

ASSOCIATED METALS IN VEIN-TYPE DEPOSITS IN JAPAN: INTERPRETATION USING THE HSAB PRINCIPLE

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ABSTRACT

Vein-type deposits in Japan associated with volcanic activity of Cretaceous to Quaternary ages can be divided into two major types based on the association of metals. The gold-silver deposits are characterized by enrichments of Hg, Te, Se, As, Sb, Cd and Tl, in addition to Au and Ag, whereas base-metal deposits are characterized by Pb, Zn, Mn, Ag, Cu, Bi, As, Sb, In, Ga, Sn and W. The HSAB (hard and soft acids and bases) principle can explain this difference successfully. Relatively soft elements (e.g., Au, Ag, Hg, Cd, Tl) tend to be enriched in the gold-silver deposits, whereas hard elements (e.g., Pb, Zn, Mn, In, Ga, Sn, W) are concentrated in the base-metal deposits. Concentrations of relatively soft ligands such as HS^- are higher in ore fluids responsible for the gold-silver deposits than in fluids responsible for the base-metal deposits. On the other hand, concentrations of relatively hard ligands such as Cl^- and CO_3^{2-} are higher in the ore fluids responsible for the base-metal deposits than those responsible for the gold-silver deposits. Thus, the difference in the ligand (Cl^- , HS^- , CO_3^{2-}) concentrations of the ore fluids can be also rationalized by the above-mentioned principle.

Keywords: vein-type deposits, epithermal deposits, gold deposits, softness, hardness, hard and soft acids and bases, HSAB principle, ore fluids, Japan.

SOMMAIRE

Les gisements en fissures japonais, qui montrent une association avec le volcanisme d'âge crétacé à quaternaire, se répartissent en deux groupes importants selon l'association des métaux. Les gisements à Au-Ag montrent un enrichissement en Au, Ag, Hg, Te, Se, As, Sb, Cd et Tl; les gisements à métaux de base sont enrichis en Pb, Zn, Mn, Ag, Cu, Bi, As, Sb, In, Ga, Sn et W. Le principe HSAB (acides et bases durs et mous) peut expliquer un tel regroupement. Les éléments relativement mous (autre Au et Ag, Hg, Cd, Tl) ont tendance à s'enrichir dans les gisements à Au-Ag, tandis que les éléments durs (e.g., Pb, Zn, Mn, In, Ga, Sn, W) sont concentrés dans les gisements à métaux de base. La concentration des ligands relativement mous, tel que HS^- , est plus élevée dans les

fluides responsables des gisements à Au-Ag. D'autre part, la concentration des ligands relativement durs, tels Cl^- et CO_3^{2-} , est plus élevée dans les fluides qui ont produit les gisements à métaux de base. C'est donc dire que la différence dans les concentrations des ligands importants dans ces fluides (Cl^- , HS^- , CO_3^{2-}) est régie par ce même principe.

(Traduit par la Rédaction)

Mots-clés: gisements en fissures, gisements épithermaux, gisements d'or, mollesse, dureté, acides et bases durs et mous, HSAB, fluides minéralisateurs, Japon.

INTRODUCTION

A large number of vein-type deposits occur in Cretaceous, Tertiary and Quaternary volcanic regions in Japan. These deposits have wide variations in their geochemical, geological and mineralogical characteristics (Shikazono 1986, Shikazono *et al.* 1990). For example, the Ag/Au ratio (by weight) in the total past production varies widely, from less than one to more than 100 (Shikazono 1986). The main metals produced from these deposits are Cu, Pb, Zn, Mn, Au and Ag. In addition, accessory metals (Bi, Hg, Sb, As, Cd, In, Ga, Sn, W, Mo) have been mined as by-products.

The location of the deposits examined is shown in Figure 1. They are associated with felsic and intermediate volcanic activity of late Cretaceous to Quaternary age. Most of the base-metal-rich deposits occur in Green Tuff region, which is composed of a thick pile of altered volcanic rocks of Tertiary age. The gold-silver-rich deposits occur in subaerial Quaternary volcanic rocks as well as in submarine Tertiary altered rocks. Some base-metal deposits occur in Cretaceous felsic volcanic rocks. The age of the mineralization, as determined by the K-Ar method, varies widely (from 68 to 1 Ma). However, most of the deposits studied have been formed in a range from 5 to 1 Ma. Vein-type

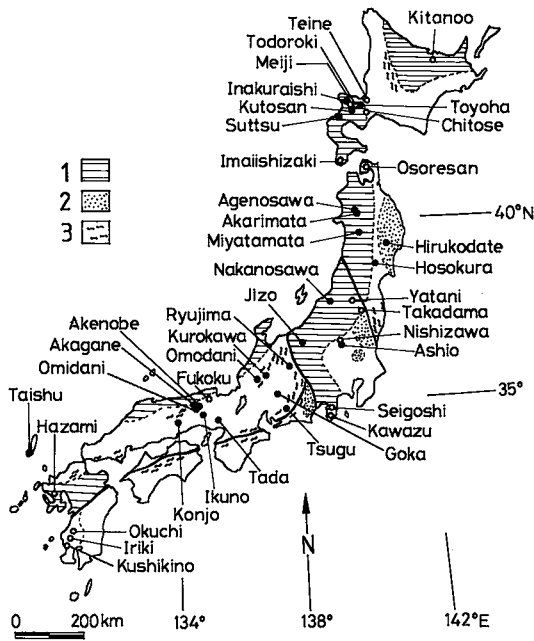


FIG. 1. A map showing location of gold-silver (open circle) and base-metal (solid circle) deposits studied. 1 Tertiary and Quaternary volcanic region, 2 Cretaceous plutonic rock region, 3 Cretaceous acidic volcanic rock region.

deposits related to Cretaceous and Tertiary felsic plutonic activity also are commonly found in the Japanese islands, but are omitted from this study.

In this paper, a summary is given of the common and accessory metals from the vein-type deposits related to volcanic activity. The differences in the metal associations, and the chemical features of the ore fluids responsible for these deposits, are interpreted in terms of the hard and soft acids and bases (HSAB) principle of Ahrlund *et al.* (1958) and Pearson (1963, 1968a,b), and softness parameter of Yamada & Tanaka (1975).

ASSOCIATED METALS IN VEIN-TYPE DEPOSITS

Vein-type deposits are classified primarily on the basis of their major ore-metals (Cu, Pb, Zn, Mn, Au and Ag) into the gold-silver type and the base-metal type. Major and accessory ore-metals from major vein-type deposits in Japan were examined by the present authors in order to assess the possible differences in the metal ratios in these two types of deposit. Characteristic major ore-me-

TABLE 1. ACCESSORY METALS FROM VEIN-TYPE DEPOSITS IN JAPAN

Gold-silver type

Metal Mine Name	Hg	Tl	Cd	Bi	Mo	Sn	W
Konoma	x						
Kitanoou	x						
Showa	x						
Meiji	x						
Takadama	x						
Hirukodate	x						
Okuchi	x						
Hazami	x						
Osoresan	x	x					
Tsugu	x				x		
Chitose			x				
Todoroki			x				
Seigoshi			x				
Kushikino			x				
Teine				x			
Nishizawa				x	x		
Kawazu				x	x	x	
Iriki					x		
Yatani					x		

Base-metal type

Metal Mine Name	Hg	Tl	Cd	Bi	Mo	Sn	W
Jizo	x						
Akenobe			x	x	x	x	x
Toyoha			x	x		x	x
Ashio			x	x		x	x
Goka			x	x			
Miyatamata			x	x			
Agenesawa			x	x			
Akarimata			x	x			
Hosokura			x	x			
Nakanosawa			x	x			
Fukoku			x	x			
Ikuno			x	x			
Taishu			x	x			
Suttu					x		
Hayakawa						x	x
Akakane						x	x
Kishu						x	x
Kutosan						x	x
Kurokawa						x	x
Goka						x	x
Omidani						x	x
Imaiishizaki						x	x
Inakuraishi						x	x
Tada						x	x
Fukoku						x	x
Omidani						x	x
Konjo						x	x
Ryujima						x	x

x: present. References used: Shikazono (1986), Shikazono *et al.* (1990).

tals are Au, Ag, Te, Se and Cu for the gold-silver deposits, and Pb, Zn, Mn, Cu and Ag for the base-metal deposits (Shikazono 1986). Accessory metals from these two types of deposit include Cd, Hg, Tl, Sb and As for the gold-silver deposits, and In, Ga, Bi, As, Sb, W and Sn for the base-metal deposits (Table 1). Minerals containing Cu, Ag, Sb and As are common in both types of deposit. They are thus not included in Table 1.

CHEMICAL FEATURES OF THE ORE FLUIDS

Earlier investigators have evaluated the physicochemical environment of formation of Japanese ore deposits considered here (*e.g.*, Shikazono 1974a,b, 1978). It is now established

that different physicochemical environments prevailed during the formation of the gold-silver and base-metal deposits (Shikazono 1974a, 1977a,b, 1978). The two types of deposit were found to have different characteristic mineralogical features. For example, mineral assemblages and chemical compositions of ore minerals (*e.g.*, iron content of sphalerite, silver content of electrum) in both types of deposit are clearly different. In the base-metal deposits, pyrrhotite occurs, whereas no pyrrhotite has been reported from the gold-silver deposits. In the gold-silver deposits, pyrite and hematite are the common minerals of iron. Iron content (FeS mole %) of sphalerite from the base-metal and gold-silver deposits ranges from 1 to 20 and from 0.1 to 2, respectively (Shikazono 1977b). These mineralogical features, combined with fluid-inclusion and thermochemical studies, have shown that sulfur fugacity [$f(S_2)$], and oxygen fugacity [$f(O_2)$] of ore fluids responsible for the gold-silver deposits were higher than those respon-

sible for the base-metal deposits (Shikazono 1974a, 1978) (Fig. 2). The predominant gangue minerals are different in both types of deposits; quartz, chalcedonic quartz, adularia, calcite, smectite, interstratified mica-smectite, interstratified chlorite-smectite, sericite, zeolites and kaolinite in the gold-silver deposits; chlorite, quartz, sericite, carbonates (calcite, rhodochrosite, siderite), and (magnetite) in the base-metal deposits. In the preceding statement, minerals mentioned in parentheses occur in small amounts in each type of deposit. Gangue mineral assemblages, fluid-inclusion analyses and thermochemical calculations indicate that CO_2 fugacity [$f(CO_2)$] for the base-metal deposits was generally higher than for the gold-silver deposits; 10^{-3} –1 atm (gold-silver deposits) and 10^{-1} –10 atm (base-metal deposits) (Shikazono 1985a).

The salinity (NaCl equivalent concentration) of ore fluids can be estimated from data on freezing temperature of fluid inclusions in minerals from these deposits. The salinity in the ore fluids responsible for the gold-silver deposits is generally lower than in the case of the base-metal deposits (*e.g.*, Enjoji & Takenouchi 1976) (Table 2). Salinities of ore fluids responsible for the gold-silver deposits and base-metal deposits are mostly within a range of 0–3 wt.% (NaCl equivalent concentration) and 3–10 wt.%, respectively.

Temperature of formation can be estimated from the temperature of homogenization of fluid inclusions and opaque mineral assemblages, such as sphalerite–electrum–argentite (or acanthite)–pyrite (Shikazono 1985b). Typical ranges of temperature of formation are from 170° to 250°C for the gold-silver, and from 200° to 300°C for the base-metal deposits (Shikazono 1985a) (Table 2).

A K-feldspar of adularia habit is a characteristic alteration and gangue mineral for the gold-silver deposits, whereas sericite is characteristic of the base-metal deposits (Shikazono 1978). The K-feldspar/sericite stability boundary is determined by the activity ratio, $a(K^+)/a(H^+)$, and temperature (*e.g.*, Montoya & Hemley 1975). The concentration of the potassium ion in the ore fluids can be estimated from the empirical relation linking Na^+/K^+ obtained from analyses of active geothermal waters (White 1965, Ellis 1969, Fournier & Truesdell 1973) and total salinity of fluid inclusions. By using this estimated concentration of potassium, salinity data on fluid inclusions and temperature from fluid inclusion studies, the probable range of pH of ore fluids can be defined (Shikazono 1978). The stability of these minerals, the salinity of fluid inclusions and estimated temperatures of formation all allow the inference that the pH of ore fluids responsible for the gold-silver deposits was higher than that of the

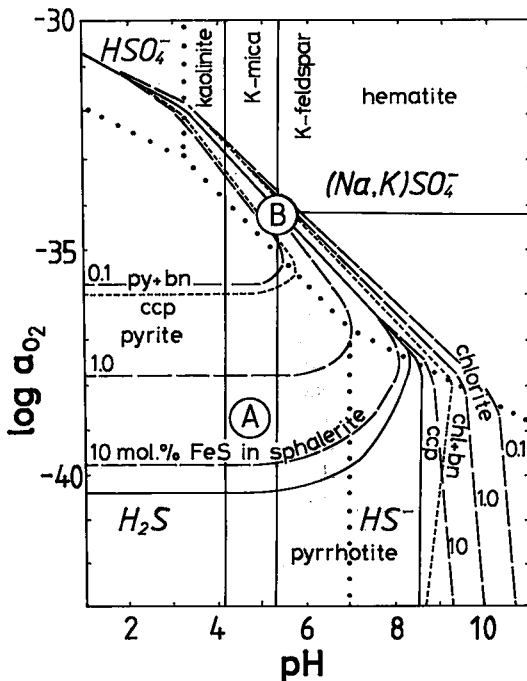


FIG. 2. $\log a(O_2)$ - pH diagram showing the typical ranges of ore fluids responsible for the gold-silver (B) and base-metal deposits (A). Temperature: 250°C, ΣS (total concentration of dissolved sulfur): 0.02 molal, total salinity: 1 molal with $Na^+/K^+ = 9$. The diagram was modified from Barton *et al.* (1977) and Hayba *et al.* (1985). Abbreviations: *py* pyrite, *bn* bornite, *ccp* chalcocopyrite, *chl* chlorite.

TABLE 2. SALINITY AND FILLING TEMPERATURES OF FLUID INCLUSIONS FROM VEIN-TYPE DEPOSITS

Gold-silver type			
Deposit	Filling temperature (°C)	NaCl eq. concentration (wt.%)	References
Sado	305-190	2.5-1.0	(1), (2)
Seigoshi	243-178	2.8-0.0	(1), (2)
Yatani	273-209	1.5-0.5	(1), (2)
Ohguchi	265-164	1.6-0.0	(1), (2)
Todoroki	240-122	1.7-0.4	(1), (3)
Koryu	300-140	1.4-0.0	(1), (4)
Chitose	300-220	2.0-1.0	(6)
Kushikino	250-210	1.1-0.6	(6), (2)
Base-metal type			
Toyoha	300-150	4.2-0.2	(7)
Oppu	330-170	18.3-1.7	(1)
Osarizawa	266-158	7.5-0.0	(1)
Hosokura	231-130	9.1-0.0	(1)
Nanetsu	306-260	7.9-4.4	(1)
Taisyu	376-160	33.5-5.0	(1)
Asahi	275-260	10.3-6.8	(1)
Ani	266-207	12.0	(1)
Oe	310-145	2.0-0.0	(1), (8)
Jokoku	250-125	6.0-3.0	(1)

References used: 1 Enjoji & Takenouchi (1976), 2 Shikazono (1985b), 3 Yoneda (1981), 4 Sugaki *et al.* (1984), 5 Sato *et al.* (1981), 6 Izawa *et al.* (1981), 7 Yajima & Ohta (1979), 8 Sato *et al.* (1980).

TABLE 3. GEOCHEMICAL FEATURES OF ORE FLUIDS RESPONSIBLE FOR THE GOLD-SILVER AND BASE-METAL VEIN-TYPE DEPOSITS

	Gold-silver type	Base-metal type	References
f(S ₂)	high (10 ⁻¹³ -10 ⁻¹⁰ atm. at 250°C)	low (10 ⁻¹⁴ -10 ⁻¹² atm. at 250°C)	(1)
f(O ₂)	high (10 ⁻³⁷ -10 ⁻³⁴ atm. at 250°C)	low (10 ⁻³⁸ -10 ⁻³⁶ atm. at 250°C)	(2)
f(CO ₂)	low (10 ⁻¹ -1 atm. at 250°C)	high (1-100 atm. at 250°C)	(3)
Salinity	low (0-3 wt.%)	high (3-10 wt.%)	(4)
S	10 ⁻² -10 ⁻³ mole/kg. H ₂ O	10 ⁻² -10 ⁻³ mole/kg. H ₂ O	(5) (6)
pH	high (5-8 at 250°C)	low (4-5 at 250°C)	(2)
Temperature	low (170-250°C)	high (200-300°C)	(7)

References used: 1 Shikazono & Shimizu (1988), 2 Shikazono (1978), 3 Shikazono (1985a), 4 Enjoji & Takenouchi (1976), 5 Shikazono (1974b), 6 Hattori (1975), 7 Shikazono (1985b).

base-metal mineralization, as shown in Figure 2 (Shikazono 1977a,b, 1978). The total concentration of dissolved sulfur species in both ore fluids, as estimated from thermochemical calculations and stability fields of ore minerals, is of nearly the same in order of magnitude ($\Sigma S = 10^{-2}$ to 10^{-3} mole/kg H₂O) (e.g., Shikazono 1974b, Hattori 1975). The concentration of HS⁻ in the ore fluids responsible for the gold-silver deposits may have been higher than that for the base-metal deposits because HS⁻ concentration increases with increasing pH at constant total concentration of dissolved sulfur and temperature (e.g., Barnes & Kullerud 1961). These geochemical features of the ore fluids are summarized in Table 3.

Using the probable ranges of temperature, concentrations of Cl⁻ and HS⁻, ΣS and pH summarized in Table 3, we can place a limit on the concentrations of ore metals in the fluid phase, as such concentrations can be represented as a function of temperature, concentrations of Cl⁻, HS⁻, ΣS and pH (e.g., Barnes 1979). Such calculations indicate that gold is dissolved dominantly as bisulfide complexes, whereas other metals such as zinc, copper and lead are present dominantly as chloro complexes (Shikazono 1974a, 1986). Mechanisms of precipitation for these ore metals (Au, Zn, Cu, Pb) in the epithermal vein-type deposits in Japan have been discussed at length (e.g., Shikazono 1974, 1978, 1986, Hattori 1975). Degassing of H₂S, mixing of fluids and oxidation were found to be important for gold precipitation, whereas decreasing temperature and increasing pH due to loss of gases (H₂S, H₂, CO₂) from ore fluids

are probably important for the precipitation of base metals (Cu, Pb, Zn, Mn) (Shikazono 1974a, 1986, Hattori 1975). Further work is needed on the mechanisms of precipitation of these ore metals. No studies on the mechanisms of precipitation of the other metals (Tl, Se, Te, As, Sb, Sn, W, Mo, Bi, Ga, In) have been carried out.

INTERPRETATION ACCORDING TO THE HSAB PRINCIPLE

Ahrland *et al.* (1958) classified a number of Lewis acids as of (a) or (b) type based on the relative affinities for various ions of the ligand atoms. The sequence of stability of complexes is different for classes (a) and (b). With acceptor metal ions of class (a), the affinities of the halide ions lie in the sequence F⁻ > Cl⁻ > Br⁻ > I⁻, whereas with class (b), the sequence is F⁻ < Cl⁻ < Br⁻ < I⁻. Pearson (1963, 1968a,b) classified acids and bases as hard [class (a)], soft [class (b)] and borderline. Class (a) acids prefer to link with hard bases, whereas the class (b) acids prefer soft bases. Yamada & Tanaka (1975) proposed a softness parameter of metal ions, on the basis of the parameters En (electron donor constant) and H (basicity constant) given by Edwards (1954). The softness parameter σ is given by $\alpha/(\alpha + \beta)$, where α and β are constants characteristic of metal ions. They indicated that the softness parameter may reasonably be considered as a quantitative measure of the softness of metal ions and is consistent with the HSAB principle by Pearson (1963, 1968a,b). Wood *et al.* (1987) have shown experimentally that

TABLE 4A. CLASSIFICATION OF METALS AND LIGANDS ACCORDING TO THE HSAB PRINCIPLE

Hard acids:	Mn ²⁺ , Ga ³⁺ , In ³⁺ , Co ²⁺ , Fe ³⁺ , As ³⁺ Sn ⁴⁺ , MoO ³⁺ , WO ⁴⁺ , CO ₂
Soft acids:	Cu ⁺ , Ag ⁺ , Au ⁺ , Tl ⁺ , Hg ⁺ , Cd ²⁺ , Hg ²⁺ , Te ⁴⁺ Tl ³⁺
Borderline acids:	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Pb ²⁺ , Sn ²⁺ , Sb ³⁺ , Bi ³⁺ , SO ₂
Hard bases:	OH ⁻ , Cl ⁻ , CO ₂ , SO ₂
Soft Bases:	H ₂ S, HS ⁻ , S ²⁻

TABLE 4B. SOFTNESS PARAMETER OF THE VARIOUS METAL IONS

Metal ions	Softness parameter	Metal ions	Softness parameter
Ag ⁺	1.03	Cu ²⁺	0.89
Hg ⁺	1.01	Bi ³⁺	0.87
Tl ⁺	0.98	Pb ²⁺	0.85
Cu ⁺	0.96	Fe ²⁺	0.84
Cd ²⁺	0.96	Mn ²⁺	0.82
Ni ²⁺	0.84	Fe ³⁺	0.78
In ³⁺	0.93	Sn ²⁺	0.73
Co ²⁺	0.92	Ga ³⁺	0.58
Zn ²⁺	0.91		

the relative solubilities of the metals in H₂O–NaCl–CO₂ solutions from 200° to 350°C are consistent with the HSAB principle; in chloride-poor solutions, the soft ions Au⁺ and Ag⁺ prefer to combine with the soft bisulfide ligand; the borderline ions Fe²⁺, Zn²⁺, Pb²⁺, Sb³⁺ and Bi³⁺ prefer water, hydroxyl, carbonate or bicarbonate ligands, and the extremely hard Mo⁶⁺ bonds only to the hard anions OH⁻ and O²⁻. Table 4 shows the classification of metals and ligands according to the HSAB principle of Ahrlund *et al.* (1958), Pearson (1963, 1968a,b) (Table 4a) and softness parameter of Yamada & Tanaka (1975) (Table 4b). Comparison of Table 4 with Table 1 makes it evident that the metals associated with the gold–silver deposits have a relatively soft character, whereas those associated with the base-metal deposits have a relatively hard (or borderline) character. For example, metals that tend to form hard acids (Mn²⁺, Ga³⁺, In³⁺, Fe³⁺, Sn⁴⁺, MoO³⁺, WO⁴⁺, CO₂) and borderline acids (Fe²⁺, Zn²⁺, Pb²⁺, Sn²⁺) are enriched in the base-metal deposits, whereas metals that tend to form soft acids (Ag⁺, Au⁺, Tl⁺, Hg⁺, Te⁴⁺, Tl³⁺) are enriched in the gold–silver deposits. Metals that have high values of the softness parameter (Ag⁺, Hg⁺, Tl⁺, Cd²⁺) are associated with the gold–silver deposits, whereas those that have low values of the softness parameter (Zn²⁺, In³⁺, Bi³⁺, Pb²⁺, Te⁴⁺, Mn²⁺, Sn²⁺, Ga³⁺) are found with the base-metal deposits. These correlations mean that the HSAB principle could be a useful approach to evaluate the geochemical behavior of metals and ligands in ore fluids responsible for the formation of the vein-type deposits examined here. Among the ligands in the ore fluids, HS⁻ and H₂S are the most likely to form complexes with the metals concentrated in the gold–silver deposits (*e.g.*, Au, Ag, Cu, Hg, Tl, Cd), whereas Cl⁻ prefers to form

complexes with the metals concentrated in the base-metal deposits (*e.g.*, Pb, Zn, Mn, Fe, Cu, and Sn) (Crerar *et al.* 1985).

Generally, the complexes with intermediate or hard ligands (*e.g.*, chloro complexes) should become more stable with increasing temperature than complexes with soft ligands (*e.g.*, bisulfide complexes) (Seward 1981, Crerar *et al.* 1985). The higher temperatures of formation of the base-metal deposits (Table 2) also are in accordance with the HSAB principle. It was shown in Table 3 that the two types of deposit studied here formed at different temperatures and concentrations of Cl⁻, HS⁻, and CO₂. Thus, it could further be inferred that the HSAB principle can be successfully applied to the genesis of these vein-type ore deposits, formed mostly at less than ca. 250°C. Crerar *et al.* (1985) noted that Pearson's rule (the HSAB principle) successfully describes speciation to about 250°C, but may break down at higher temperatures, as all metals become harder.

A few applications of the HSAB principle to hydrothermal ore deposits have been carried out (Crerar *et al.* 1985, Wood 1987). These studies demonstrate that the HSAB principle is useful in interpretations of the metal ratios in ore deposits. The results of these previous studies are roughly in agreement with those of the present study, although the types of deposit studied here are different from those studied by previous investigators. For example, Wood (1987) has shown that gold is transported by lower salinity fluids than the base metals, and this difference in salinity is a significant factor in the separation of gold and base metals in Archean deposits in greenstone belts. Cathles (1986) also has indicated that the solubility of gold is much greater in low-salinity solutions; this can explain the bimodal populations of base-metal-rich, gold-poor deposits (stratiform deposits similar to Kuroko deposits in Japan) and base-metal-poor, gold-rich deposits in greenstone belts (lode gold deposits). Such differences in the salinity of ore fluids responsible for the epithermal gold deposits and Kuroko and base-metal vein-type deposits in Japan have been pointed out also by Shikazono (1988). Therefore, it could be inferred that the difference in salinity is a main cause for a separation of gold and base metals in mineralized zones in young (Tertiary to Quaternary) Japanese vein-type and Kuroko-type deposits in volcanic terranes and in Archean deposits in greenstone terranes. However, the concentration of CO₂ in ore fluids responsible for Japanese gold–silver deposits and Archean lode gold deposits in greenstone belt seems to be different; CO₂ concentration is low (0.01–0.1 molal) for Japanese deposits (Shikazono 1985a), whereas it is high (0.05 – 2 molal) for Archean deposits (Wood 1987). The reason of this

difference is not known. To answer this question, further work on the nature of fluid inclusions and the influence of postdepositional processes on the chemistry of fluid inclusions will be necessary.

SUMMARY

The associated metals and geochemical features of the Japanese vein-type deposits related to volcanic activity indicate the following:

1. Ore deposits can be divided into two types, gold-silver and base metal, according to the major ore-metals produced.
2. The gold-silver deposits are characterized by the association Au, Ag, Se, Te, Cu, Sb, As, Hg and Cd, whereas the base-metal deposits contain the association Pb, Zn, Mn, Cu, Sb, As, Sn, W, Mo, Bi, In and Ga.
3. Ore fluids responsible for the gold-silver deposits are characterized by a neutral pH, low Cl^- , high HS^- , and low CO_2 concentrations and high $f(\text{S}_2)$ and $f(\text{O}_2)$, whereas ore fluids for the base metal deposits have a low pH, high Cl^- , low HS^- and high CO_2 concentrations, and low $f(\text{S}_2)$ and $f(\text{O}_2)$.

The above-mentioned differences in the associated metals and chemical features of ore fluids are in good accord with the HSAB principle, according to which relatively soft metals and ligands are enriched in the gold-silver deposits, whereas relatively hard metals and ligands are enriched in the base-metal deposits. Most of the deposits formed at less than 250°C. At these conditions of temperature, the differences in metals enriched in the deposits studied are consistent with the HSAB principle (Crerar *et al.* 1985). A similar relationship between salinity and type of deposits (gold-rich *versus* base-metal-rich) can be found for Japanese vein-type deposits studied here and also for Archean deposits in greenstone belt (Cathles 1986, Wood 1987).

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