Physico-chemical properties of ore-forming solution responsible for the formation of Toyoha Pb-Zn deposits, Hokkaido, Japan

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Abstract—Physico-chemical properties of ore-forming solution responsible for the formation of Toyoha Pb-Zn vein type deposits, Japan are estimated on the basis of the studies on mineral assemblage and fluid inclusions. The concentration of total dissolved sulfur is estimated in a range from 10^{-2} to 10^{-3} mol/l which is consistent with that of hot springs accompanying sulfide deposition. The probable ranges of the other variables such as pH, NaCl and base metal contents of ore-forming solution are also calculated. These estimated values are compared with those of hot springs, Broadland geothermal area, New Zealand, now depositing sulfide minerals. It is concluded that both hydrothermal solutions are very similar with respect to physico-chemical properties and both are characterized by (1) total dissolved sulfur in excess over base metals, (2) neutral to slightly alkaline pH, and (3) low NaCl content. These characteristic features are very different from those of Salton Sea geothermal brine which is now depositing sulfide minerals with total dissolved sulfur insufficient for base metals, slightly acid to neutral, and has high NaCl content.

INTRODUCTION

Information on the physico-chemical properties of ore-forming solution is necessary for interpreting genesis of hydrothermal ore deposits. Nature of the ore-forming solution has been fairly well elucidated on the theoretical studies on stability relations between minerals, aqueous and gaseous phases, chemical analyses of hot springs and hot brines accompanied by deposition of sulfide minerals, and experimental works on partition of elements between aqueous hydrothermal solution and minerals.

BARTON (1959) calculated and estimated the possible region for ore-forming solution from the stability relations between minerals commonly observed in hydrothermal mineral deposits and from data on the solubility product of these minerals. He intended especially to give a limitation to the ratio of activities of simple anions in the possible hydrothermal region. Concentration of total dissolved anions, however, would be a more important factor limiting the physico-chemical properties of ore-forming solution than activities of simple anions, because equilibrium relation of hydrothermal ore-

forming system can be generally expressed as a function of temperature, gaseous fugacities, ionic strength, pH, and total dissolved concentrations of elements contained in the system. Among the concentrations of chemical species concerned, concentration of total dissolved sulfur is probably the most important factor for limiting the physico-chemical environment of hydrothermal ore deposition along with that of chlorine, because recently data which suggest that dominant chemical states of base metal elements in the ore-forming solution are chloride complexes or sulfur-containing complexes (bisulfide, sulfide, or polysulfide complexes) have been accumulating. The concentration of total dissolved sulfur in the ore-forming solution responsible for the formation of Toyoha Pb-Zn vein deposits, Hokkaido, Japan, is estimated in this paper, equilibria between pyrite, pyrrhotite, hydrothermal ore-forming solution, and gaseous phases being assumed. In addition, data on chemical analyses of hot spring waters and hot brines now depositing sulfide minerals are summarized for estimating the order of magnitude of the concentration of total dissolved sulfur in the hydrothermal ore-forming solution. Then, characteristic features of the hydrothermal ore-forming solution responsible for the formation of Toyoha deposits are compared with those of hot spring water of Broadland geothermal area, New Zealand with regard to the ratio of the concentration of total dissolved sulfur and to those of base metals in these solutions. It is concluded consequently that the natures of these solutions are very similar to each other.

TOYOKA DEPOSITS

The Toyoka mine is most productive of lead and zinc ores in Japan. Lead and zinc veins of the mine occur in the so-called Green Tuff region of Miocene in Hokkaido. The deposits are considered to belong to the so-called epithermal veins in Lindgren's sense. The veins are structurally divided into two groups, E-W system represented by the Tajima vein and N-W system represented by the Soya vein. The Tajima vein shows characteristic features of disseminated and vuggy structures. On the contrary, Soya vein has distinctly banded structures. A detailed description of the distribution of minerals, mineral assemblage, mineralogy, and discussion on the nature of mineralization of the Toyoka deposits will be published in future (SHIKAZONO, in preparation).

ESTIMATION OF THE CONCENTRATION OF TOTAL DISSOLVED SULFUR IN ORE-FORMING SOLUTION RESPONSIBLE FOR THE FORMATION OF THE TOYOKA DEPOSITS

General statements

Based on the previous works on the chemical states of sulfur-containing species in solution (GARRELS and NAESER, 1958; CLOKE, 1963;

BARNES and KULLERUD, 1961; ELLIS and GIGGENBACH, 1971), it is probably a good assumption that four species of H_2S , HS^- , HSO_4^- , and SO_4^{2-} among them are most predominant in comparison with the other species such as polysulfide and S^{2-} ions under the condition of hydrothermal ore deposition. The species including sodium or potassium such as NaHSO_4 , NaSO_4^- , KHSO_4 , and KSO_4^- would be neglected when the salinity of ore-forming solution is not so high. Low concentration of ore-forming solution is deduced from the depression of freezing point of fluid inclusions for ore-forming solution responsible for the formation of so-called epithermal vein deposits (TAKENOCHI, 1970; ROEDDER, 1967; ENJOI, 1972; SHIKAZONO, unpublished data).

Recently, thermochemical studies on the hydrothermal aqueous solution have been developed both by theoretical considerations (COBBLE, 1964; CRISS and COBBLE, 1964; HELGESON, 1964, 1967, 1969; KHODAKOVSKY, 1969) and by experimental works (KOZINTSEVA, 1964; Lietzke *et al.*, 1961; MARSHALL and JONES, 1966; ELISS and GIGGENBACH, 1971). Therefore, we can estimate chemistry of ore-forming solution on the basis of these data. However, one must very carefully treat these thermochemical data, because most of the thermochemical parameters, especially those of dissociation constants of weak electrolytes, change rapidly in the probable hydrothermal region from 150°C to 300°C.

Table 1. *Chemical equilibrium reactions*

Concentration of total dissolved sulfur

The concentration of total dissolved sulfur is expressed as a function of sulfur fugacity, oxygen fugacity, activity of liquid H_2O , activity coefficients of the aqueous species, temperature, and pH on the basis of chemical equilibrium reactions of (1) to (3) shown in Table 1. The expression is as follows.

$$\Sigma \text{S} = \frac{K_1 K_2 a_{\text{H}_2\text{O}} f_{\text{S}}^{\frac{1}{2}}}{\delta_{\text{H}_2\text{S}} f_{\text{O}_2}^{\frac{1}{2}}} \left(1 + \frac{K_3}{a_{\text{H}^+} \delta_{\text{HS}}} \right)$$

where a , δ , and f refer to activity, activity coefficient, and fugacity of subscribed species, respectively, and K_i refers to equilibrium constants for the reactions. In order to derive equation (1), it is assumed that ore-forming system remained in a state where reduced sulfur species were predominant and concentration of total dissolved reduced

sulfur species, H_2S and HS^- , was fairly higher than that of base metal complexes combined with these species. For estimating order of magnitude of the concentration of total dissolved sulfur, we have to know ranges of the other physico-chemical parameters.

Ionic strength Ionic strength of a hydrothermal ore-forming solution can be estimated from the determination of depression of freezing point of fluid inclusions. The depression measured for fluid inclusions in quartz and sphalerite from Toyoha deposits ranges from -1.9°C to $-0.1^\circ\text{C} \pm 0.2^\circ\text{C}$. The data and mode of occurrence of the fluid inclusions are shown in Table 2. When the ore-forming solution is assumed to be a $\text{NaCl} - \text{H}_2\text{O}_{\text{liq}}$ binary mixture, the depression of freezing point of -1.9°C corresponds to 3.7 wt % of NaCl. Considering the uncertainty of the measurements, we estimate 4 wt % of NaCl to be the maximum value for the concentration of NaCl in the ore-forming solution considered. Maximum ionic strength of 0.5 for the solution can be estimated from 4 wt%. Then, it is reasonable to regard the ionic strength to be from 0.5 to 0.0.

Table 2. *Depression of freezing point of fluid inclusions*

Minerals	Locality	Mode of occurrence	Depression of freezing point
Quartz	Soya-180 mL-No.16	Veinlet in wallrock	-0.4°C
Quartz	Soya-0 mL-No.35	In sphalerite-pyrite band	-0.1°C to -0.3°C
Quartz	Soya-60 mL-No.35	In sphalerite-pyrite band	-0.1°C
Quartz	Soya-60 mL-No.35	In quartz-calcite band	-0.1°C
Sphalerite	Tajima-150 mL-No.20	Disseminated sphalerite in quartz	-1.8°C
Sphalerite	Tajima-175 mL-No.25	Disseminated sphalerite in quartz	-1.9°C

Activity of liquid water HELGESON (1969) calculated activity of liquid water for the solutions of NaCl of 1.0, 2.0, and 3.0 mol/l on the basis of experimental work on the osmotic coefficient of NaCl– H_2O system (GARDNER *et al.*, 1963). According to his calculated values of activity of liquid water, it is a good assumption that it nearly equals unity when ionic strength of the solution is from 0.5 to 0.0.

Activity coefficient of ions and neutral species Debye-Hückel's equation can be applied to strong electrolyte solution having values of ionic strength smaller than 0.001 at 25°C . Deviation from its equation is conspicuous at low temperatures (GARRELS and CHRIST, 1965). However, under high temperature and low salinity conditions now under consideration, activity coefficients of ions are to be calculated using

Debye-Hückel's equation.

Although experiments on solubility of gaseous species into the $\text{H}_2\text{O}_{\text{liq}} - \text{NaCl}$ system at elevated temperatures have not sufficiently been carried out, it would be reasonable to regard the value of activity coefficient of neutral aqueous species as unity under the low salinity condition.

Fugacities of sulfur and oxygen gases

When we assume chemical equilibrium between pyrrhotite and pyrite, we can give a limitation on the range of fugacities of sulfur and oxygen gases. Pyrrhotite coexisting with pyrite occurs fairly commonly in Toyoha deposits. Mode of occurrence of the pyrrhotite is generally divided into two kinds. In the first case, the mineral occurs as a constituent of band in the vein and the other is microscopic grains included in other sulfides. Pyrrhotite generally occurs in Soya vein, but not commonly in Tajima vein. Mineralization for the formation of Soya vein is divided into two stages, namely early stage of sulfide formation and later stage of carbonate formation. Pyrrhotite occurring in the megascopic band exists at the inner most part of sulfide bands. Under the microscope, it seems texturally that the pyrrhotite has not been equilibrated with pyrite. Whereas pyrrhotite is observed as microscopic grains in other sulfides over all stages of early mineralization. The textural relationship between pyrrhotite and coexisting pyrite shows that equilibrium relation between pyrite and pyrrhotite has been attained at the time of their deposition.

TOULMIN and BARTON (1964) gave a relationship between composition of hexagonal pyrrhotite and sulfur fugacity and temperature. If this relationship is assumed to be extrapolated to a temperature region lower than 320°C , the value of sulfur fugacity is obtained at a given temperature. Pyrite-pyrrhotite assemblage also gives a limitation on the range of oxygen fugacity from consideration on the stability relation in the Fe-S-O-C system (HOLLAND, 1965).

Rewriting equation (1) in logarithmic form, we obtain

$$\log \Sigma S = \frac{1}{2} \log f_{\text{S}_2} - \frac{1}{2} \log f_{\text{O}_2} + \log \phi$$

$$\text{where } \phi = \frac{K_1 K_2 a_{\text{H}_2\text{O}}}{\delta_{\text{H}_2\text{S}}} \left(1 + \frac{K_3}{a_{\text{H}^+} \delta_{\text{HS}^-}} \right)$$

Thus, the iso-total dissolved sulfur contour (Figs. 1 and 2) is drawn as a line of 45° slope on a $\log f_{\text{S}_2} - \log f_{\text{O}_2}$ diagram at a given temperature (RAYMAHASHAY and HOLLAND, 1969). The contour moves with change in the pH value and ionic strength on the diagram. When ore-forming solution has constant values of pH, fugacity of CO_2 gas, ionic strength and temperature, maximum concentration of total dissolved sulfur for the solution can be obtained from the iso-total dissolved sulfur contour which passes the intersection of pyrite-pyrrhotite phase boundary line and carbon- CO_2 gas phase boundary line which moves toward lower f_{O_2} region with decreasing

f_{CO_2} in Figs. 1 and 2. Minimum concentration of total dissolved sulfur can be obtained from the other contour which passes pyrite-pyrrhotite-magnetite tripple point.

Fig. 1. Iso-total dissolved sulfur contours (a and b) on $\log f_{\text{S}_2}$ - $\log f_{\text{O}_2}$ diagram at 200°C. a and b lines are the same as in Table 3.

Fig. 2. Iso-total dissolved sulfur contours (a and b) on $\log f_{\text{S}_2}$ - $\log f_{\text{O}_2}$ diagram at 250°C. a and b lines are the same as in Table 3.

Table 3. Calculated concentration of total dissolved sulfur at the point of graphite- CO_2 gas-pyrrhotite-pyrite (a), and pyrrhotite-pyrite-magnetite assemblages (b)

Temp. (°C)		250			200		
pH		7.7	8.0	9.0	7.2	8.0	9.0
$\log \Sigma \text{S}$	a	-1.6	-1.0	0.0	-2.8	-2.3	-1.3
	b	-4.8	-4.5	-3.5	-3.8	-3.0	-2.0

Condition: $f_{\text{H}_2\text{O}} = 40\text{atm}$ at 250°C and 16atm at 200°C. $f_{\text{CO}_2} = 1\text{atm}$ at 250°C and 10^{-1}atm at 200°C. Ionic strength = 0.5 in (a) and 0.0 in (b)

Results of calculation

Results of calculation are shown in Figs. 1 and 2, and in Table 3. Thermochemical data for equations (1) and (2) in Table 1 were taken from HOLLAND (1965) and KOZINTSEVA (1964), respectively, and those for equations (3) and (4) from ELLIS and GIGGENBACH (1971). Ionic strength affects the position of the iso-total dissolved sulfur contours. Ionic strengths giving the maximum and minimum concentrations of total dissolved sulfur are taken to be 0.5 and 0.0, respectively, since the iso-total dissolved sulfur contour moves toward higher f_{O_2} and lower f_{S_2} region with increasing ionic strength. In H_2S dominant region, iso-total dissolved sulfur contour does not move with changing pH. While the contour moves

with changing pH in HS^- dominant region, calculation was performed at pH = 8 and 9 in the HS^- dominant region. A temperature range from 200°C to 250°C is assumed on the basis of measured filling temperatures of fluid inclusions in quartz from Toyoha deposits. In consequence, order of magnitude of the total dissolved sulfur is estimated to range from 10^0 to 10^{-5} mol/l with changing pH, ionic strength and temperature. However, it ranges from 10^{-2} to 10^{-3} mol/l when taking the most probable conditions temperature = 200°C, pH in HS^- dominant or both H_2S and HS^- dominant region, and ionic strength = 0.5.

DISCUSSION AND CONCLUSION

Comparison of the estimated concentrations of total dissolved sulfur in ore-forming solution responsible for the formation of Toyoha deposits with those in hot springs or hot brines depositing sulfide minerals

Although many hot springs accompanied by Hg deposits have been reported, those which are now precipitating HgS are rather rare. They are for example Suphur Bank, California, Steamboat Springs, Nevada, and probably Ngawha Springs, New Zealand (White, 1967). Hot springs or hot brines now precipitating other sulfide minerals besides HgS are limited to a few localities. From hot brine in the Salton Sea geothermal area, California, metal rich siliceous scale is precipitating about 2 ~ 3 tons per month (SKINNER *et al.*, 1967). LEBEDEV (1967) reported sulfides and native lead precipitating from hot brine at Cheleken Peninsula, U.S.S.R. Sulfide minerals were found in six drilling cores from the Broadland geothermal area, New Zealand (BROWNE, 1971). BROWNE showed that the solution with low salinity, neutral to slightly alkaline pH, and low concentrations of base metal elements is also a probable ore-forming solution along with that of high salinity and high concentrations of base metal elements reported for the Salton Sea geothermal area.

The chemical analytical data of these hot springs and hot brines are shown in Table 4. The concentration of total dissolved sulfur for these solutions approximately coincides with that estimated for the ore-forming solution responsible for the formation of Toyoha deposits.

The ratio of concentration of total dissolved sulfur to those of base metal elements

Base metal contents of ore-forming solution can not be estimated when chemical states of base metal elements in hydrothermal aqueous solution are unknown. Although we cannot precisely deduce base metal contents of ore-forming solution, we may estimate at least that base metal contents of the ore-forming solution responsible for the formation of Toyoha deposits were very low, for instance, probably from 10^{-4} to 10^{-10} molal for Zn considering that a) pH range remained from neutral to slightly alkaline and concentration of chloride was very low for the ore-forming solution (SHIKAZONO, unpublished data) and b) chloride complex or bisulfide complex was

Table 4. *Representative chemical composition of hot springs or hot brines accompanied by the deposition of sulfide minerals (ppm)*

Locality	pH	SO ₄ ²⁻	H ₂ S	Na ⁺	Cl ⁻
1. Sulphur Bank, Lake Co., California	6.8	598	12	1190	644
2. Steamboat Springs, Washoe Co., Nevada	6.1	107	8	50400	824
3. Ngawha Springs, New Zealand	6.4	347	6	830	1250
4. Salton Sea, California	5.5	5.4	16	50400	155000
5. Cheleken Peninsula, U.S.S.R.	5.5-6.6	153.7-278.6		69740-79647	145020-161330
6. Broadland, New Zealand	8.55	564	64	1300	1823

predominant under the condition now in consideration. Detailed calculation will be given elsewhere. Therefore, the concentration of total dissolved sulfur would have been higher than those of base metal elements. It is to be noted that the estimated physicochemical properties of ore-forming solution responsible for the formation of the Toyoha epithermal Pb-Zn vein deposits are very similar to those of hot springs now depositing sulfide minerals in the Broadland geothermal area, New Zealand, especially with regard to order of magnitude of concentration of total dissolved sulfur, pH, NaCl and base metal contents. Not only the ore-forming solution responsible for the formation of Toyoha deposits, but also that for the other so-called epithermal vein deposits would be very similar with respect to their physico-chemical properties. Comparison of the chemistry of ore-forming solution for the formation of Toyoha deposits with that of hot springs in the Broadland geothermal area is summarized in Table 5.

Table 5. *Characteristic features of hydrothermal solutions responsible for Toyoha deposits and in the Broadland geothermal area*

	Toyoha deposits	Broadland geothermal area
Temperature	150°C to 250°C	130°C to 280°C
pH	6 to 9	6.5 to 8.5
NaCl content	0.1 to 0.5 mol/l	0.1 mol/l
Concentration of total dissolved sulfur	10 ⁻² to 10 ⁻³ mol/l	10 ⁻² to 10 ⁻³ mol/l
Concentration of total dissolved carbon	10 ⁻¹ to 10 ⁻⁴ mol/l	10 ⁻¹ to 10 ⁻³ mol/l
Base metal contents	Zn: 10 ⁻⁴ to 10 ⁻¹⁰ mol/l	Zn: 0.015 ppm Cu: 0.012 ppm Pb: 0.005 ppm Ag: 0.002 ppm Au: 0.0001 to 0.001 ppm

SUMMARY

There are many ways for estimating physico-chemical properties of ore-forming solution. In this paper thermochemical equilibria in the solution are used for the estimation of the concentration of total dissolved sulfur in the solution which formed Toyoha deposits. Together with the estimated temperature, ionic strength and pH of ore-forming solution and the results of studies on fluid inclusions and mineral assemblage, the equilibrium relation between pyrite and pyrrhotite suggests the concentration of total sulfur to be in a range between 10^{-2} and 10^{-3} mol/l. Except for the Salton Sea geothermal area, hot springs and brines depositing sulfide minerals also generally show sulfur concentration from 10^{-2} to 10^{-3} mol/l. Physico-chemical variables such as pH, NaCl and base metal contents of hot springs in the Broadland geothermal area are nearly the same as to the estimated corresponding values for the ore-forming solutions of Toyoha deposits and other epithermal vein deposits. These solutions are characterized by the presence of excess sulfur which is not present in the ore-forming solution in the Salton Sea geothermal area.

As shown by BROWNE (1971) hydrothermal solution with low salinity, neutral or slightly alkaline pH and with low concentrations of base metal elements also is a probable ore-forming solution, as well as hydrothermal solution with high salinity and high concentrations of base metal elements such as reported for the solution in the Salton Sea geothermal area.

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