposit. WATANABE (1976, 1979), by means of fluid inclusions, discussed formation temperature, origin, and state of the ore fluids responsible for the Neogene mineralization, as a whole. For an outline of the Neogene mineralization and mineralogical descriptions of ore specimens from more than 30 mines, see WATANABE (1976).

In the Neogene ore deposits under consideration, particularly in the copper-lead-zinc deposits, one of the mineralogical features is a ubiquitous occurrence of barite, though such observation is against that of LAMBERT and SATO (1974). Generally speaking, the mineral association, chalcopyrite-pyrite-galena-sphalerite-barite-sericite-chlorite-quartz, is essentially characteristic of the Neogene mineralization. Here adopted is a view point throughout the present study that wide-spread distribution of the ore deposits in the Green Tuff region is regarded as a single geological event, despite the difference in a field of formation, or in type of ore deposits. In other words, they were formed in association with the geosynclinal evolution. Such a view point may be supported by a striking similarity in lead isotope ratio among the Miocene ore leads (SATO et al., 1973). Then, genetical discussions on the Neogene mineralization can be reduced to those of the mineral assemblage mentioned before. On the basis of the field and laboratory observations, mineral assemblages found, fluid inclusion data, sphalerite composition, and thermochemical calculations, the present article makes it the aim to discuss the overall geochemical environments of the Neogene ore formation in the Green Tuff region of Japan.

Acknowledgements: I would like to thank Prof. A. TSUSUE for critical reading of the manuscript. I am also indebted to Drs. M. DOI, A. SOEDA, S. TAKENO, and the late M. WATANABE for their comments, advises, and encouragements during the course of this work. I wish to express my deep gratitude to Profs. T. Tatsumi, T. Fujii, A. Tsusue, and H. Sakai for their helpful suggestions and criticisms in the initial phases of this study. I am grateful to Profs. T. Tatsumi, A. Sugaki, and H. Shima for permission to use microprobe analyser and its operation to Drs. T. Urabe and A. Kitakaze.

II. Composition of sphalerite coexisting with pyrite

In evaluation of depositional environments of ores, the ternary system Fe–Zn–S is of great importance. Generally observed in the Neogene ore deposits is the mineral assemblage, pyrite and sphalerite, belonging to the system, with some exception in which pyrrhotite-bearing lead-zinc veins are noted.

Barton and Toulmin (1966) revealed that iron content in sphalerite coexistent with pyrite is very sensitive to variations in temperature and sulfur fugacity. In the following discussion, assumptions are made that:

(1) Equilibrium
$2FeS$ (in sphalerite solid solution) $+S_2=2FeS_2$ (pyrite)
was achieved at the time of ore deposition, and then preserved.

(2) The dependency of composition of sphalerite on activity does not change significantly with temperature.

The latter was experimentally confirmed by Barton and Toulmin (1966) at the relatively higher temperatures in the FeS-rich portion. Interpolation of the FeS activity-FeS mol. % relation leads to the Henry's Law constant of 2.5 to 4.0 in the FeS-poor portion (Yui and Czamanske, 1971). A value of 2.5 as that constant is employed throughout the present article. Furthermore, as experimentally demonstarated by Kullerud and Yorder (1959), pyrite does not deviate measurably from stoichiometric composition, FeS_2.

Thus, following a calculation similar to Barton and Toulmin (1966), activity of FeS in sphalerite coexisting with pyrite can be expressed as a function of temperature and sulfur fugacity.

In order to know the distribution of iron contents of sphalerites within a single ore deposit, those of sphalerites in various occurrences in the Daikoku deposit of the Ainai mine (Watanabe, 1970, 1974), one of the typical Kuroko deposits, have been analysed by the same method described in Urabe (1974a) using electronmicroprobe analyser, J. E. O. L. Model JXA with take-off angle of 40°. Corrections for absorption, fluorescence, ionization, and backscattering effects have been made by the method proposed by Sweatman and Long (1969). Special attention has been paid to the analyses of low-copper portion in sphalerites as much as possible. The analytical results are given in Table 1. For brief descriptions of the samples analysed and analytical conditions, reference should be made to Watanabe (1976). The calibration curve method of which details were described by Sugaki et al. (1970) has also been employed for the determination of FeS content, based on comparison with those of synthetic ZnS (0, 5, 10, 15, 20 mol. % FeS) with the results shown in Table 2.

For comparison, a series of unit cell parameter measurements of sphalerites of known composition have been performed by means of X-ray diffractometer with Ni-filtered Cu–Kα radiation, using reagent sodium chloride as an internal standard at room temperautre. Consequently, the FeS contents calculated from experimental formula by Barton and

TABLE 1. MICROPROBE ANALYSES OF SPHALERITES COEXISTING WITH PYRITE FROM THE DAIKOKU ORE DEPOSIT, AINAI MINE

No.	Zn*	Fe*	Cu*	Mn*	Cd*	S*	Sum*	FeS**
(1)	65.42	0.41	0.00	0.00	0.36	32.84	99.23	0.7
(2)	65.87	0.23	0.04	0.00	0.23	32.39	98.76	0.3
(3)	66.10	0.08	0.04	0.01	0.31	32.27	98.82	0.1
(4)	65.79	0.08	0.00	0.01	0.31	32.25	98.44	0.1
(5)	64.73	1.25	0.18	0.02	0.24	33.10	99.53	1.9
(6)	65.32	0.58	0.28	0.00	0.31	32.77	99.27	0.6
(7)	65.14	0.66	0.12	0.02	0.19	33.45	99.59	1.0
(8)	64.83	1.43	0.19	0.00	0.23	33.11	99.79	2.2
(9)	61.79	4.29	0.01	0.01	0.33	33.37	99.79	7.4
(10)	64.66	0.52	0.35	0.00	0.23	32.28	98.04	0.4
(11)	64.61	0.68	0.70	0.00	0.36	32.01	98.36	0.1
(12)	61.86	3.47	0.02	0.05	0.82	32.53	98.73	6.1
(13)	63.93	1.47	0.13	0.00	0.85	32.26	98.65	2.4
(14)	64.88	0.23	0.47	0.01	0.40	32.25	98.26	0.4
(15)	64.18	0.17	0.61	0.04	0.52	32.64	98.17	0.3
(16)	66.43	0.08	0.01	0.00	0.33	32.79	99.63	0.1
(17)	66.14	0.07	0.03	0.00	0.32	32.80	99.37	0.1
(18)	66.56	0.18	0.23	0.03	0.50	32.52	100.01	0.3
(19)	66.50	0.11	0.02	0.03	0.52	33.01	100.18	0.1
(20)	65.90	0.07	0.07	0.00	0.37	32.99	99.40	0.1
(21)	66.75	0.62	0.00	0.00	0.18	32.44	99.99	1.1
(22)	66.58	0.58	0.02	0.02	0.29	33.08	100.58	1.0
(23)	66.55	0.61	0.01	0.00	0.16	33.03	100.37	1.0
(24)	65.58	0.13	0.80	0.01	0.22	33.16	99.88	0.2
(25)	65.82	0.26	0.07	0.01	0.28	33.37	99.80	0.4
(26)	66.32	0.13	0.06	0.03	0.26	32.30	99.09	0.1
(27)	66.60	0.23	0.00	0.00	0.39	32.43	99.65	0.4
(28)	66.15	0.43	0.01	0.01	0.38	32.76	99.74	0.8
(29)	65.24	1.43	0.01	0.00	0.54	32.68	99.90	2.5
(30)	66.16	0.57	0.00	0.00	0.31	32.31	99.36	1.0
(31)	65.88	0.37	0.13	0.01	0.47	31.99	98.84	0.5
(32)	64.40	0.75	0.81	0.00	0.27	31.76	98.01	0.1

* in weight %

** Corrected values in mol. % FeS assuming all copper in sphalerite contributed by minor inclusions of chalcopyrite.

TOULMIN (1966) appear to be significantly high compared with those by microprobe analyses. The reason for this lies in the difficulties of separating clean samples and in that contributions made by manganese and cadmium present in sphalerite solid solutions are not included in the data from X-ray diffraction method employed here. In addition to the above data, iron contents in sphalerites coexisting with pyrite from other Neogene ore deposits are reproduced from the literatures in Table 3. From Tables 1 to 3, we are

TABLE 2. IRON CONTENTS OF SPHALERITES COEXISTING WITH PYRITE FROM THE DAIKOKU DEPOSIT, AINAI MINE.

No.	FeS mol. %	No.	FeS mol. %
(33)	0.3–1.0	(41)	1.0–5.5
(34)	0–0.3	(42)	0.7–1.9
(35)	0	(43)	0.7–1.2
(36)	0.7–2.7	(44)	1.0–5.7
(37)	0–3.6	(45)	0.3–1.9
(38)	0.3–2.8	(46)	0.7–2.7
(39)	1.0–3.6	(47)	0.9–3.6
(40)	0.3–2.2		

TABLE 3. SUMMARY OF DATA FOR IRON CONTENTS OF SPHALERITES COEXISTING WITH PYRITE IN THE NEOGENE ORE DEPOSITS IN THE GREEN TUFF REGION, JAPAN.

Ore type	FeS mol. %	Sources
(A) Kuroko deposits		
Kosaka-Uchinotai (W)	0.30–0.55	(1)
Kosaka-Uchinotai (E)	0.04–1.97	(2), (2)
Kosaka-Uwamuki	<a few mol. %	(3)
Iwami		(3)
Ainai-Daikoku		(4)
(B) Au–Ag veins of volcanic affinity		
Fuke-Honpi	1–3	(5)
Kushikino	1.4	(6)
Omori	0.2–0.3	(7)
Seikoshi	0.5–0.9	(6)
Yugashima	0.9–1.5	(6)
Toi	0.2–0.3	(6)
Kawazu	0.3–1.0	(6)
Yatani-Kanizawa	0–3.8	(6)
Konomai	0.2–0.5	(6)
Todoroki	0.3–0.7	(6)
(C) Cu–Pb–Zn–Mn veins of volcanic affinity		
Oe	0.3–0.7	(7)
Inakuraishi	0.4–0.7	(7)
Jokoku	0.3	(7)
(D) Pb–Zb veins of volcanic affinity		
Toyoha-Soya	1.0–5.0	(7)
Yatani	10±	(6)

Sources: (1) SATO (1969); (2) LU (1970); (3) URABE (1974a); (4) this study; (5) TAGUCHI (1975); (6) HATTORI (1975); (7) SHIKAZONO (1973, 1975) allowed to estimate that concentrations of iron in sphalerites coexistent with pyrite in the Neogene ore deposits are mostly in the range of 0.3 to 3.0 mol. % FeS.

III. EVALUATION OF GAS FUGACITY PREVAILING DURING THE NEOGENE MINERALIZATION

Then, informations on the formation temperatures are required for evaluation of physicochemical depositional environments of ores. WATANABE (1976, 1979) investigated extensively the fluid inclusions in the Neogene ore deposits and concluded that most of the Neogene ore formation took place in the temperature range of 200° to 250°C, being in harmony with those obtained from sulfur isotope geothermometry (TATSUMI, 1965; KAJIWARA, 1971; KIYOSU, 1973) and electrum tarnish method (KAJIWARA, 1971; HATTORI, 1975). Therefore, this range of 200°C to 250°C is used throughout the present article, yielding sulfur fugacity (in atmosphere) of −12.7 to −14.7 at 200°C and −9.8 to −11.8 at 250°C (in log scale unless otherwise noted), which are presented in Table 4.

TABLE 4. A RELATIONSHIP OF SULFUR FUGACITY (IN LOG SCALE) TO IRON CONTENTS OF SPHALERITES COEXISTING WITH PYRITE. (EQUILIBRIUM CONSTANTS TAKEN FROM HELGESON (1969)

FeS mol. %	150	200	250	300°C
10	−19.3	−15.8	−12.9	−10.4
5	−18.7	−15.2	−12.3	−9.8
3	−18.3	−14.7	−11.8	−9.4
1	−17.3	−13.8	−10.8	−8.4
0.3	−16.3	−12.7	−9.8	−7.4
0.1	−15.3	−11.8	−8.9	−6.4
0.01	−13.3	−9.8	−6.9	4.4
0.001	−9.3	−5.8	−2.9	−0.4

Now, following a calculation similar to HOLLAND (1959, 1965), it is possible to set limits on oxygen and carbon dioxide fugacity prevailing during the mineralization. Equilibrium constants or free energy data used for calculations throughout are avialable from HOLLAND (ditto) and HELGESON (1969), which are listed in Table 5. Then, noting the presence of pyrite and absence of magnetite with or without hematite as commonly observed in the uppermost part of the Kuroko deposits and veins, we are capable of limiting the upper limit on oxygen fugacity from the reactions: $3FeS_2+2O_2=Fe_3O_4+3S_2$, or $2FeS_2+3/2O_2=Fe_2O_3+2S_2$ (Table 5) and sulfur fugacity calculated above. This indicates that oxygen fugacity was smaller than −38.1 at 200°C and −32.6 at 250°C. On the contrary, the lower limit for oxygen fugacity depends on whether anhydrite is present or not. Because of the presence of the mineral as a discrete phase such as associating with the Kuroko deposits and some vein and of the absence of oldahmite, this can be defined by the reaction: $CaS+2O_2=CaSO_4$, resulting in the values −42.5 at 200°C and −37.7 at 250°C. While if barite is present instead of anhydrite as mentioned before,

TABLE 5. EQUILIBRIUM REACTIONS AND EQUILIBRIUM CONSTANTS USED IN CALCULATIONS.

		200°C	250°C	Sources
(1)	$2FeS_2=2FeS+S_2$	−11.7	−14.1	(a)
(2)	$Cu_5FeS_4+4FeS_2=5CuFeS_2+S_2$	−11.1	−8.5	(a)
(3)	$3FeS_2+2O_2=Fe_3O_4+3S_2$	+38.1	+35.8	(a)
(4)	$4FeS_2+3O_2=2Fe_2O_3+4S_2$	+63.4	+58.7	(a)
(5)	$4Fe_3O_4+O_2=6Fe_2O_3$	+37.9	+32.9	(a)
(6)	$CaS+2O_2=CaSO_4$	−42.5	−37.7	(b)
(7)	$BaS+2O_2=BaSO_4$	−46.8	−41.4	(b)
(8)	$PbS+2O_2=PbSO_4$	−36.3	−31.9	(b)
(9)	$C+O_2=CO_2$	+43.6	+39.4	(b)
(10)	$CaCO_3+SiO_2=CaSiO_3+CO_2$	−1.7	−0.8	(b)
(11)	$2CaCO_3+S_2+3O_2=2CaSO_4+2CO_2$	+130.8	+116.4	(b)
(12)	$2CaS+O_2+2CO_2=2CaCO_3+S_2$	+42.0	+36.6	(b)
(13)	$2BCO_3+S_2+3O_2=2BaSO_4+2CO_2$	+137.2	+122.2	(b)
(14)	$2MnS+2CO_2+O_2=2MnCO_3+S_2$	+30.8	26.0	(b)
(15)	$2H_2S+O_2=S_2+2H_2O$	+35.05	+30.6	(a)
(16)	$H_2S=H^++HS^-$	−6.96	−7.35	(a)
(17)	$HS^-=H^++S^{2-}$	−9.57	−8.61	(a)
(18)	$S^{2-}+2O_2=SO_4^{2-}$	+83.74	+72.7	(a)
(19)	$H_2S+2O_2=H^++HSO_4^-$	+71.62	+62.5	(a)
(20)	$4CuFeS_2=4Cu^{2+}+4Fe^{2+}+8S^{2-}$	−184.8	−174.8	(a)
(21)	$2FeS_2=2Fe^{2+}+2S^{2-}+S_2$	−48.4	−44.5	(a)
(22)	$4Cu^{2+}+2H_2O=4Cu^++4H^++O_2$	−33.4	−26.6	(a)
(23)	$4Fe^{3+}+2H_2O=4Fe^{2+}+4H^++O_2$	+4.6	+0.4	(a)
(24)	$PbS=Pb^{2+}+S^{2-}$	−20.4	−19.1	(a)
(25)	$ZnS=Zn^{2+}+S^{2-}$	−19.8	−18.9	(a)
(26)	$BaSO_4=Ba^{2+}+SO_4^{2-}$	−9.8	−10.3	(a)
(27)	$CaSO_4=Ca^{2+}+SO_4^{2-}$	−7.2	−8.1	(a)

Sources: (a) HELGESON (1969) (b) HOLLAND (1959, 1965)

the reaction: $BaS+2O_2=BaSO_4$ is useful in defining the condition, leading to oxygen fugacity of −46.8 at 200°C and −41.4 at 250°C. The absence of graphite fixes the upper limit for carbon dioxide fugacity by the reaction: $C+O_2=CO_2$. They are in the range of +5.5 at 200°C and +6.8 at 250°C. On the other hand, the lower limit is calculated from the reaction: $CaCO_3+SiO_2=CaSiO_3+CO_2$. This is based on the observation that wollastonite has never been discovered as a discrete phase in the Neogene ores under discussion. From the reaction, we obtain carbon dioxide fugacity −1.7 at 200°C and −0.8 at 250°C. The range estimated for the fugacity is significantly larger than those by HOLLAND (1965) for the generalized hydrothermal system. This may be ascribable, in part, to the low iron content in sphalerite from the Neogene ore deposits of concern.

IV. CHEMISTRY OF ORE FLUIDS RESPONSIBLE FOR THE NEOGENE MINERALIZATION

In order to calculate the concentrations of major dissolved species in the ore fluids, required are the following chemical parameters: activity coefficients of individual ions, activity of water in concentrated salt solution, pH values, and gas fugacity values at given temperatures and ionic strength. Generally supported is that ore fluids can be approximated by the system NaCl–H_2O with or without CO_2 (e.g. ROEDDER, 1967). According to the fluid inclusion data, salinity of the ore fluids responsible for the Neogene mineralization falls within a range 0 to 1 m NaCl, in most cases (e.g. WATANABE, 1976, 1979). Comparatively speaking, ionic strength of 0.7 is accepted for the normal sea water (GARRELS and THOMPSON, 1962). Thus, in the following discussions, the thermochemical calculations are made on 1 molal sodium chloride solution.

Various extended forms of the Debye-Hückel equation can be used to approximate individual activity coefficients at elevated temperatures (HELGESON, 1967). Here adopted is the delta approximation proposed by HELGESON (1964), which is expressed as

$$\mathrm{Log}\ \gamma_i(\mathrm{I, T}) = \frac{-\mathrm{ZA(T)I}^{1/2}}{1+\mathring{a}\mathrm{B(T)I}^{1/2}} + \mathrm{Log}\ \gamma_{\mathrm{H_2CO_3}}\ (\mathrm{I, T})$$

where γ_i, Z_i, $\gamma_{\mathrm{H_2OC_3}}$, å, I, A, and B, respectively, indicate activity coefficient of the i-th species, charge of the i-th species, activity coefficient of H_2CO_3 in supporting electrolyte, effective diameter of ion (assumed to be independent of temperature), ionic strength, and the Debye-Hückel electrostatic parameters. Activity coefficient for hydrated molecular species, H_2CO_3 used in the delta approximation can be estimated from the solubility data of carbon dioxide by MALININ (1960) and ELLIS and GOLDING (1963) in water and NaCl solutions. For the system whose vapor is assumed to be a perfect gas, activity of water in concentrated solutions can be evaluated by means of osmotic coefficients (GARDNER et al. 1963). Thus, we can estimate individual activity coefficients of major dissolved ions such as sulfur and metal species present in the ore fluids at given temperature and ionic strength. The results are shown in Table 6.

TABLE 6. VALUES OF ACTIVITY COEFFICIENTS OF INDIVIDUAL IONS (IN LOG SCALE) BASED ON IONIC STRENGTH OF 1.0.

	SO_4^{2-}	HSO_4^-	HS^-	S^{2-} Ba^{2+}, Sr^{2+}, Cd^{2+}
150°C	(−1.05)	(−0.22)	−0.25	−0.94
200°C	(−1.21)	(−0.25)	−0.29	−1.08
250°C	(−1.41)	(−0.27)	−0.31	−1.25
300°C	(−1.71)	(−0.27)	−0.32	−1.51
	Ag^+	Pb^{2+}	K^+	Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}
150°C	(−0.31)	(−1.01)	−0.28	−0.83
200°C	(−0.35)	(−1.16)	−0.32	−0.95
250°C	(−0.40)	(−1.35)	−0.35	−1.09
300°C	(−0.43)	(−1.64)	−0.37	−1.31

Parenthetical values are averages.

Then, some limits are placed on pH values of the ore fluids using stability relation of associated silicate minerals. As was stated previously, sericite assumed to be similar in thermodynamic properties to those of muscovite, chlorite, and quartz are an essential assemblage in the Neogene ore deposits. Adularia and kaolin-group mineral are sometimes observed in the gold-silver veins and the Kuroko deposits. The pH values, in general, should lie within the stability field of muscovite which is defined by the following equilibrium reactions:

$$\underset{\text{muscovite}}{2KAl_3Si_3O_{10}(OH)_2}+2H^+ +3H_2O=\underset{\text{kaolinite}}{3AlSi_2O_5(OH)_4}+2K^+$$

$$\underset{\text{adularia}}{3KAlSi_3O_8}+2H^+=\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_{22}}+\underset{\text{quartz}}{6SiO}+2K^+$$

Equilibrium constants for the reactions are taken from HELGESON (1969). According to ROEDDER (1967), RAYMAHASHAY and HOLLAND (1969), TAKENOUCHI (1970), and ENJOJI (1972), concentration of potassium present in ore fluids generally ranges from 0.001 to 0.1 m. Based on the assumption of 0.01 to 0.1 m for the potassium concentration, pH range obtained is summarized in Table 7. Thus, from the chemical parameters and equilibrium reactions listed in Table 5, we are capable of calculating the concentrations of major dissolved species. The results are discussed in the following chapter.

TABLE 7. A pH RANGE FOR THE NEOGENE ORE FLUIDS.

	muscovite-kaolinite		adularia-muscovite	
	$m_{K^+}=10^{-2}$	10^{-1}	$m_{K^+}=10^{-2}$	10^{-1}
200°C	pH=5.8	4.8	pH=6.5	5.5
250°C	pH=5.4	4.4	pH=6.4	5.4

V. RESULTS AND DISCUSSIONS

A. Gas fugacity

The aforementioned depositional environments for the Neogene mineralization are summarized on Log f_{S_2}–Log f_{O_2} diagram (Figs. 1 and 2), and Log$_{CO_2}$–Log f_{O_2} diagram (Figs. 3 and 4). As is evident in the gas fugacity diagrams, it should be emphasized except for lead-zinc veins such as Toyoha (Hokkaido), the stable region for the Kuroko deposits is fairly wide compared with those for other ore-type, possibly reflecting a special geologic environment of formation. This is compatible with a conclusion derived from the genetical consideration of ore textures observed in the Kuroko deposits (WATANABE, 1974).

Then, taking of the fact that low-iron sphalerite, that is, less than 0.1 mol. % FeS, sometimes occurs with or without the mineral assemblage pyrite-bornite-chalcopyrite, such as in the Daikoku deposit of the Ainai mine (WATANABE, 1970, 1974), the range of sulfur fugacity obtained above becomes somewhat wide, resulting in the upper limit for sulfur fugacity fixed by the univariant assemblage. A mineral, rhodochrosite with or without alabandite is also recognized, particularly in the vein-type deposits. Hence, it would be a logical conclusion that the overall geochemical conditions prevailing at the time of the Neogene mineralization lie in a region bounded by the following phase boundaries: (i) pyrite-pyrrhotite; (ii) pyrite-magnetite (or pyrite-hematite); (iii) alabandite-

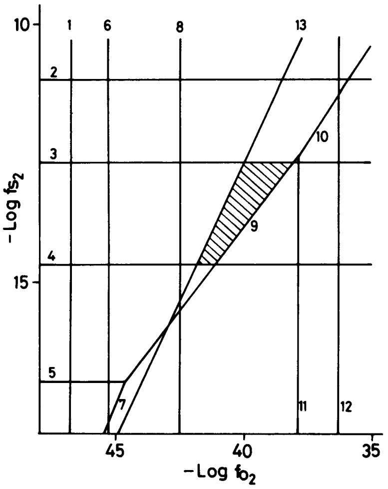

FIG. 1. Isothermal section at 200°C, limiting depositional environments of the Neogene mineralization based on iron contents in sphalerites coexisting with pyrite. Numbers attached to the lines indicate: 1. BaS–$BaSO_4$; 2. FeS_2–Cu_5FeS_4–$CuFeS_2$; 3. fixed sulfur fugacity (0.3 mol. % FeS); 4. fixed sulfur fugacity (3 mol. % FeS); 5. FeS_2–FeS; 6. C–CO_2; 7. FeS–Fe_3O_4; 8. CaS–$CaSO_4$; 9. FeS_2–Fe_3O_4; 10. FeS_2–Fe_2O_3; 11. Fe_2O_3–Fe_3O_4; 12. PbS–$PbSO_4$; 13. MnS–$MnCO_3$.

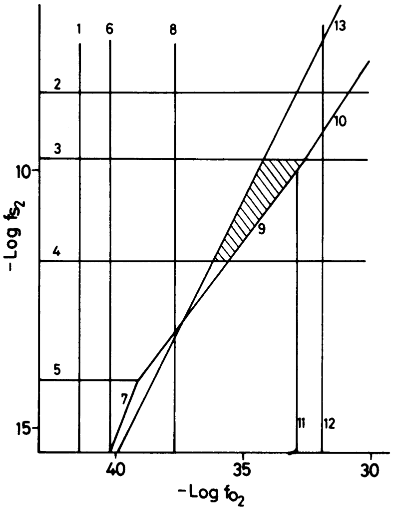

FIG. 2. Isothermal section at 250°C, limiting depositional environments of the Neogene mineralization based on iron contents in sphalerites coexisting with pyrite. Numbers attached to the lines are the same as in Fig. 1.

rhodochrosite; (iv) graphite-carbon dioxide; (v) fixed oxygen fugacity line by oldahmite-anhydrite boundary and fixed iron content in sphalerite. On the basis of the foregoing discussion and works on veins by SHIKAZONO (1973, 1974a, 1974b) and HATTORI (1975), we can make generalization concerning the physicochemical environments of the Neogene ore deposition, including pyrrhotite-bearing lead-zinc veins, in the Green Tuff region of Japan. According to HOLLAND (1965), a reasonable range of carbon dioxide fugacity during low-temperature ore deposition is assumed to be $+2$ to -2 atm. Thus, Figs. 5 and 6 give a summary of them which is based on fixed temperature and carbon dioxide fugacity, -1 at 200°C and 0 at 250°C. These are superimposed on Fig. 7. In general, the figure leads to the conclusion that the geochemical environments for the Neogene mineralization are roughly classified into two types, those characterized by high to inter-

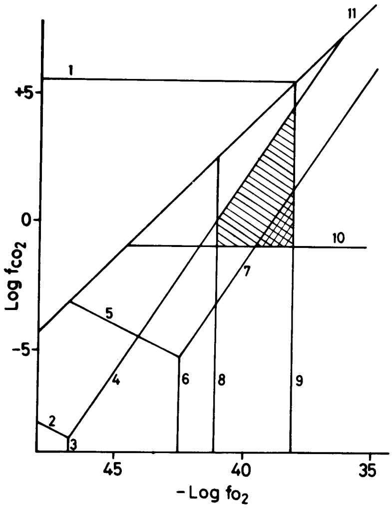

Fig. 3. Isothermal section at 200°C, limiting depositional environments of the Neogene mineralization based on iron contents in sphalerites coexisting with pyrite. Hatched area shows stability region for coexistence of barite and calcite, while cross-hatched area indicates anhydrite stability field under the given condition. Numbers attached to the lines indicate: 1. upper limit for carbon dioxide fugacity (graphite absent); 2. $BaCO_3$–BaS; 3. BaS–$BaSO_4$; 4. $BaCO_3$–$BaSO_4$; 5. $CaCO_3$–CaS; 6. CaS–$CaSO_4$; 7. $CaCO_3$–$CaSO_4$; 8. lower limit for oxygen fugacity (3 mol. % FeS); 9. upper limit for oxygen fugacity (0.3 mol. % FeS); 10. lower limit for carbon dioxide fugacity ($CaCO_3$–SiO_2–$CaSiO_3$); 11. C–CO_2.

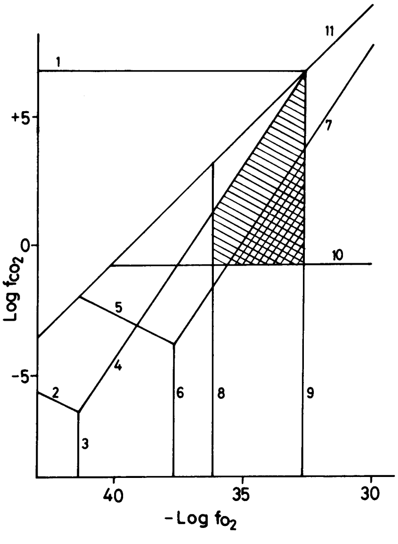

Fig. 4. Isothermal section at 250°C, limiting depositional environments of the Neogene mineralization based on iron contents in sphalerites coexisting with pyrite. Numbers attached to the lines are the same as in Fig. 3.

mediate oxygen and sulfur fugacity and those characterized by intermediate to low oxygen and sulfur fugacity. The former, including the Kuroko deposits, gold-silver veins, copper-lead-zinc-manganese veins, and pyrrhotite-free lead-zinc veins, is a region surrounded by the following phase boundaries: pyrite-magnetite (or pyrite-hematite); galena-anglesite; magnetite-hematite; pyrite-bornite-chalcopyrite; alabandite-rhodochrosite; oldahmite-anhydrite; and fixed iron content of sphalerite. On the other hand, the latter, including lead-zinc veins with or without pyrrhotite, is a region bounded by the mineral assemblages: alabandite-rhodochrosite; pyrite-pyrrhotite; oldahmite-anhydrite; graphite-carbon dioxide; and pyrite-magnetite. The deduced oxidation states prevailing during the Neogene mineralization lend support to a conclusion independently reached by

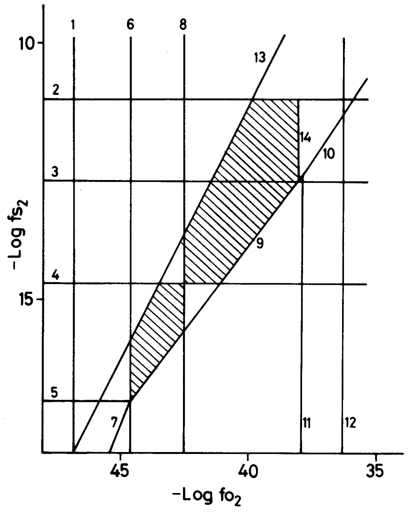

FIG. 5. Generalized depositional environments for the Neogene mineralization in the Green Tuff region, Japan. (T= 200°C and Log f_{CO_2} = −1 atm). Numbers attached to the lines are the same as in Fig. 1. No. 14 indicates oxygen fugacity at fixed sulfur fugacity (3 mol. % FeS). See the text for discussion on the hatched area.

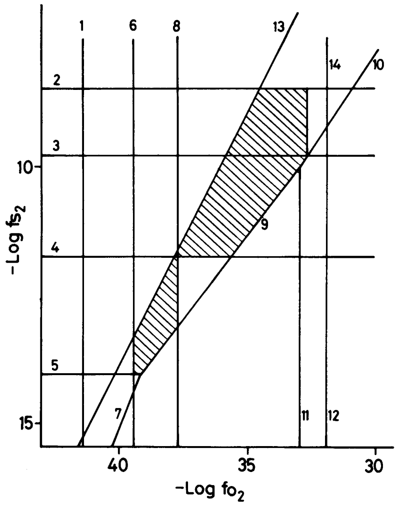

FIG. 6. Generalized depositional environments for the Neogene mineralization in the Green Tuff region, Japan. (T= 250°C and Log f_{CO_2}=0 atm). Numbers attached to the lines are the same as in Fig. 5.

SHIKAZONO (1973, 1974b) and HATTORI (1975), indicating the following order of increasing oxidation state: from pyrrhotite-bearing lead-zinc veins (e.g. Toyoha-Soya, Hokkaido), through pyrrhotite-free lead-zinc veins (e.g. Yatani, Yamagata), to copper-lead-zinc-manganese veins (Osarizawa-Shichinenhi, Akita), Kuroko deposits (e.g. Ainai and Kosaka, Akita), and epithermal gold-silver veins (e.g. Yatani-Kanizawa, Yamagata; Seikoshi, Shizuoka). Based on theoretical consideration and composition of minerals, SHIKAZONO (1973, 1974a, 1974b, 1975) emphasized that a role played by oxygen fugacity, that is, reduction of circulating waters is of prime importance for hydrothermal ore deposition, as well as temperature decrease. Here, it may be worthy of particular attention that the mineral assemblage pyrite-bornite-chalcopyrite is commonly observed in the Kuroko deposits, whereas the primary assemblage is very rare in the vein-type

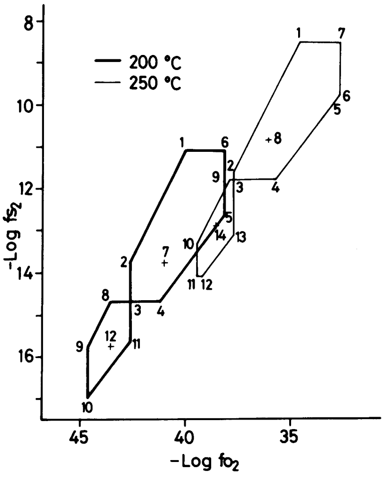

Fig. 7. The stable region for the Neogene mineralization, on which calculations of concentrations of major sulfur and metal species present in the model ore fluids have been made. For gas fugacity values at a given point see Table 8.

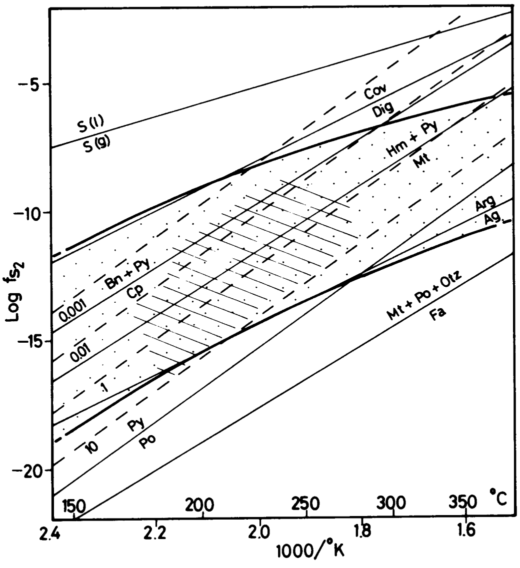

Fig. 8. Generalized Neogene ore-forming environments (hatched area) superimposed on the "Main-line" ore-forming environments (dotted area). Numbers attached to the line indicate mol. % FeS in sphalerites coexisting with pyrite. Abbreviations are: S, sulfur; Cov, covelline; Dig, digenite; Bn, bornite; Py, pyrite; Po, pyrrhotite; Cp, chalcopyrite; Hm, hematite, Mt, magnetite; Arg, argentite; Ag, native silver; Qtz, quartz; Fa, fayalite; l, liquid; and g, gas.

deposits throughout the Green Tuff region. As mentioned before, this means that there are differences in sulfur fugacity, if formation temperature and other chemical parameters do not significantly differ among the deposits. Qualitatively speaking, the differences in oxidation state of ore fluids may be interpreted as varying rates of incorporation of organic materials present in the surrounding rocks or mixing of oxidative surface waters such as sea water. Unlike the case of oxygen fugacity, much difficulties are encountered in explaining the difference in sulfur fugacity prevailing at the time of each ore deposition. Thus, there still remains the problem to be answered.

In Fig. 8, the overall geochemical environments of the Neogene ore formation are superimposed on the "Main-line" ore-forming environment depicted on Log f_{S_2}–T diagram which was proposed by BARTON (1970). The Neogene ore-forming environments thus discussed lie within the Barton's generalized depositional environments.

B. Chemistry

There have been some chemical models of ore-forming environments, such as those of WHITE (1968), HELGESON (1970), KAJIWARA (1971), SATO (1972, 1973), ANDERSON (1975), ICHIKUNI (1975), and SHIKAZONO (1974b).

Under the usual hydrothermal conditions of geological interest, SO_4^{-2}, HSO_4^-, H_2S, H^-S, and S^{-2} are only potentially important sulfur species present in ore solution (BARNES and KULLERUD, 1961). Since the depositional environments are quite different between the two groups just-mentioned, calculations are made on the individudal group, under the conditions which are indicated by a number in or arround the stable region shown in Fig. 7 and listed in Table 8. Also, carbon dioxide fugacity is fixed. Thus, the calculated results are given in Tables 9 and 10 for the former group and in Tables 11 and 12 for the latter group, together with those of Ba^{+2} and Ca^{+2}.

TABLE 8. GAS FUGACITY VALUES USED IN CALCULATIONS OF CONCENTRATIONS OF MAJOR SULFUR AND METAL IONS DISSOLVED IN MODEL ORE FLUIDS.

	$-\text{Log } f_{S_2}^{*}$	$-\text{Log } f_{O_2}^{*}$	$-\text{Log } f_{S_2}^{**}$	$-\text{Log } f_{O_2}^{**}$
(1)	11.0	39.9	8.5	34.4
(2)	13.8	42.6	11.7	37.7
(3)	14.7	42.6	11.8	37.7
(4)	14.7	41.1	11.8	35.7
(5)	12.7	38.1	10.0	32.9
(6)	11.1	38.1	9.8	32.6
(7)	14.1	41.0	8.5	32.6
(8)	14.7	43.5	10.9	36.0
(9)	15.8	44.6	11.8	37.8
(10)	17.0	44.6	13.4	39.4
(11)	15.7	42.6	14.1	39.4
(12)	15.8	43.5	14.1	39.1
(13)			13.2	37.7
(14)			12.9	38.5

* 200°C
** 250°C

Unfortunately, data for the effective diameters used in the calculation of individual activity coefficients of Ag^+ and Cu^+ are lacking at the present time. For this reason, we introduce the stoichiometric individual activity coefficient, γ_i, which was proposed by

Table 9. Calculated Concentration of Major Sulfur Species Dissolved in the Model Ore Fluids. (T=200°C)

(200°C, Case-1)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.8*	6.5**	4.8*	5.5**
Log m_i				
H_2S	−3.2	−3.2	−3.2	−3.2
HS^-	−3.9	−3.2	−4.9	−4.2
S^{2-}	−6.9	−5.5	−8.9	−7.5
SO_4^{2-}	−2.9	−1.5	−4.9	−3.5
HSO_4^-	−5.3	−4.6	−6.3	−5.6
Ca^{2+}	−3.2	−4.6	−1.2	−2.6
Ba^{2+}	−5.8	−7.2	−3.8	−5.2

*,**: Asterisks in Tables 9, 11, 14, and 16 indicate, unless otherwise noted, pH defined by the boundary kaolinite-muscovite, and pH defined by the boundary muscovite-adularia.

(200°C, Case-2)

Log m_i				
H_2S	−3.2	−3.2	−3.2	−3.2
HS^-	−3.9	−3.2	−4.9	−4.2
S^{2-}	−6.9	−5.5	−6.9	−7.5
SO_4^{2-}	−8.3	−6.9	−10.3	−8.9
HSO_4^-	−10.7	−10.0	−11.7	−11.0
Ca^{2+}	+2.2	+0.8	+4.2	+2.8
Ba^{2+}	−0.4	−1.8	+1.6	+0.2

(200°C, Case-3)

Log m_i				
H_2S	−3.7	−3.7	−3.7	−3.7
HS^-	−4.4	−3.7	−5.4	−4.7
S^{2-}	−7.4	−6.0	−9.4	−8.0
SO_4^{2-}	−8.8	−7.4	−10.8	−9.4
HSO_4^-	−11.2	−10.5	−12.2	−11.5
Ca^{2+}	+2.7	+1.3	+4.7	+3.3
Ba^{2+}	+0.1	−1.3	+2.1	+0.7

(200°C, Case-4)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.8*	6.5**	4.8*	5.5**
Log m_i				
H_2S	−4.4	−4.4	−4.4	−4.4
HS^-	−5.1	−4.4	−6.1	−5.4
S^{2-}	−8.1	−6.7	−10.1	−8.7
SO^{4-}	−6.5	−5.1	−8.5	−7.1
HSO_4^-	−8.9	−8.2	−9.9	−9.2
Ca^{2+}	+0.4	−1.0	+2.4	+1.0
Ba^{2+}	−2.2	−3.6	−0.2	−1.6

(200°C, Case-5)

Log m_i				
H_2S	−4.9	−4.9	−4.9	−4.9
HS^-	−5.9	−4.9	−6.9	−5.9
S^{2-}	−8.6	−7.2	−10.6	−9.2
SO_4^{2-}	−1.0	+0.4	−3.0	−1.6
HSO_4^-	−3.4	−2.6	−4.3	−3.6
Ca^{2+}	−5.1	−6.5	−3.1	−4.5
Ba^{2+}	−7.7	−9.1	−5.7	−7.1

(200°C, Case-6)

Log m_i				
H_2S	−4.1	−4.1	−4.1	−4.1
HS^-	−4.8	−4.1	−5.8	−5.1
S^{2-}	−7.8	−6.4	−9.8	−8.4
SO_4^{2-}	−0.2	+1.2	−2.2	−0.8
HSO_4^-	−2.6	−1.9	−3.6	−2.9
Ca^{2+}	−5.9	−7.3	−3.9	−5.3
Ba^{2+}	−8.5	−9.9	−6.5	−7.9

(200°C, Case-7)

Log m_i				
H_2S	−3.8	−3.8	−3.8	−3.8
HS^-	−4.7	−4.0	−5.7	−5.0
S^{2-}	−7.7	−6.3	−9.7	−8.3
SO_4^{2-}	−5.9	−4.5	−7.9	−6.5
HSO_4^-	−8.3	−7.6	−9.3	−8.6
Ca^{2+}	−0.2	−1.6	+1.8	+0.4
Ba^{2+}	−2.8	−4.2	−0.8	−2.2

TABLE 10. CALCULATED CONCENTRATION OF MAJOR SULFUR SPECIES DISSOLVED IN THE MODEL ORE FLUIDS. (T=250°C)

(250°C, Case-1)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.4*	6.4**	4.4*	5.4**
Log m_i				
HS_2	−2.4	−2.4	−2.4	−2.4
HS^-	−4.1	−3.1	−5.1	−4.1
S^{2-}	−6.4	−4.4	−8.4	−6.4
SO_4^{2-}	−2.3	−0.3	−4.3	−2.3
HSO_4^-	−3.0	−2.0	−4.0	−3.0
Ca^{2+}	−4.6	−6.6	−2.6	−4.6
Ba^{2+}	−6.8	−8.8	−4.8	−6.8

*, **: Asterisks in Tables 10, 12, 15 and 17 indicate, unless otherwise noted, pH defined by the boundary kaolinite-muscovite, and pH defined by the boundary muscovite-adularia.

(250°C, Case-2)

Log m_i				
HS_2	−2.3	−2.3	−2.3	−2.3
HS^-	−4.0	−3.0	−5.0	−4.0
S^{2-}	−6.3	−4.3	−8.3	−6.3
SO_4^{2-}	−8.8	−6.8	−10.8	−8.8
HSO_4^-	−9.5	−8.5	−10.5	−9.5
Ca^{2+}	−1.9	−0.1	+3.9	−1.9
Ba^{2+}	−0.3	−2.3	+1.7	−0.3

(250°C, Case-3)

Log m_i				
HS_2	−2.5	−2.5	−2.5	−2.5
HS^-	−4.1	−3.1	−5.1	−4.1
S^{2-}	−6.4	−4.4	−8.4	−6.4
SO_4^{2-}	−8.9	−6.9	−10.9	−8.9
HSO_4^-	−9.6	−8.6	−10.6	−9.6
Ca^{2+}	+2.0	0.0	+4.0	+2.0
Ba^{2+}	−0.2	−2.2	+1.8	−0.2

(250°C, Case-4)

Log m_i				
HS_2	−3.4	−3.4	−3.4	−3.4
HS^-	−5.0	−4.0	−6.0	−5.0
S^{2-}	−7.3	−5.3	−9.3	−7.3
SO_4^{2-}	−6.0	−4.0	−8.0	−6.0
HSO_4^-	−6.4	−5.4	−7.4	−6.4
Ca^{2+}	−0.9	−2.9	+1.1	−0.9
Ba^{2+}	−3.1	−5.1	−1.1	−3.1

(250°C, Case-5)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.8*	6.5**	4.8*	5.5**
Log m_i				
HS_2	−4.0	−4.0	−4.0	−4.0
HS^-	−5.6	−4.6	−6.6	−5.6
S^{2-}	−7.9	−5.9	−9.9	−7.9
SO_4^{2-}	−0.8	+1.2	−2.8	−0.8
HSO_4^-	−1.5	−0.5	−2.5	−1.5
Ca^{2+}	−6.1	−8.1	−4.1	−6.1
Ba^{2+}	−8.3	−10.3	−6.3	−8.3

(250°C, Case-6)

Log m_i				
HS_2	−4.0	−4.0	−4.0	−4.0
HS^-	−5.6	−4.6	−6.6	−5.6
S^{2-}	−7.9	−5.9	−9.9	−7.9
SO_4^{2-}	−0.2	+1.8	−2.2	−0.2
HSO_4^-	−0.9	+0.1	−1.9	−0.9
Ca^{2+}	−6.7	−8.7	−4.7	−6.7
Ba^{2+}	−8.9	−10.9	−6.9	−8.9

(250°C, Case-7)

Log m_i				
HS_2	−3.4	−3.4	−3.4	−3.4
HS^-	−5.0	−4.0	−6.0	−5.0
S^{2-}	−7.3	−5.3	−9.3	−7.3
SO_4^{2-}	+0.4	+2.4	−1.6	+0.4
HSO_4^-	−0.3	+0.7	−1.3	−0.3
Ca^{2+}	−7.3	−9.3	−5.3	−7.3
Ba^{2+}	−9.5	−11.5	−7.5	−9.5

(250°C, Case-8)

Log m_i				
HS_2	−2.9	−2.9	−2.9	−2.9
HS^-	−4.5	−3.5	−5.5	−4.5
S^{2-}	−6.8	−4.8	−8.8	−6.8
SO_4^{2-}	−12.7	−10.7	−14.7	−12.7
HSO_4^-	−6.6	−5.6	−7.6	−6.6
Ca^{2+}	+5.8	+3.8	+7.8	+5.8
Ba^{2+}	+3.6	+1.6	+5.6	+3.6

TABLE 11. CALCULATED CONCENTRATION OF MAJOR SULFUR SPECIES DISSOLVED IN THE MODEL ORE FLUIDS. (T=200°C).

(200°C, Case-8)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.8*	6.5**	4.8*	5.5**
Log m_i				
H_2S	−3.1	−3.1	−3.1	−3.1
HS^-	−3.9	−3.2	−4.9	−4.2
S^{2-}	−6.9	−5.5	−8.9	−7.5
SO_4^{2-}	−10.1	−8.7	−12.1	−10.7
HSO_4^-	−12.5	−11.8	−13.5	−12.8
Ca^{2+}	+4.0	+2.6	+6.0	+4.6
Ba^{2+}	+1.4	0.0	+3.4	+2.0

(200°C, Case-9)

Log m_i				
H_2S	−3.2	−3.2	−3.2	−3.2
HS^-	−3.9	−3.2	−4.9	−4.9
S^{2-}	−6.9	−5.5	−8.9	−7.5
SO_4^{2-}	−12.3	−10.9	−14.3	−12.9
HSO_4^-	−14.7	−14.0	−15.7	−15.0
Ca^{2+}	+6.2	+4.8	+8.2	+6.8
Ba^{2+}	+3.6	+2.2	+5.6	+4.2

(200°C, Case-10)

Log m_i				
H_2S	−3.8	−3.8	−3.8	−3.8
HS^-	−4.5	−3.8	−5.5	−4.8
S^{2-}	−7.5	−6.1	−9.5	−8.1
SO_4^{2-}	−12.9	−11.5	−14.9	−13.5
HSO_4^-	−15.3	−14.6	−16.3	−15.6
Ca^{2+}	+6.8	+5.4	+8.8	+7.4
Ba^{2+}	+4.2	+2.8	+6.2	+4.8

(200°C, Case-11)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.4*	6.4**	4.4*	5.4**
Log m_i				
H_2S	−4.2	−4.2	−4.2	−4.2
HS^-	−4.9	−4.2	−5.9	−5.2
S^{2-}	−7.9	−6.5	−9.9	−8.5
SO_4^{2-}	−9.3	−7.9	−11.3	−9.9
HSO_4^-	−11.7	−11.0	−12.7	−12.0
Ca^{2+}	+3.2	+1.8	+5.2	+3.8
Ba^{3+}	+0.6	−0.8	+2.6	+1.2

(200°C, Case-12)

Log m_i				
H_2S	−3.6	−3.6	−3.6	−3.6
HS^-	−4.5	−3.8	−5.5	−4.8
S^{2-}	−7.5	−6.1	−9.5	−8.1
SO_4^{2-}	−10.7	−9.3	−12.7	−11.3
HSO_4^-	−13.1	−12.4	−14.1	−13.4
Ca^{2+}	+4.6	+3.2	+6.6	+5.2
Ba^{2+}	+2.0	+0.6	+4.0	+2.6

TABLE 12. CALCULATED CONCENTRATION OF MAJOR SULFUR SPECIES DISSOLVED IN THE MODEL ORE FLUIDS. (T=250°C)

(250°C, Case-9)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.4*	6.4**	4.4*	5.4**
Log m_i				
H_2S	−2.3	−2.3	−2.3	−2.3
HS^-	−4.0	−3.0	−5.0	−4.0
S^{2-}	−6.3	−4.3	−8.3	−6.3
SO_4^{2-}	−9.0	−7.0	−11.0	−9.0
HSO_4^-	−9.7	−8.7	−10.7	−9.7
Ca^{2+}	+2.1	+0.1	+4.1	+2.1
Ba^{2+}	−0.1	+2.1	+1.9	−0.1

(250°C, Case-10)

Log m_i				
H_2S	−3.8	−3.8	−3.8	−3.8
HS^-	−4.5	−3.8	−5.6	−4.8
S^{2-}	−6.3	−4.3	−8.3	−6.3
SO_4^{2-}	−12.9	−11.5	−14.9	−13.5
HSO_4^-	−15.3	−14.6	−16.3	−15.6
Ca^{2+}	+6.8	+5.4	+8.8	+7.4
Ba^{2+}	+4.2	+2.8	+6.2	+4.8

(250°C, Case-11)

Log m_i				
H_2S	−2.6	−2.6	−2.6	−2.6
HS^-	−4.4	−3.4	−5.4	−4.4
S^{2-}	−6.7	−4.7	−8.7	−6.7
SO_4^{2-}	−12.6	−10.6	−14.6	−12.6
HSO_4^-	−13.3	−12.3	−14.3	−13.3
Ca^{2+}	+5.7	+3.7	+7.7	+5.7
Ba^{2+}	+3.5	+1.5	+5.5	+3.5

(250°C, Case-12)

	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
pH	5.4*	6.4**	4.4*	5.4**
Log m_i				
H_2S	−2.8	−2.8	−2.8	−2.8
HS^-	−4.5	−3.5	−5.5	−4.5
S^{2-}	−6.8	−4.8	−8.8	−6.8
SO_4^{2-}	−12.1	−10.1	−14.1	−12.1
HSO_4^-	−12.8	−11.8	−13.8	−12.8
Ca^{2+}	+5.2	+3.2	+7.2	+5.2
Ba^{2+}	+3.0	+1.0	+5.0	+3.0

(250°C, Case-13)

Log m_i				
H_2S	−3.2	−3.2	−3.2	−3.2
HS^-	−4.8	−3.8	−5.8	−4.8
S^{2-}	−7.1	−5.1	−9.1	−7.1
SO_4^{2-}	−9.6	−7.6	−11.6	−9.6
HSO_4^-	−10.3	−9.3	−11.3	−10.3
Ca^{2+}	+2.7	+0.7	+4.7	+0.5
Ba^{2+}	+0.5	−1.5	+2.5	+0.5

(250°C, Case-14)

Log m_i				
H_2S	−2.6	−2.6	−2.6	−2.6
HS^-	−4.2	−3.2	−5.2	−4.2
S^{2-}	−6.5	−4.5	−8.5	−6.5
SO_4^{2-}	−12.4	−10.4	−14.4	−12.4
HSO_4^-	−11.3	−10.3	−12.3	−11.3
Ca^{2+}	+5.5	+3.5	+7.5	+5.5
Ba^{2+}	+3.3	+1.3	+5.3	+3.3

TABLE 13. STOICHIOMETRIC INDIVIDUAL ACTIVITY COEFFICIENTS FOR SOME CATIONS DISSOLVED IN 1 MOLAL CHLORIDE SOLUTIONS. (DATA TAKEN FROM HELGESON (1969))

	$-\mathrm{Log}\ \gamma_i$						
	Cu^+	Cu^{2+}	Fe^{2+}	Fe^{3+}	Pb^{2+}	Zn^{2+}	Ag^+
200°C	5.4	3.7	1.0	5.5	2.5	4.3	4.3
250°C	6.0	4.8	1.2	6.6	2.9	5.2	4.2

TABLE 14. CALCULATED CONCENTRATION OF SOME METAL IONS DISSOLVED IN THE MODEL ORE FLUIDS. (T=200°C)

(200°C, Case-1)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.8*	6.5**	4.8*	5.5**
Log $a_{S^{2-}}$	−8.0	−6.6	−10.0	−8.6
Log m_i				
Fe***	−9.7	−11.1	−7.7	−9.1
Cu***	−6.7	−7.4	−5.7	−6.4
Pb	−9.9	−11.3	−7.9	−9.3
Zn	−7.5	−8.9	−5.5	−6.9

***: Ferric and cupric ions are negligibly small in amount, compared with those of ferrous and cuprous ions under the conditions throughout the calculations.

(200°C, Case-2)

Log $a_{S^{2-}}$	−8.0	−6.6	−10.0	−8.6
Log m_i				
Fe***	−8.4	−9.8	−6.4	−7.8
Cu***	−7.3	−8.0	−6.3	−7.0
Pb	−9.9	−11.3	−7.9	−9.3
Zn	−7.5	−8.9	−5.5	−6.9

(200°C, Case-3)

Log $a_{S^{2-}}$	−8.5	−7.1	−10.5	−9.1
Log m_i				
Fe***	−7.4	−8.8	−5.4	−6.8
Cu***	−7.3	−8.0	−6.3	−7.0
Pb	−9.4	−10.8	−7.4	−8.8
Zn	−7.0	−8.4	−5.0	−6.4

(200°C, Case-4)

Log $a_{S^{2-}}$	−9.2	−7.8	−11.2	−9.8
Log m_i				
Fe***	−6.7	−8.1	−4.7	−6.1
Cu***	−7.0	−7.7	−6.0	−6.7
Pb	−8.7	−10.1	−6.7	−8.1
Zn	−6.3	−7.7	−4.3	−5.7

(200°C Case-5)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.8*	6.5**	4.8*	5.5**
Log $a_{S^{2-}}$	−9.7	−8.3	−11.7	−10.3
Log m_i				
Fe***	−7.2	−8.6	−5.2	−5.9
Cu***	−6.2	−6.9	−5.2	−5.9
Pb	−8.2	−9.6	−6.2	−7.6
Zn	−5.8	−7.2	−3.8	−5.2

(200°C, Case-6)

Log $a_{S^{2-}}$	−8.9	−7.5	−10.9	−9.5
Log m_i				
Fe***	−8.8	−10.2	−6.2	−8.2
Cu***	−6.2	−6.9	−5.2	−5.9
Pb	−9.0	−10.4	−7.0	−8.4
Zn	−6.6	−8.0	−4.6	−6.0

(200°C, Case-7)

Log $a_{S^{2-}}$	−8.8	−7.4	−10.8	−9.4
Log m_i				
Fe***	−7.6	−9.0	−5.6	−7.0
Cu***	−6.9	−7.6	−5.9	−6.6
Pb	−9.1	−10.5	−7.1	−8.5
Zn	−6.7	−6.7	−5.9	−6.6

TABLE 15. CALCULATED CONCENTRATION OF SOME METAL IONS DISSOLVED IN THE MODEL ORE FLUIDS. (T= 250°C)

(250°C, Case-1)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.4*	6.4**	4.4*	5.4**
Log $a_{S^{2-}}$	−7.6	−5.6	−9.6	−7.6
Log m_i				
Fe***	−9.2	−11.2	−7.2	−9.2
Cu***	−4.8	−5.8	−3.8	−4.8
Pb	−8.6	−10.6	−6.6	−8.6
Zn	−6.1	−8.1	−4.1	−6.1

(250°C, Case-2)

Log $a_{S^{2-}}$	−7.5	−5.5	−9.5	−7.5
Log m_i				
Fe***	−7.7	−9.7	−5.7	−7.7
Cu***	−5.6	−6.6	−4.6	−5.6
Pb	−8.7	−10.7	−6.7	−8.7
Zn	−6.2	−8.2	−4.2	−6.2

(250°C, Case-3)

Log $a_{S^{2-}}$	−7.6	−5.6	−9.6	−7.6
Log m_i				
Fe***	−7.6	−9.6	−5.6	−7.6
Cu***	−5.5	−6.5	−4.5	−5.5
Pb	−8.6	−10.6	−6.6	−8.6
Zn	−6.1	−8.1	−4.1	−6.1

(250°C, Case-4)

Log $a_{S^{2-}}$	−8.5	−6.5	−10.5	−8.5
Log m_i				
Fe***	−6.7	−8.7	−4.7	−6.7
Cu***	−5.1	−6.1	−4.1	−5.1
Pb	−7.7	−9.7	−5.7	−7.7
Zn	−5.2	−7.2	−3.2	−5.2

(250°C, Case-5)

	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
pH	5.4*	6.4**	4.4*	5.4**
Log $a_{S^{2-}}$	−9.1	−7.1	−11.1	−9.1
Log m_i				
Fe***	−7.0	−9.0	−5.0	−7.0
Cu***	−4.3	−5.3	−3.3	−4.3
Pb	−7.1	−9.1	−5.1	−7.1
Zn	−4.6	−6.6	−2.6	−4.6

(250°C, Case-6)

Log $a_{S^{2-}}$	−9.1	−7.1	−11.1	−9.1
Log m_i				
Fe***	−7.1	−9.1	−5.1	−7.1
Cu***	−4.3	−5.3	−3.3	−4.3
Pb	−7.1	−9.1	−5.1	−7.1
Zn	−4.6	−6.6	−2.6	−4.6

(250°C, Case-7)

Log $a_{S^{2-}}$	−8.5	−6.5	−10.5	−8.5
Log m_i				
Fe***	−8.3	−10.3	−6.3	−8.3
Cu***	−4.3	−5.3	−3.3	−4.3
Pb	−7.7	−9.7	−5.7	−7.7
Zn	−5.2	−7.2	−3.2	−5.2

(250°C, Case-8)

Log $a_{S^{2-}}$	−7.5	−5.5	−9.5	−7.5
Log m_i				
Fe***	−6.6	−8.6	−4.6	−6.6
Cu***	−6.2	−7.2	−4.2	−6.2
Pb	−8.7	−10.7	−6.7	−8.7
Zn	−6.2	−8.2	−4.2	−6.2

Table 16. Calculated Concentration of Some Metal Ions Dissolved in the Model Ore Fluids. (T=200°C)

(200°C, Case-8)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.8*	6.5**	4.8*	5.5**
Log a_{S2-}	−8.0	−6.6	−10.0	−8.6
Log m_i				
Fe***	−7.9	−9.3	−5.9	−7.3
Cu***	−7.6	−8.3	−6.6	−7.3
Pb	−9.9	−11.3	−7.9	−9.3
Zn	−7.5	−8.9	−5.5	−6.9

(200°C, Case-9)

Log a_{S2-}	−8.0	−6.6	−10.0	−8.6
Log m_i				
Fe***	−7.4	−8.8	−5.4	−6.8
Cu***	−7.8	−8.5	−6.8	−7.5
Pb	−9.9	−11.3	−7.9	−9.3
Zn	−7.5	−8.9	−5.5	−6.9

(200°C, Case-10)

pH	$m_{K^+}=10^{-1}$		$m_{K^+}=10^{-2}$	
	5.8*	6.5**	4.8*	5.5**
Log a_{S2-}	−8.6	−7.2	−10.6	−9.2
Log m_i				
Fe***	−6.2	−7.6	−4.2	−5.6
Cu***	−7.8	−8.5	−6.8	−7.5
Pb	−9.3	−10.7	−7.3	−8.7
Zn	−6.9	−8.3	−4.9	−6.3

(200°C, Case-11)

Log a_{S2-}	−9.0	−7.6	−11.0	−9.6
Log m_i				
Fe***	−3.5	−4.9	−1.5	−2.9
Cu***	−10.2	−10.9	−9.2	−9.9
Pb	−8.9	−10.3	−6.9	−8.3
Zn	−6.5	−7.9	−4.5	−5.9

(200°C, Case-12)

Log a_{S2-}	−8.6	−7.2	−10.6	−9.2
Log m_i				
Fe***	−6.8	−8.2	−4.8	−6.2
Pb	−9.3	−10.7	−7.3	−8.7
Zn	−6.9	−8.3	−4.9	−6.3

Helgeson (1969). The coefficient is defined as follows:

$$\gamma_i = a_i/m_{t,i}$$

where a_i and $m_{t,i}$ designate the activity and total molality of the i-th ion present in small concentrations in the sodium chloride solution. They are reproduced from Helgeson (1969) in Table 13. The calculated molal concentrations of major ore components are given in Tables 14 and 15 for the aforementioned former group and in Tables 16 and 17 for the latter group. From Tables 9 to 15, it can be said that the realtive metal concentrations are as follows: in the low oxygen fugacity region generally, $\mathrm{Pb}<\mathrm{Cu}<\mathrm{Zn}\leqq\mathrm{Fe}$ and $\mathrm{Pb}<\mathrm{Fe}\leqq\mathrm{Cu}$ Zn at 200°C and 25°C0, respectively, while in the high oxygen fugacity region generally, $\mathrm{Pb}<\mathrm{Fe}<\mathrm{Cu}\leqq\mathrm{Zn}$ at 200°C and 250°C. In the low to intermediate oxygen fugacity environments such as those of lead-zinc veins, Ba^{+2} and Ca^{+2} concentrations are abnormally high. This is consistent with the field observatoin that primary sulfates are very rare to occur in such ore deposits. Summarized in Tables 18 and 19 are the aforementioned calculated molal concentrations of major sulfur and metal species dissolved in the Neogene ore fluids. Table 20 gives a summary of the metal contents in the brines with or without ore-grade precipitates from the currently active geothermal fields. There are considerable differences in temperatures and other chemical parameters between the Neogene ore fluids and the geothermal discharges. As an inevitable consequence, this leads to a rough comparison. From Tables 9 to 17 and

TABLE 17. CALCULATED CONCENTRATION OF SOME METAL IONS DISSOLVED IN THE MODEL ORE FLUIDS. (T=250°C)

(250°C, Case-9)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.4*	6.4**	4.4*	5.4**
Log a_S2-	−7.5	−5.5	−9.5	−7.5
Log m_l				
Fe***	−7.7	−9.7	−5.7	−7.7
Cu***	−5.6	−6.6	−4.6	−5.6
Pb	−8.7	−10.7	−6.7	−8.7
Zn	−6.2	−8.2	−4.2	−6.2

(250°C, Case-10)

Log a_S2-	−7.5	−5.5	−9.5	−7.5
Log m_l				
Fe***	−6.9	−8.9	−4.9	−6.9
Cu***	−6.0	−7.0	−5.0	−6.0
Pb	−8.7	−10.7	−6.7	−8.7
Zn	−6.2	−8.2	−4.2	−6.2

(250°C, Case-11)

Log a_S2-	−7.9	−5.9	−9.9	−7.9
Log m_l				
Fe***	−6.1	−8.1	−4.1	−6.1
Cu***	−6.0	−7.0	−5.0	−6.0
Pb	−8.3	−10.3	−6.3	−8.3
Zn	−5.8	−7.8	−3.8	−5.8

(250°C, Case-12)

pH	$m_{K^+}=10^{-2}$		$m_{K^+}=10^{-1}$	
	5.4*	6.4**	4.4*	5.4**
Log a_S2-	−8.0	−6.0	−10.0	−8.0
Log m_l				
Fe***	−6.0	−8.0	−4.0	−6.0
Cu***	−6.0	−7.0	−5.0	−6.0
Pb	−8.2	−10.2	−6.2	−8.2
Zn	−5.7	−7.7	−3.7	−5.7

(250°C, Case-13)

Log $a2_S-$	−8.3	−6.3	−10.3	−8.3
Log m_l				
Fe***	−6.2	−8.2	−4.2	−6.2
Cu***	−5.5	−6.5	−4.5	−5.5
Pb	−7.9	−9.9	−5.9	−7.9
Zn	−5.4	−7.4	−3.4	−5.4

(250°C, Case-14)

Log a_S2-	−7.6	−5.6	−9.6	−7.6
Log m_l				
Fe***	−6.4	−8.4	−4.4	−6.4
Cu***	−6.2	−7.2	−5.2	−6.2
Pb	−8.6	−10.6	−6.6	−8.6
Zn	−6.1	−8.1	−4.1	−6.1

Table 20, it is suggested that the geothermal brines from New Zealand (e.g. Wairakei, Champagne Pool, Broadlands) and possibly sea water have a similar composition to those of the Neogene ore fluids of high to intermediate oxidation state at 200°C. On the other hand, the geothermal brines from the Discovery Deep, Red Sea and Matupi, T. P. N. G. are similar in chemical composition to those of the Neogene ore fluids of low to intermediate oxidation state at 250°C. Of the active geothermal fluids shown in Table 20, those from the Salton Sea area, California are most enriched in heavy metals. With respect to the above, attention should be paid to the fact that comparison made here is based on the molal concentrations in log scale. In addition, we must bear in mind that the Helgeson's second dissociation constant of hydrogen sulfide differs by order of magnitude compared with that derived by ELLIS and GIGGENBACH (1971), resulting in significant differences in the calculated results.

TABLE 18. SUMMARY OF CALCULATED MOLAL CONCENTRATIONS OF MAJOR SULFUR SPECIES DISSOLVED IN THE NEOGENE ORE FLUIDS.

			−Log concentration		
	m_{K^+}	pH	H_2S	HS^-	S^{2-}
200°C	10^{-2}	5.8	3.1~ 5.0	3.9~ 5’7	6.9~ 8.7
		6.5	3.1~ 5.0	3.2~ 5.0	5.5~ 7.3
	10^{-1}	4.8	3.1~ 5.0	4.9~ 6.7	8.9~10.7
		5.5	3.1~ 5.0	4.2~ 6.0	7.5~ 9.3
250°C	10^{-2}	5.4	2.3~ 4.0	4.0~ 5.6	6.3~ 7.9
		6.4	2.3~ 4.0	3.0~ 4.6	4.3~ 5.9
	10^{-1}	4.4	2.3~ 4.0	5.0~ 6.6	8.3~ 9.9
		5.4	2.3~ 4.0	4.0~ 5.6	6.3~ 7.9
			SO_4^{2-}	HSO_4^-	
200°C	10^{-2}	5.8	0.2~12.9	2.6~15.3	
		6.5	−1.2~11.5	1.9~14.6	
	10^{-1}	4.8	2.2~14.9	3.6~16.3	
		5.5	0.8~13.5	2.9~15.6	
250°C	10^{-2}	5.4	−0.4~12.6	0.3~13.3	
		6.4	−2.4~10.6	−0.7~12.3	
	10^{-1}	4.4	1.6~14.6	1.3~14.3	
		5.4	−0.4~12.6	0.3~15.3	

TABLE 19. SUMMARY OF CALCULATED CONCENTRATIONS OF SOME METAL IONS DISSOLVED IN THE NEOGENE ORE FLUIDS.

				−Log concentration		
	m_{K^+}	pH	Fe	Cu	Pb	Zn
300°C	10^{-2}	5.8	3.5~ 9.7	6.1~10.2	8.1~ 9.9	5.7~7.5
		6.5	4.9~11.1	6.8~10.9	9.5~11.3	7.1~8.9
	10^{-1}	4.8	1.5~ 7.7	5.1~ 9.2	6.1~ 7.9	3.7~5.5
		5.5	2.9~ 9.1	5.8~ 9.9	7.5~ 9.3	5.1~6.9
250°C	10^{-2}	5.4	6.0~ 9.2	4.3~ 6.2	7.1~ 8.7	4.6~6.2
		6.4	8.0~11.2	5.3~ 7.2	9.1~10.7	6.6~8.2
	10^{-1}	4.4	4.0~ 7.2	3.3~ 5.2	5.1~ 6.7	2.6~4.2
		5.4	6.0~ 9.2	4.3~ 6.2	7.1~ 8.7	4.6~6.2

As to the origin of the Neogene ore fluids, the subject will be discussed from stable isotope geochemistry in a forthcoming paper (WATANABE and SAKAI, in print).

In order to conduct investigations into the Neogene mineralization more systematically and more quantitatively, the following informations are required:

(1) Precise determination of thermodynamic properties of chemical species concerned.

(2) Estimation of absolute amounts precipitated in the Green Tuff region.

TABLE 20. COMPARISON OF METAL CONCENTRATION IN WATERS FROM THE CURRENTLY ACTIVE GEOTHERMAL AREAS.

	−Log concentration					
	Fe	Cu	Pb	Zn	K	Ba
(1) Agerage Wairakei drill holes, N. Z.	5.8	5.9	8.0	6.7	2.2*	n.d.
(2) Champagne Pool, Waiotapu, N. Z.	6.1	5.7	8.3	7.0	2.4**	n.d.
(3) Br-7, Broadlands, N. Z.	n.d.	6.7	7.6	6.6	2.2	n.d.
(4) R-152, Cheleken, U. S. S. R.	3.7	4.9	4.8	4.2	n.d.	n.d.
(5) 56°C Brine, Red Sea	2.8	5.4	5.5	4.1	1.3	5.2
(6) Discovery Deep Brine, Red Sea	3.3	6.0	6.1	4.9	1.3	5.5
(7) Tavurvur Shore, Matupi, T. P. N. G.	3.8	6.1	6.4	4.4	1.7	n.d.
(8) I. I. D. No. 1, Salton Sea, U. S. A.	1.4	3.9	3.3	2.1	0.4	2.8
(9) Ocean Water	6.8	7.3	9.8	6.8	2.0	6.7

* Hole 44, Wairakei ** Hole 6, Waiotapu

Sources: (1) and (2), ELLIS (1967)
(3), BROWNE (1971)
(4), LEBEDEV (1967)
(5) and (6), BREWER and SPENCER (1969)
(7), FERGUSON and LAMBERT (1972)
(8) and (9), WHITE (1968)

(3) Chemical and stable isotopic composition of minerals and fluid inclusions.
(4) Lead and rubidium-strontium data on ores and surrounding rocks.
(5) Data of trace element distribution in minerals.
(6) Age determination data on ore constituents and surrounding rocks.
(7) How the Neogene mineralization does stand geologically with respect to the geosynclinal evolution in the Green Tuff region?

VI. SUMMARY AND CONCLUSIONS

According to the foregoing discussions, the following conclusions can be drawn:

1) Iron contents coexisting with pyrite from the Neogene ore deposits lie mostly in the range of 0.3 to 3.0 mol. % FeS.

2) Following a calculation similar to that of HOLLAND (1959, 1965), limits have been placed on gas fugacity prevailing at the time of ore deposition.

3) The overall geochemical environments for the Neogene mineralization are roughly classified into two types; those characterized by high to intermediate oxygen and sulfur

fugacity and those characterized by intermediate to low oxygen and fulfur fugacity. The former, including the Kuroko deposits, gold-silver veins, copper-lead-zinc-manganese veins, and pyrrhotite-free lead-zinc veins, is a region surrounded by the following phase boundaries: alabandite-rhodochrosite; pyrite-magnetite (or pyrite-hematite); galena-anglesite; pyrite-bornite-chalcopyrite; oldahmite-anhydrite; and fixed iron content of sphalerite (3 mol. % FeS). On the other hand, the latter, including lead-zinc veins with or without pyrrhotite, is a region surrounded by the boundaries: alabandite-rhodochrosite; pyrite-pyrrhotite; oldahmite-anhydrite; graphite-carbon dioxide; and pyrite-magnetite.

4) Of the mineral assemblages above, pyrite-bornite-chalcopyrite assemblage is characteristic of the typical Kuroko deposits, suggesting that relatively high sulfur fugacity environments prevailed during their formation.

5) Based on the assumption of mineral-solution equilibrium, the major sulfur and metal species present in the ore fluids responsible for the Neogene ore deposition has been evaluated. The relative metal concentrations are as follows: in the low oxygen fugacity region in general, $Pb<Cu<Zn\leqq Fe$ at 200°C and $Pb<Fe<Cu\leqq Zn$ at 250°C, and in the high oxygen fugacity region in general, $Pb<Fe<Cn\leqq Zn$ at 200°C and 250°C.

6) Comparison of the calculated concentrations of major metal species dissolved in the Neogene ore fluids with those of the active geothermal brines, based on molal concentrations in log scale, leads to the following conclusion: the geothermal brines from New Zealand (e.g. Wairakei, Champagne Pool, and Broadlands) and possibly sea water have a similar composition to those of the Neogene ore fluids of high to intermediate oxidation state at 200°C, while the brines from the Discovery Deep, Red Sea and Matupi, T. P. N. G. are similar in chemical composition to those of the Neogene ore fluids of low to intermediate oxidation state at 250°C.

⟨Addendum⟩ Since completion of this work some years ago, several papers dealing with mineralogical and geochemical aspects of the Neogene mineralization in the Green Tuff region have been published, for example, YAMAOKA (1976), HATTORI and SAKAI (1979), and WATANABE and SOEDA (1981).

REFERENCES

ANDERSON, G. M. (1975): Precipitation of Mississippi Valley-type ores. *Econ. Geol.*, 70, 937–942.

BARNES, H. L. and KULLERUD, G. (1961): Equilibria in sulfur-containing aqueous solution in the system Fe–S–O, and their correlation during ore deposition. *Econ. Geol.*, 56, 648–688.

——— and CZAMANSKE, G. K. (1967): Solubility and transport of ore minerals. In: *Geochemistry of Hydrothermal Ore Deposits*, H. L. BARNES, Ed., 334–381, Holt Rinehart Winston, New York.

BARTON, P. B., Jr (1970): Sulfide petrology. *Miner. Soc. Amer. Spec. Paper*, No. 3, 187–198.

——— and TOULMIN, P., III. (1966): Phase relations involving sphalerite in the Fe–Zn–S system. *Econ. Geol.*, 61, 815–849.

——— and SKINNER, B. J. (1967): Sulfide mineral stabilities. In: *Geochemistry of Hydrothermal Ore Deposits*, H. L. BARNES, Ed., 236–333, Holt Rinehart Winston, New York.

BREWER, P. G. and SPENCER, D. W. (1969): A note on the chemical composition of the Red Sea brines. In: *Hot Brines and Recent Heavy Metal Deposits in the Red Sea*, E. T. DEGGENS and D. A. ROSS, Ed., 174–179, Springer-Verlag, New York.

BROWNE, P. R. L. (1971): Mineralization in the Broadlands geothermal fields, Taupo volcanic zone, New Zealand. *Soc. Mining Geol. Jap., Spec. Issue* No. 2, 64–75.

ELLIS, A. J. (1967): The chemistry of some explored geothermal systems. In: *Geochemistry of Hydothermal Ore Deposits*, H. L. BARNES, Ed., 465–514, Holt Rinehart Winston, New York.

——— and GOLDING, R. M. (1963): The solubility of carbon dioxide in water and in sodium chloride solutions. *Amer. Jour. Sci.,* 261, 47–60.

——— and GIGGENBACH, W. F. (1971): Hydrogen sulphide ionization and sulfur hydrolysis in high temperature solution. *Geochim. Cosmochim. Acta,* 35, 247–260.

ENJOJI, M. (1972): Studies on fluid inclusions as the media of the ore formation. *Sci. Repts. Tokyo Kyoiku Daigaku, Sec. C,* 11, 106, 79–126.

FURGASON, J. and LAMBERT, I. B. (1972): Volcanic exhalations and metal enrichments at Matupi Harbor, New Britain, T. P. N. G. *Econ. Geol.,* 67, 25–37.

GARDNER, E. R., JONES, P. J., and NORDWALL, H. J. De (1963): Osmotic coefficients of some aqueous soldium chloride solutions at high temperatures. *Trans. Farady Soc.,* 59, 1994–2000.

GARRELS, R. M. and THOMPSON, M. E. (1962): A chemical model for sea water at 25°C and one atmosphere total pressure. *Amer. Jour. Sci.,* 260, 57–66.

HATTORI, K. (1975): Geochemistry of ore deposition at the Yatani lead-zinc and gold-silver deposit, Japan. *Econ. Geol.,* 70, 677–693.

——— and SAKAI, H. (1979): D/H ratios, origins, and evolution of the Neogene ore-forming fluids for the Neogene veins and Kuroko deposits. *Econ. Geol.,* 74, 535–555.

HELGESON, H. C. (1964): Complexing and Hydrothermal Ore Deposition. *Pergamon Press,* New York.

——— (1967): Solution chemistry and metamorphism. In: *Researches in Geochemistry,* P. H. ABELSON, Ed., Vol. 2, 241–259, Wiley, New York.

——— (1969): Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Amer. Jour. Sci.,* 276, 729–804.

——— (1970): A chemical and thermodynamic model of ore deposition in hydrothermal system. *Miner. Soc. Amer. Spec. Paper* No. 3, 155–186.

HOLLAND, H. D. (1959): Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates, and carbonates of ore and gangue minerals. *Econ. Geol.,* 54, 184–223.

——— (1965): Some applications of thermochemical data to problems of ore deposits. II. Mineral assemblages and the composition of the ore-forming fluids. *Econ. Geol.,* 60, 1101–1166.

ICHIKUNI, M. (1975): A chemical model for black ore-forming solution (in Japanese). *Japan. Assoc. Min. Petrol. Econ. Geol.,* 70, 71–80.

KAJIWARA, Y. (1970): Some limitations on the physicochemical environment of deposition of the Kuroko ore. In: *Volcanism and Ore Genesis,* T. TATSUMI, Ed., 367–380, University of Tokyo Press, Tokyo.

——— (1971): Sulfur isotope study of the Kuroko-ores of the Shakanai No. 1 deposits, Akita Prefecture, Japan. *Geochem. Jour.,* 4, 157–181.

——— (1973a): Chemical composition of ore-forming fluids responsible for Kuroko type mineralization in Japan. *Geochem. Jour.,* 6, 141–149.

——— (1973b): A simulation of the Kuroko type mineralization in Japan. *Geochem. Jour.,* 6, 193–209.

——— and HONMA, H. (1972): Lead content of barite coexisting with galena. -An indicator of oxygen fugacity during ore formation. *Mining Geol.,* 22, 457–465.

KIYOSU, Y. (1973): Sulfur isotopic fractionation among sphalerite, galena, and sulfide ions. *Geochem. Jour.,* 7, 191–200.

KULLERUD, G. (1953): The FeS–ZnS system, a geological thermometer. *Norsk. Geol. Tidsskr.,* 32, 61–147.

——— and YORDER, H. S. Jr. (1959): Pyrite stability relations in the Fe–S system. *Econ. Geol.,* 54, 533–572.

——— (1967): Sulfide studies. In: *Researches in Geochemistry,* P. H. ABELSON, Ed., Vol. 2, 286–321, Wiley, New York.

LAMBERT, I. B. and SATO, T. (1974): The Kuroko and associated ore deposits of Japan: A review of their features and metallogenesis. *Econ. Geol.,* 69, 1215–1236.

LEBEDEV, L. M. (1967): Contemporary deposition of native lead from hot Cheleken thermal brines. *Dokl. Akad. Nauk, SSR.*, 174, 197–200.

LU, K. I. (1970): Geology and ore deposits of the Uchinotai-higashi deposits, Kosaka mine. *Unpub. Dr. Sc. thesis, University of Tokyo.*

MALININ, S. D. (1959): The system water-carbon dioxide at high temperatures and pressures. *Geochemistry,* no. 3, 292–306.

MEYER, C. and HEMLEY, J. J. (1967): Wall rock alteration. In: *Geochemistry of Hydrothermal Ore Deposits,* H. L. BARNES, Ed., 166–235, Holt Rinehart Winston, New York.

NRIAGU, J. O. (1971a): Expressions for calculating the solubilities of metal sulfides in hydrothermal solution. *Canad. Jour. Earth.,* 8, 813–819.

———— (1971b): Experimental investigation of a portion of the system $PbS–NaCl–HCl–H_2O$ at elevated temperatures. *Amer. Jour. Sci.,* 271, 157–169.

OHMOTO, H. (1972): Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.,* 67, 551–578.

RAYMAHASHAY, B. C. and HOLLAND, H. D. (1969): Redox reactions accompanying hydrothermal wall rock alteration. *Econ. Geol.,* 64, 291–305.

ROBINSON, B. W. (1974): The origin of mineralization at the Tui mine, Te Aroha, New Zealand, in the light of stable isotope studies. *Econ. Geol.,* 69, 910–925.

ROEDDER, E. (1967): Fluid inclusions as samples of ore fluids. In: *Geochemistry of Hydrothermal Ore Deposits* H. L. BARNES, Ed., 515–574, Holt Rinehart Winston, New York.

SATO, K., SLAWSON, W. F., and KANASEWICH, E. R. (1973): Additional isotopic measurements of Japanese ore leads. *Geochem. Jour.,* 7, 115–122.

SATO, T. (1969): An estimation of physico-chemical environments of formation of the Kuroko deposits based on their mineral parageneses (in Japanese). *Koshogaku-Note* 7, 1–6.

———— (1972a): Metallogenesis of Neogene base metal and Au-Ag deposits in Japan with special reference to Kuroko deposits (in Japanese). *Soc. Mining Geol. Jap., Spec. Issue* 4, 185–204, 185–204.

———— (1972b): Model for ore-forming solutions and ore-forming environments: Kuroko vs. veins in Miocene "Green Tuff" region of Japan. *Bull. Geol. Surv. Jap.,* 23, 13–22.

———— (1973): A chloride complex model for Kuroko mineralization. *Geochem. Jour.,* 7, 245–270.

SHIKAZONO, N. (1973): Sphalerite-carbonate-pyrite assemblage in hydrothermal veins and its bearing on limiting the environment of their deposition. *Geochem. Jour.,* 7, 97–114.

———— (1974a): Physicochemical properties of ore-forming solution responsible for the formation of Toyoha Pb-Zn deposits. *Geochem. Jour.,* 8, 37–46.

———— (1974b): Physicochemical environment and mechanism of volcanic hydrothermal ore deposition in Japan, with special reference to oxygen fugacity. *Univ. Tokyo Fac. Sci. Jour., Sec. II,* 19, 27–56.

———— (1975): Mineralization and chemical environment of the Toyoha lead-zinc vein-type deposits, Hokkaido, Japan. *Econ. Geol.,* 70, 694–705.

———— (1976a): Chemical composition of Kuroko ore-forming solution (in Japanese). *Japan. Assoc. Min. Petrol. Econ. Geol.,* 71, 201–215.

———— (1976b): Chemical characteristics of ore-forming solution and mechanism of ore deposition (in Japanese). *Soc. Mining Geol. Jap., Spec. Issue* 7, 117–131.

SUGAKI, A., SHIMA, H., and KITAKAZE, A. (1970): Fundamental study on the quantitative analysis of sulfide minerals by electron micro probe analyses (in Japanese) (I). *Tech. Rept. Yamaguchi Univ.,* 1, 209–219.

SWEATMAN, T. B. and LONG, J. V. P. (1969): Quantitative electron probe microanalysis of rock-forming minerals. *Jour. Petrol.,* 10, 332–379.

TAGUCHI, S. (1975): Precipitation condition of electrum estimated from compositional variation of sphalerite. *Sanko-Gakkai Ann. Mtg. Abstract at Yamanashi Univ., Kofu.*

TAKENOUCHI, S. (1970): Fluid inclusion study by means of heating-stage and freezing-stage microscope (in Japanese). *Mining Geol.,* 20, 345–354.

TATSUMI, T. (1965): Sulfur isotope fractionation between coexisting sulfide minerals from some Japanese ore deposits. *Econ. Geol.,* 60, 1645–1659.

URABE, T. (1974a): Iron content of sphalerite coexisting with pyrite from some Kuroko deposits. *Soc. Mining Geol. Jap., Spec. Issue* 6, 377–384.

——— (1974b): Mineralogical aspects of the Kuroko deposits in Japan and their implications. *Mineral. Deposita* (*Berl.*), 9, 309–324.

WATANABE, M. (1970): Geology and ore deposit of the Daikoku deposit, Ainai mine, Akita Prefecture, with special reference to the fluid inclusion study on the ore-forming minerals. *Unpub. Master's thesis, University of Tokyo.*

——— (1974): On the textures of ores from the Daikoku ore deposit, Ainai mine, Akita Prefecture, Northeast Japan, and their implications in the ore genesis. *Soc. Mining Geol. Jap., Spec. Issue* 6, 337–348.

——— (1976): Geological and geochemical studies on the Neogene mineralization in the Green Tuff region, Japan, with special reference to the natures and origins of the ore-forming fluids. *Unpub. Dr. Sc. thesis, Hiroshima University.*

——— (1979): Fluid inclusions in some Neogene ore deposits in the Green Tuff region, Japan. *Mining Geol.* 29, 307–321.

———, HATTORI, K., and SAKAI, H. (1976): Origin of ore-forming fluids from hydrogen isotopic ratio (in Japanese). *Soc. Mining Geol. Jap., Spec. Issue* 7, 101–116.

——— and SOEDA, A. (1981): Some characteristics of the Neogene mineralization in the Sanin Green Tuff region, Southwest Japan. *Mining Geol.,* 31, 1–11.

——— and SAKAI, H. (in print): Stable isotope geochemistry of sulfates from the Neogene ore deposits in the Green Tuff region, Japan. *Econ. Geol.*

WHITE, D E (1968): Environments of generation of some base-metal ore deposits. *Econ. Geol.,* 63, 301–335.

YAMAOKA, K. (1976): On the genetical problems of the vein-type deposits of the Neogene age in the Inner Belt of Northeast Japan (in Japanese). *Soc. Mining Geol. Jap., Spec. Issue* 7, 59–74.

YUI, S. and CZAMANSKE, G. K. (1971): Iron content of sphalerite from the Iimori mine, Japan. *Soc. Mining Geol. Jap., Spec. Issue* 3, 277–279.

Makoto WATANABE
INSTITUTE OF GEOLOGY AND MINERALOGY,
FACULTY OF SCIENCE, HIROSHIMA UNIVERSITY,
HIROSHIMA 730, JAPAN