

## Mineralizations of Base Metal Deposits of Acid-Sulfate Type Coexisting with Adularia-Sericite Type

Hideki IMAI\*

**Abstract:** Two types of ores are recognized in the Huanzala mine, Peru. Zinc and lead ore of adularia-sericite type, is accompanied by pyrite body and skarn. Orthoclase (adularia), sericite and calcite are found in the skarn and altered country rocks. On the other hand, copper and silver (tin) ore of acid-sulfate type, is characterized by enargite, luzonite and bornite, accompanied by tin, silver and tellurium minerals. Although sericite and calcite are found only at the earlier stage in the mineralization of acid-sulfate type, kaolinite appears in the country rocks at a subsequent stage. It is interpreted that the ore-forming fluid of the acid-sulfate type separated from the adularia-sericite type by boiling in the early stage of mineralization. The separated fluid was nearly neutral just after boiling and changed into acidic by the oxidation of  $H_2S$  into  $HSO_4^-$ . Both types of mineralizations are studied in terms of  $f_{O_2}$ - $f_{S_2}$ -pH-temperature diagrams. The adularia-sericite type might correspond to the hot-water system of a geothermal area, and the acid-sulfate type to the vapor-dominated system.

The copper ores from the Teine mine, Hokkaido, Japan and the Chinkuashih mine, Taiwan are acid-sulfate type, characterized by the occurrence of enargite and luzonite. However, zinc and lead ores of the adularia-sericite type are also present in these deposits. Both types in the Teine and Chinkuashih deposits are supposed to have formed in the similar relation as in the Huanzala deposits. The enargite and luzonite ores in the Hokuetsu mine, Japan are closely associated with native sulfur of solfataric origin.

### 1. Introduction

In the Huanzala deposits, Peru, zinc and lead deposits coexist with copper and silver deposits (Imai et al., 1985; Imai, 1986). According to Hayba et al. (1985) and Heald et al. (1987), the zinc and lead ore in the deposits corresponds to adularia-sericite type, while copper ore corresponds to the acid-sulfate type. Although Hayba et al. (1985) and Heald et al. (1987) proposed the acid-sulfate and adularia-sericite types applied only to epithermal deposits, here I apply these terms to xenothermal, mesothermal, pyrometamorphic and porphyry copper deposits in addition to epithermal deposits.

Studies by Imai et al. (1988, 1996) of the relation between geothermal systems of volcanic regions in Japan and volcanic-hosted precious- and base-metal deposits containing enargite and luzonite, suggested a different interpretation from given by Imai et al. (1985) and Imai (1986). In the present paper, I revise some parts of my previous papers, and propose that the acid-sulfate type is separated from the adularia-sericite type by boiling in the course of mineralization. Further discussion on the rele-

vant problems in the other deposits will be given.

### 2. Genesis of the Huanzala Deposits, Peru

#### 2.1. Geological setting of the Huanzala deposits

According to the previous works (Imai et al., 1985; Imai, 1986; Soler et al., 1986), geological setting of the Huanzala deposits are summarized as follows. The mine is situated in central Peru, about 250 km north of Lima. This region is underlain by Lower Cretaceous sedimentary rocks correlated with the Goyllarisquizma Group. In the mining area, the Cretaceous sedimentary rocks are, from lower to upper, chert (Chim Formation), limestone (Santa Formation) and an alternating unit of sandstone and slate (Carhuaz Formation). The Huanzala deposits occur in the Santa limestone (Fig. 1). Sheet dikes of Miocene or Pliocene age are intruded in this area. The ore bodies are composed of (A) pyrite, zinc and lead ores including sporadic skarn minerals, and (B) copper and silver ores accompanied by tin-tungsten and tellurium minerals (Table 1). The (A) ore bodies are characterized by the altered country rocks containing orthoclase (adularia) and/or sericite. Widely developed pyrite ore bodies belong to the same adularia-sericite type. The (B) ore bodies are characterized by enargite (luzonite) associated with the country rock containing kaolinite. Thus, the former corresponds to adularia-sericite type, and the latter corresponds to acid-sulfate type (Hayba et al., 1985; Heald et al., 1987; Berger and Henley, 1989).

---

Received on June 10, 1999; accepted on September 20, 1999

\* 1-53, Haramachi, Shinjuku-ku, Tokyo 162-0053, Japan

Keywords: acid-sulfate type deposit, adularia-sericite type deposit, vapor-dominated geothermal system, hot-water geothermal system, enargite, luzonite, bornite, wurtzite, Huanzala mine, Teine mine, Chinkuashih mine, Hokuetsu mine.

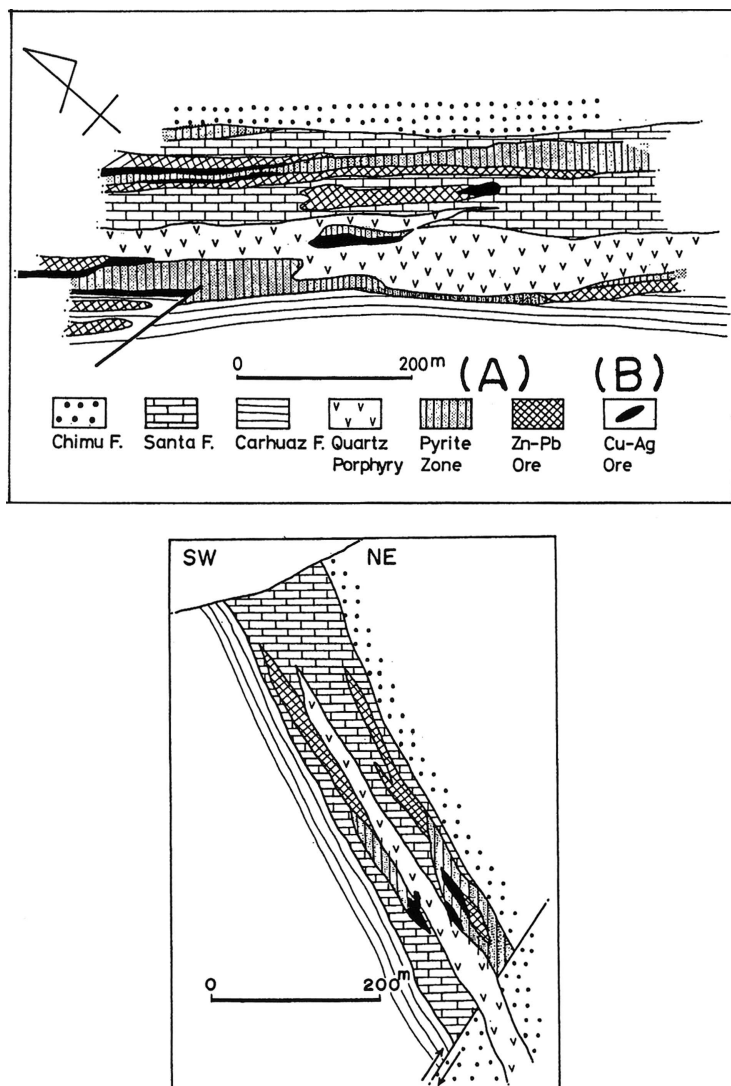


Fig. 1 Schematic geological map and section of the Huanzala mine (revised from Imai et al., 1985). (A) adularia-sericite type, (B) acid-sulfate type.

## 2. 2. Some problems on the mineralization of the Huanzala deposits

In the previous papers (Imai et al., 1985; Imai, 1986), it is interpreted that the zinc and lead mineralization of adularia-sericite type was succeeded by the copper-silver ore of acid-sulfate type in the continuous series of ore deposition. However, I have recognized that the solution for acid-sulfate type could be separated from the original ore-forming fluid in the course of mineralization by boiling, and the residual liquid solution yielded the adularia-sericite type (Imai et al., 1988, 1996). In the following pages, I try to apply this model of separation of two solutions by boiling to the Huanzala and other deposits. For this speculation, I referred some papers by Krauskopf (1957, 1964, 1965), Heinrich and Eadington

(1986), and Spycher and Reed (1989).

Table 1 shows the paragenesis observed in the Huanzala deposits, as revised from the previous paper (Imai et al., 1985). The mineralization of adularia-sericite type ((A) in Table 1) commenced by the formation of pyrite and pyrrhotite (hexagonal), perhaps below 500°C (490°C) (Imai et al., 1985), followed by skarnization and iron-rich sphalerite, accompanied by orthoclase (adularia), albite (emphasized by quadrangles in Table 1) and prehnite. Main skarn minerals and iron-rich sphalerite would be deposited at 400–330°C. The iron-rich sphalerite was succeeded by iron-poor sphalerite, which was formed by the extraction of iron from the iron-rich sphalerite by the copper-bearing solution to form chalcopyrite dots in sphalerite (Imai et al., 1985). The iron-poor sphalerite is accompanied by sericitized (phlogopitic) and carbonatized (calcite) country rocks (quadrangle in Table 1). The temperature of iron-poor sphalerite formation would be 330–250°C. Pyrite ore bodies are widely developed in the limestone. Pyrite is partly replaced by skarn minerals.

The acid-sulfate type ((B) in Table 1) is characterized by enargite and bornite. The enargite often occurs in parallel growth with luzonite (epitaxial growth) (Fig. 2) (Imai, 1943, 1978). As stated in the previous papers (Imai et al., 1985; Imai, 1986), ore fluid responsible for the acid-sulfate type could be separated from that for adularia-sericite type, probably at 400–300°C by boiling. Sericite, calcite and other carbonate minerals are only found at the initial stage of the acid-sulfate type. Instead kaolinite and halloysite appear in the country rocks at the later stage (quadrangle in Table 1). Enargite and luzonite are associated with silver, tin-tungsten and tellurium minerals such as argentite, hessite, cassiterite, scheelite, tungstenite and others (Table 1). This mineralization continued below 200°C. This type of the ore deposit might have been called xenothermal deposit (Buddington, 1935).

I speculate that the mechanism of separation could be similar to that of vapor-dominated system from hot-water system by boiling in geothermal systems (Imai et al., 1988, 1996). Namely, the zinc and lead ores correspond to the hot-water system, and copper and silver ores correspond to the vapor-dominated system in a geothermal area (White et al., 1971; Truesdell and White, 1973, Imai et al., 1988, 1996). The separated vapor of acid-sulfate type

Table 1 Paragenesis of the minerals in the Huanzala mine ( revised from Imai et al., 1985).

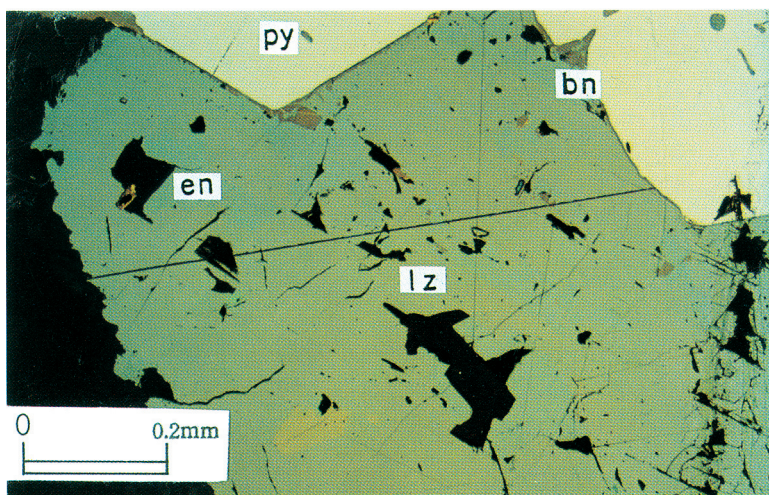
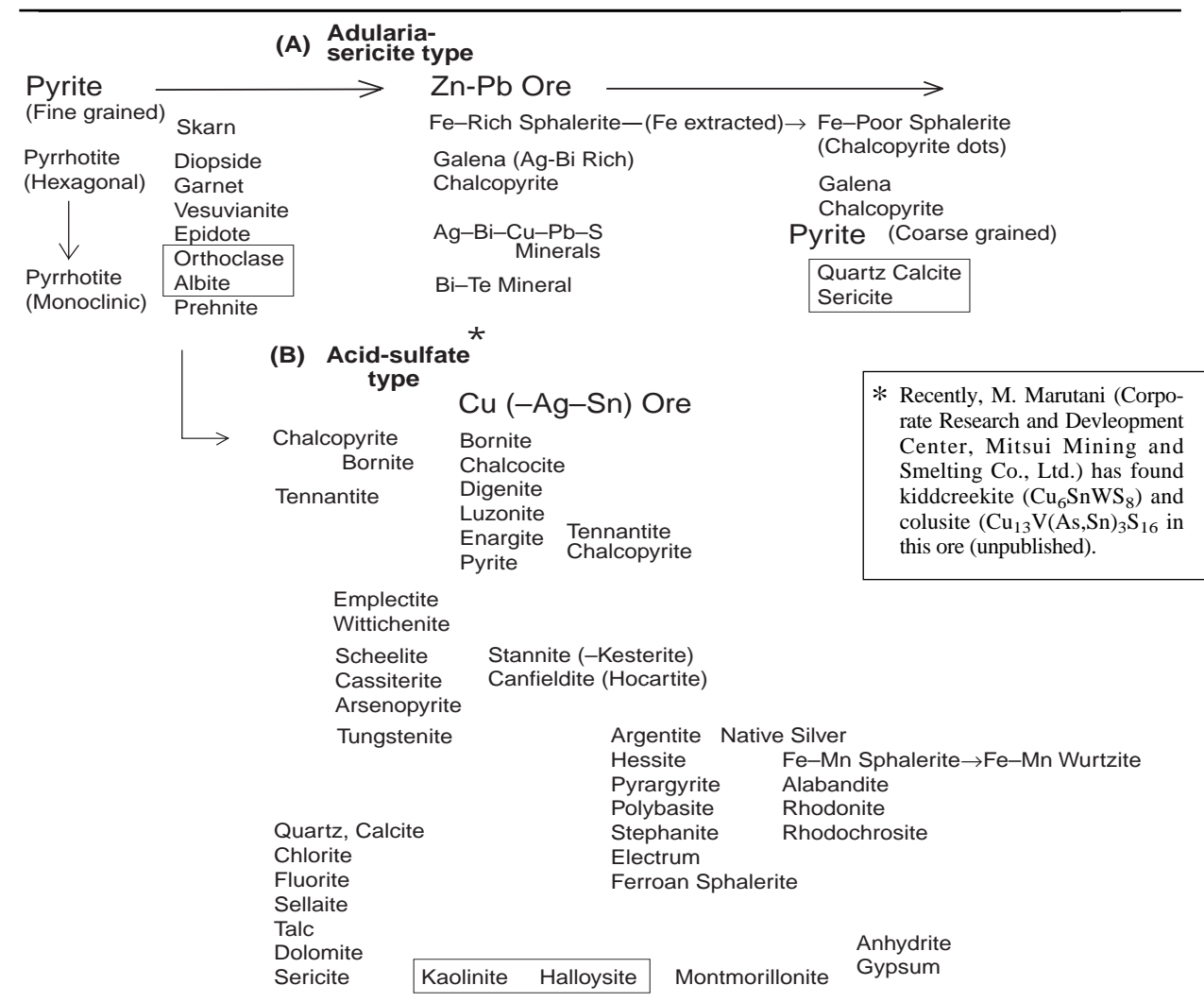
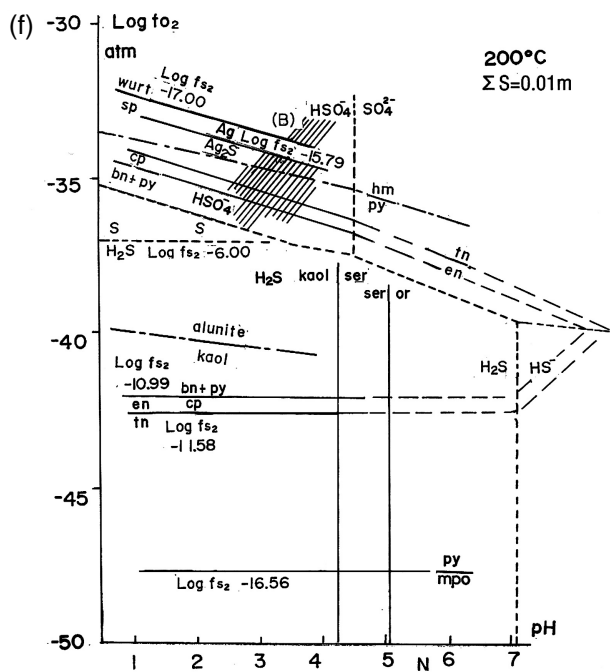
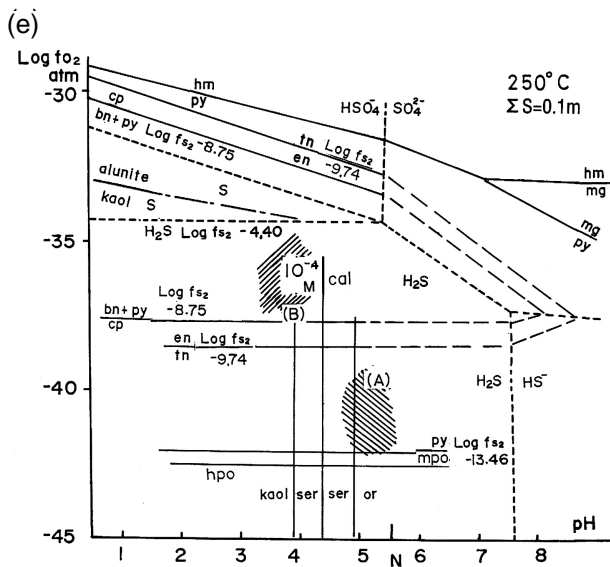
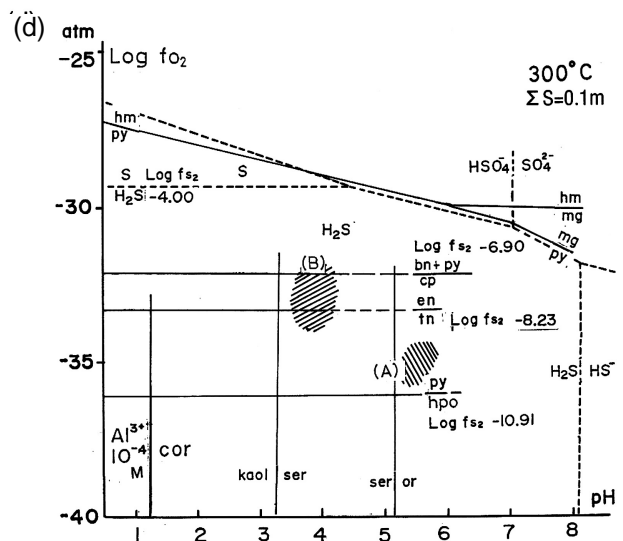
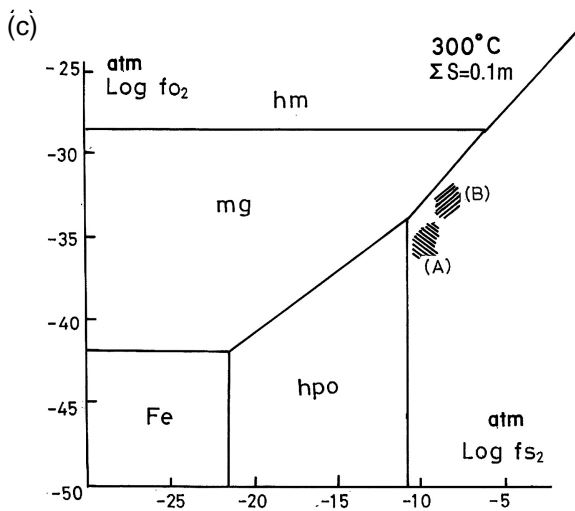
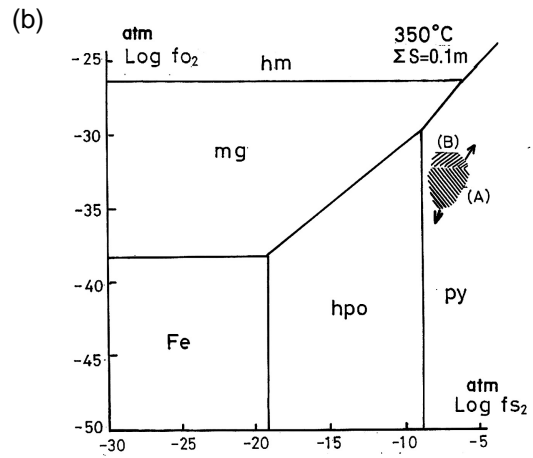
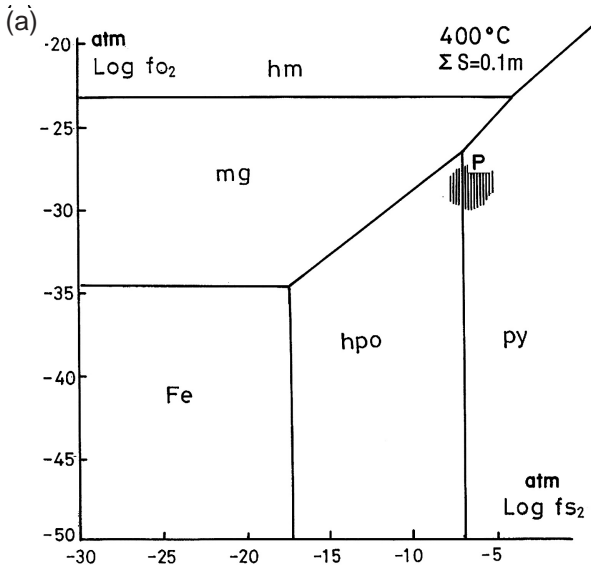


Fig. 2 Photomicrograph of polished section. Reflected light. Enargite and luzonite in epitaxy from the Huanzala deposit. grey (en), enargite; pink (lz), luzonite; py, pyrite; bn, bornite.

(B) is nearly neutral just after boiling, and yields sericitization, calcitization and other carbonatization in the country rocks. Then, it changes gradually into acidic by the oxidation of H<sub>2</sub>S into HSO<sub>4</sub><sup>-</sup>, yielding kaolinite and halloysite in the country rocks.

2. 3. Geological environments of the mineralizations of the Huanzala deposits

The changes of physicochemical conditions of mineralization processes in the two types, (A) adularia (orthoclase)-sericite type and (B) acid-sulfate type in the Huanzala deposits are estimated and depicted in Figure 3. Figures 3(a), (b) and (c) are log f<sub>o2</sub> -log f<sub>s2</sub> diagrams at 400°, 350° and 300°C, respectively, while Figures 3(d), (e) and (f) are log f<sub>o2</sub> -log f<sub>s2</sub>-



pH relations at 300°, 250° and 200°C. In the following discussions, I assume that  $\Sigma S = 0.1$  m,  $\Sigma K = 0.1$  m and  $CO_2 = 26.28$  m (datum at the Nigorikawa hot spring, Yoshida, 1991) in Figures 3(a), (b), (c), (d), (e) and  $\Sigma S = 0.01$  m,  $\Sigma K = 0.1$  m in Figure 3(f). In Figure 3(a), the original mineralization fluid (P) is placed in the range of  $\log f_{S_2} -7 - -8$  atm and  $\log f_{O_2} -28 - -29$  atm, depositing pyrite with small amount of hexagonal pyrrhotite.

In Figures 3(b) and (c), the original fluid (P) is going to separate into liquid (A) and vapor (B) by boiling. From (A) adularia (orthoclase)-sericite type ore is produced, and from (B) acid-sulphate type is produced. In this stage,  $H_2S$  content in the vapor phase (B) is higher than the liquid phase (A). Thus the  $f_{S_2}$  of the former is higher than the latter. In the adularia-sericite type (A), the  $f_{O_2}$  of the boundaries of pyrite/pyrrhotite (hexagonal or monoclinic) become lower with the temperature drop (Figs. 3(d), (e) and (f)). Hexagonal pyrrhotite in the deposits was replaced by the monoclinic pyrrhotite (Table 1) (Imai et al., 1985). According to Bezmen and Smolyarova (1976), monoclinic pyrrhotite is the low-temperature form, and exists below about 250°C with the relation shown in Figure 3(e). The decrease of  $f_{O_2}$  (in (A)) results in the decrease of  $f_{S_2}$ , as shown in Figure 3(e). Monoclinic pyrrhotite would be the latest phase of the adularia-sericite type mineralization (Table 1). This means that the mineralization continued to at least 250°C. The pH condition of this type is almost unchanged, i.e. around neutral.

In Figures 3(d) and (e), the oxidation of  $H_2S$  in volatilized fluid (B) (vapor and condensed hot-water) proceeds upwards along the fissures, gradually condensing and transforming into  $HSO_4^-$ , with a consequent drop in pH. Calcite does not exist at the lower pH beyond the solubility boundary in Figure 3(e). The alteration mineral in the country rocks changes to kaolinite from sericite (Fig. 3(e)). In the process of flowing upwards, enargite (luzonite) and bornite would be deposited between 300-200°C in the condensing environment of  $H_2S$ -bearing fluid (Figs. 3(d) and (e)). In this stage,  $f_{O_2}$  tends to

decrease (Figs. 3(d) and (e)). It would be due to the decrease of dissociation of  $H_2O$  by the temperature drop. Passing the  $H_2S-HSO_4^-$  boundary and entering into the environment of  $HSO_4^-$  at about 200°C,  $f_{S_2}$  of the condensed solution diminishes with the increase of the  $f_{O_2}$  near the surface (Fig. 3(f)). At the latest stage of the mineralization of acid-sulfate type, wurtzite is deposited (Table 1 and Fig. 3(f)). The mineralization of acid-sulfate type continued below 200°C (Imai et al., 1985).

Namely, the successive mineralization environments accompanied by temperature drop are concluded as follows. In case of adularia-sericite type (A),  $f_{O_2}$  and  $f_{S_2}$  move towards lower values during the mineralization, while pH condition is almost unchanged and neutral. In the acid-sulfate type (B), the pH of the condensing fluid becomes lower at the stages of enargite (luzonite) and bornite depositions in the  $H_2S$ -bearing environment. After the condensed solution crosses the boundary of  $H_2S-HSO_4^-$ , the  $f_{S_2}$  of the solution decreases with the increase of  $f_{O_2}$  in the  $HSO_4^-$  predominant field near the surface (Fig. 3(f)).

### 3. Teine Gold-Enargite-Luzonite Deposit in Hokkaido, Japan

The Teine mine was a gold and copper producer in a suburb of Sapporo City (Watanabe, 1936; Watanabe, 1943a, 1943b, 1944; Sugimoto, 1952; Imai, 1978). The area consists of Late Miocene andesitic tuff breccia and mudstone, extruded by the altered andesite (propylite). The veins occur mainly in altered andesite. The veins are grouped into Mitsuyama, Koganezawa and Bannozawa areas as shown in Figure 4.

The vein deposits in the Mitsuyama area belong to acid-sulfate type. The main ore minerals are enargite, luzonite and native gold, accompanied by pyrite, tetrahedrite (tennantite), chalcocopyrite, bornite, chalcocite, sylvanite, petzite, rickardite, pyrargyrite, native tellurium, bismuthinite, emplectite, klaprothite, goldfieldite (?), stib-

Fig. 3 The relation of  $f_{O_2}$ - $f_{S_2}$ -pH-temperature on the minerals from the Huanzala deposit. (A) adularia-sericite type, (B) acid-sulfate type. The hatched areas represent the environments of mineralization. The arrows show the trend of mineralization in the cases  $\Sigma S = 0.1$  m at 400, 350, 300 and 250°C and  $\Sigma S = 0.01$  m at 200°C.  $\Sigma K = 0.1$  in all cases.  $CO_2 = 26.28$  m (Nigorikawa hot spring; Yoshida, 1991). (a)  $f_{O_2}$ - $f_{S_2}$  at 400°C. (b)  $f_{O_2}$ - $f_{S_2}$  at 350°C. (c)  $f_{O_2}$ - $f_{S_2}$  at 300°C. (d)  $f_{O_2}$ - $f_{S_2}$ -pH at 300°C. (e)  $f_{O_2}$ - $f_{S_2}$ -pH at 250°C. (f)  $f_{O_2}$ - $f_{S_2}$ -pH at 200°C. Abbreviations are: hm, hematite; mg, magnetite; py, pyrite; hpo, hexagonal pyrrhotite; mpo, monoclinic pyrrhotite; cp, chalcocopyrite; bo, bornite; en, enargite; tn, tennantite (tetrahedrite); kaol, kaolinite; ser, sericite; or, orthoclase (adularia); cor, corundum; ca, calcite; sp, sphalerite; wurt, wurtzite; N, neutral point. (P) original mother fluid. Bornite+pyrite-chalcocopyrite boundary, Barton and Toulmin (1964); enargite-tennantite boundary, Craig and Barton (1973); pyrite-hexagonal pyrrhotite-magnetite-hematite-Fe boundaries and  $Ag_2S$ -Ag boundary, Helgeson (1969), Robie et al. (1978), Barton and Skinner (1979), Crerar and Barnes (1976), Muntean et al. (1990); sphalerite-wurtzite, Scott and Barnes (1972); hexagonal and monoclinic pyrrhotite boundary, Bezmen and Smolyarova (1976), Kaneda et al. (1980); sulfur compounds, Barnes and Kullerud (1961), Crerar and Barnes (1976), Muntean et al. (1990); kaolinite-sericite-orthoclase boundaries, Helgeson (1969); alunite-kaolinite boundary, Stoffregen (1987), Muntean et al. (1990); Al,  $10^{-4}$  M-diaspore boundary, Kharaka and Barnes (1973); Ca,  $10^{-4}$  M-calcite (solubility) boundary, Ichikuni (1972).

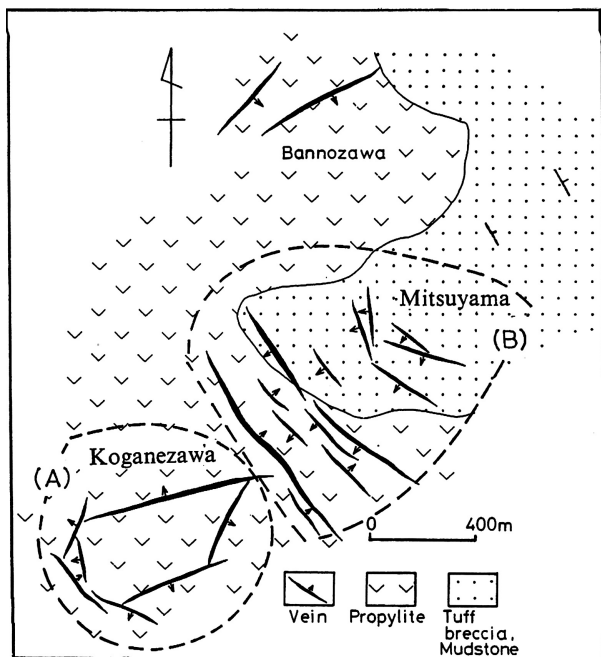


Fig. 4 Geological map of the Teine mine (revised from Imai, 1978). (A) adularia-sericite type, (B) acid-sulfate type.

nite, marcasite, teineite and others (Watanabe, 1936, 1943a, 1943b, 1944). The gangue minerals are quartz and barite. Calcite is lacking in the Mitsuyama area. The country rocks are kaolinized and silicified.

The vein group of the Koganezawa area belongs to adularia-sericite type. The ore minerals are sphalerite, galena, chalcopryrite, pyrite, native gold, stibnite, realgar and orpiment. The gangue minerals are quartz and calcite, while barite is lacking. Chloritization is recognized as the alterations of country rocks. Thus, in this mine, acid-sulfate type of deposits coexist with the adularia-sericite type, and the former is the main deposits.

#### 4. Chinkuashih Gold-Enargite and Chiufen Chalcopryrite Deposits in Taiwan

The Chinkuashih and Chiufen mines are situated in the northern end of Taiwan island (Watanabe, 1940, 1943, 1951; Yen, 1941; Huang, 1955, 1960, 1965, 1973; Folinsbee et al., 1972; Wang, 1973; Huang and Chou: 1975; Yen, 1976; Huang and Yeh, 1977; Imai, 1978; Hwang and Meyer, 1982). This area is composed of mainly Miocene sandstone and shale intruded by chonolith of dacite. The deposits occur in the dacite and the surrounding Miocene sediments (Fig. 5). The deposits of Chinkuashih belong to acid-sulfate type. The faults are mineralized as veins, along which there are some pipe-like ore bodies or irregular masses formed by replacement or impregnation. The ore minerals at Chinkuashih are

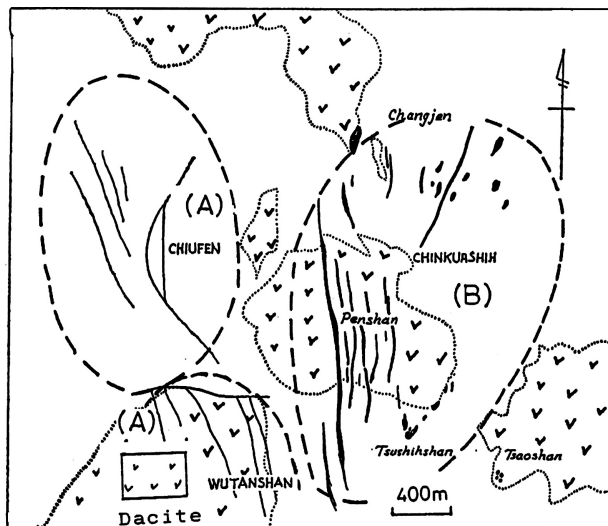


Fig. 5 Geological map of the Chinkuashih and Chiufen mines (revised from Huang and Yeh, 1977). (A) adularia-sericite type, (B) acid-sulfate type.

pyrite, enargite, luzonite, famatinite, tetrahedrite, tennantite, chalcopryrite, sphalerite and native gold with small amounts of bournonite, cinnabar, wurtzite, calaverite (Hwang and Meyer, 1982) and marcasite. The gangue minerals are quartz, barite, alunite, kaolinite, diaspore and native sulfur. The alteration halo in the Chinkuashih area is characterized by a well-developed assemblage of quartz, kaolinite and alunite in the center, successively outwards enveloped by kaolinite, sericite, montmorillonite and chlorite zones (Wang, 1973). Calcite does not exist.

Wang (1973) studied the filling temperatures of the fluid inclusions in quartz mainly from the silicified zone of the deposits. They range between 290-210°C. He concluded that the physicochemical environments of deposition might be as follows; pH 3.5-4.5; log  $f_{O_2}$  -30 - -34 atm; log  $f_{S_2}$  -6 - -8 atm, with the high activities of  $SiO_2$ ,  $K^+$  and  $SO_4^{2-}$ . Huang (1955) and Wang (1973) stated that mineralizing solution might be alkaline in the earlier stage and somewhat acidic in the later stage. Yen (1976) showed a distribution of the homogenization temperatures ranging from 300 to 160°C, and the existence of the fluid inclusions containing liquid  $CO_2$ . According to Folinsbee et al. (1972), sulfur isotopes for the sulfide minerals in the deposits yield values close to meteoritic, typical of magmatic hydrothermal, and the equilibrated sulfate species of barite is 25 ‰ heavier in  $\delta^{34}S$ . Data on barite-pyrite pair suggest the formation temperatures in the range of 305-255°C, a range compatible with fluid inclusion temperatures in barite.

The Chiufen mine is adjacent to the Chinkuashih mine to the west. The deposits of this mine belong to adularia-sericite type. The ore minerals are chalcopryrite, native gold, sphalerite, galena, stibnite and realgar. Calcite is

abundant, whereas barite is in very small amount. Alunite does not exist (Watanabe, 1940; Yen, 1941; Hwang and Meyer, 1982). Thus, in this mining area, acid-sulfate type of deposits coexist with adularia-sericite type.

### 5. Some Problems Related to Acid-Sulfate Deposits

As discussed above, some of the acid-sulfate type deposits are accompanied by adularia-sericite type deposits; alike, Butte, Montana (Sales, 1948; Meyer et al., 1967), Cerro de Pasco, Peru (Graton and Bowditch, 1936; Cerro de Pasco Corporation, 1970; Einaudi, 1977); Tintic, Utah (Lovering, 1949), Lake City, Colorado (Slack, 1980). The acid-sulfate type at Mankayan, Philippines is associated with the porphyry copper deposit which might be regarded as adularia-sericite type (Gonzalez, 1956; Imai, 1978; Hedenquist et al., 1998). The deposits similar to Mankayan are distributed in the Andean Cordillera of Chile (Sillitoe, 1991).

Likewise, some of the deposits of adularia-sericite type are associated with small amounts of acid-sulfate type deposit, such as in Yauricocha and Cobriza in Peru (Cerro de Pasco Corporation, 1970). In Kuroko deposits in Japan, small amounts of enargite-luzonite and diaspore-alunite-pyrophyllite-kaolinite assemblages are associated with the main Cu-Zn-Pb ore bodies belonging to adularia-sericite type (Matsukuma and Horikoshi, 1970; Utada, 1981).

In Hokuetsu mine, Niigata prefecture, Japan (Watanabe, 1943, 1951; Imai, 1978), the ore is composed of quartz, enargite, luzonite, sphalerite and galena, accompanied by native sulfur. The deposits are situated in the dissected walls of caldera of the Quaternary volcano Mt. Sumon. Watanabe (1943, 1951) stated that the deposits are of solfataric origin. The country rocks underwent silicification and kaolinization. The environment of the mineral association is shown in Figure 6 assuming  $\Sigma S = 0.1$  m and  $\Sigma K = 0.1$  m.

Native sulfur occurs in the silicified zone of Akeshi mine of gold- and enargite-bearing acid-sulfate type deposit (Hedenquist et al., 1994; Imai et al., 1996).

The sulfur deposits in Japan are distributed in the Quaternary volcanic areas. They are due to the steam (mixture of hot-water and vapor), containing  $H_2O$ ,  $CO_2$  and  $H_2S$ . The steam corresponds to vapor-dominated system separated from hot-water system by boiling. The separated fluid ascends along vents or fissures, gradually condenses into hot-water and is oxidized to form  $HSO_4^-$  and/or  $S$ . The sulfur is deposited in the stability field of sulfur as shown in Figure 6, replacing or impregnating andesite or tuff. In the same area, solfataras are distributed, discharging the same kind of vapor or steam, i.e. it is a vapor-dominated system.

The volcanic sulfur deposits in Japan are generally surrounded by kaolinite, alunite, montmorillonite and

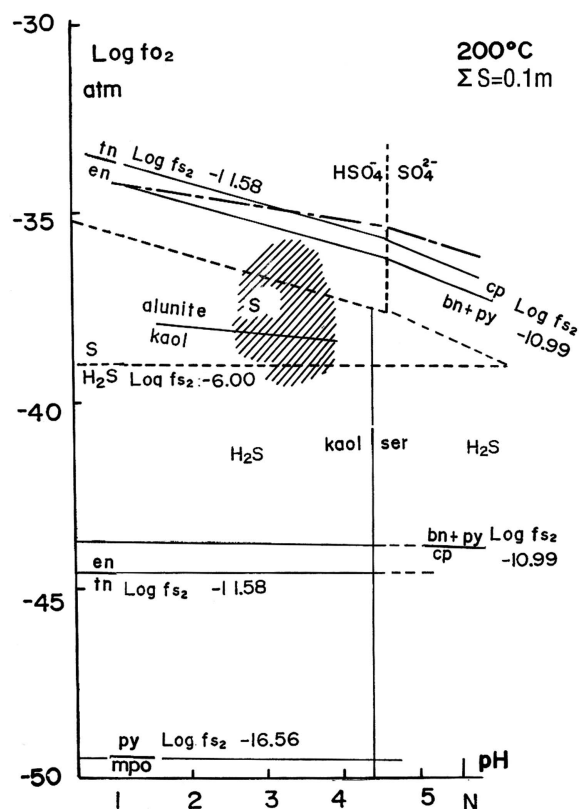


Fig. 6 The relationship of  $fO_2$ - $fS_2$ -pH on the minerals (enargite, luzonite, pyrite (marcasite), native sulfur and kaolinite). The hatched area represents the environment of the mineralization at the Hokuetsu deposit. The abbreviations are after Figure 3.  $\Sigma S = 0.1$  m and  $\Sigma K = 0.1$  m.

opal, and sporadically contain sulfide minerals, such as pyrite, marcasite; rarely chalcocite, covellite, cinnabar, bismuthinite, antimony-bearing bismuthinite (horobetsuite  $(Bi,Sb)_2S_3$ ) (Hayase, 1955) and livingstonite  $(HgSb_4S_8)$  (Japan Mining Industry Association, 1968). In Quaternary volcanic districts in Japan, especially in caldera areas (e.g., in Onikobe and Hakone), many hot springs of NaCl-bearing and nearly neutral hot water circulate along the fissures (Ozawa and Nagashima, 1975; Oki, 1983), corresponding to the hot-water systems in geothermal areas. They are associated with vapor-dominated systems represented by fumaroles (Imai et al., 1996).

In some solfataras,  $SO_2$  gas is predominant, and often accompanied by HCl gas (Iwasaki et al., 1966). The genetical problem on the relation of  $H_2S$  and  $SO_2$  gases in solfataras is unknown.

### 6. Summary

This paper gives the revised discussion to our previous papers on mineralization and paragenesis of the Huanzala deposits, central Peru. The deposits are composed zinc and lead ores of adularia-sericite type, and copper and sil-

ver (tin) ores of acid-sulfate type. Here it is proposed that the fluid of the acid-sulfate type is separated from that of the adularia-sericite type by boiling in the course of mineralization at about 400–300°C. As the fluid of the acid-sulfate type flows upwards, H<sub>2</sub>S in the fluid is gradually oxidized to transform into HSO<sub>4</sub><sup>-</sup>, and consequently the fluid becomes acidic. It is speculated that the similar phenomena would occur in the ore deposits in which acid-sulfate type coexists with adularia-sericite type, such as in the Teine and Chinkuashih deposits.

**Acknowledgments:** I wish to thank Dr. Masami Ichikuni and Dr. Hitoshi Sakai who gave me suggestions from geochemical standpoints; Professor Yuan Wang, National Taiwan University who kindly sent me some unpublished papers on Chinkuashih and Chiufen mines; Dr. Edwin Reodder, Harvard University, who gave me many advices; Professor Hiroaki Kaneda who helped me to get literatures; Mr. Masashi Kawasaki and Mr. Atsushi Gomi who sent me the ore samples from the Huanzala mine; Mr. Wakaba Sakurai, Mr. Mitsuo Yamaguchi, Mr. Hirobumi Furuta who admitted me to use the Corporate Research and Development Center of Mitsui Mining and Smelting Co., Ltd. and helped my laboratory works. I am grateful to all of them.

## References

- 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.
- Barton, P. B. and Toulmin, P. (1964) Experimental determination of the reaction chalcopyrite + sulfur = pyrite + bornite from 350°C to 500°C. *Econ. Geol.*, 59, 747–752.
- Barton, P. B. and Skinner, B. (1979) Sulfide mineral stabilities. *in* *Geochemistry of Hydrothermal Ore Deposits*. 2nd edn., (Barnes, H. L., ed.), 278–403, John Wiley and Sons.
- Berger, B. R. and Henley, R. W. (1989) Advances in the understanding of epithermal gold-silver deposits, with special reference to the western United States. *Econ. Geol. Monograph*, 6, 405–423.
- Bezmen, N. I. and Smolyarova, T. A. (1976) Ental'piia ovrazovaniia monokludnogo pirrotina i ego ustoichivost' v sisteme FeS. *Geologiya Rudnykh Mestorozhdenii*, 9, 115–120 (in Russian).
- Buddington, A. F. (1935) High-temperature mineral associations at shallow to moderate depth. *Econ. Geol.*, 30, 205–222.
- Cerro de Pasco Corporation (1970) *Geologia de los yacimientos minerales*. Congr. Latinoamer. Geol., 115 p.
- Craig, J. R. and Barton, P. B. (1973) Thermochemical approximation of sulfosalts. *Econ. Geol.*, 68, 493–506.
- Crerar, D. A. and Barnes, H. L. (1976) Ore solution chemistry, V. Solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solutions at 200°C to 350°C. *Econ. Geol.*, 71, 772–794.
- Einaudi, M. (1977) Environment of ore deposition at Cerro de Pasco, Peru. *Econ. Geol.*, 72, 893–924.
- Folinsbee, R. E., Kirkland, K., Nekolaichuk, A. and Smejkal, V. (1972) A gold-pyrite-enargite-barite hydrothermal deposit in Taiwan. *Geol. Soc. Amer. Mem.*, 135, 323–335.
- Gonzalez, A. (1956) Geology of the Lepanto copper mine, Mankayan, Mountain Province. *in* *Copper Deposits in Philippines, Part 1*, (Kinkel, A., Santos-Ynigo, L. M., Samaiego, S. and Cripsin, O., eds.), 17–50, Philippine Bureau of Mines.
- Graton, L. C. and Bowditch, S. I. (1936) Alkaline and acid solution in hypogene zoning at Cerro de Pasco. *Econ. Geol.*, 31, 651–698.
- Hayba, D. O., Bethke, P. M., Heald, P. and Foley, N. K. (1985) Geologic, mineralogic and geochemical characteristics of volcanic-hosted epithermal, precious-metal deposits. *in* *Geology and Geochemistry of Epithermal Systems* (Berger, B. R. and Bethke, P. M., eds.), Rev. Econ. Geol., 2, 129–167.
- Hayase, K. (1955) Minerals bismuthinite-stibnite series, with special reference to horobetsuite from Horobetsu mine, Hokkaido, Japan. *Mineral. Jour.*, 1, 189–197.
- Heald, P., Foley, N. K. and Hayba, D. O. (1987) Comparative anatomy of volcanic-hosted epithermal deposits; acid-sulfate and adularia-sericite types. *Econ. Geol.*, 82, 129–167.
- Hedenquist, J. W., Matsuhisa, Y., Izawa, E., White, N. C., Giggenbach, W. F. and Aoki, M. (1994) Geology, geochemistry and origin of high sulfidation Cu-Au mineralization in the Nansatsu district, Japan. *Econ. Geol.*, 89, 1–30.
- Hedenquist, J. W., Arribas, A. and Reynold, T. J. (1998) Evolution of an intrusion-centered hydrothermal system; Far Southeast Lepanto porphyry and epithermal Cu-Au deposits, Philippines. *Econ. Geol.*, 93, 373–404.
- Heinrich, C. A. and Eadington, P. J. (1986) Thermodynamic predictions of hydrothermal chemistry of arsenic and their significance for the paragenetic sequence of some cassiterite-arsenopyrite-base metal sulfide deposits. *Econ. Geol.*, 81, 511–529.
- Helgeson, H. C. (1969) Thermodynamics of hydrothermal system at elevated temperatures and pressures. *Amer. Jour. Sci.*, 267, 729–804.
- Huang, C. K. (1955) Gold-copper deposit of the Chinkuashih mine, with special reference to the mineralogy. *Acta Geol. Taiwanica*, no. 7, 1–20.
- Huang, C. K. (1960) Gold deposits of the Wutanshan area and their relation to the Chinkuashih deposit. *Acta Geol. Taiwanica*, no. 8, 13–25.
- Huang, C. K. (1965) Further notes on the mineralogy of the Chinkuashih gold-copper deposits, Taiwan. *Acta Geol. Taiwanica*, no. 11, 31–42.
- Huang, C. K. (1973) Minor gangue minerals of the Chinkuashih gold-copper deposits, Taiwan. *Acta Geol. Taiwanica*, no. 16, 31–38.
- Huang, C. K. and Chou, S. A. (1975) Paragenesis of enargite and luzonite-famatinitite in the Chinkuashih gold-copper deposits, Taiwan. *Acta Geol. Taiwanica*, no. 18, 26–35.
- Huang, C. K. and Yeh, K. (1977) Special features of the ore deposits of the Changjen series, Chinkuashih mine, Taiwan. *Acta Geol. Taiwanica*, no. 19, 1–12.
- Hwang, J. Y. and Meyer, H. E. O. (1982) The mineral chemistry and genesis of the Chinkuashih deposits, Chinkuashih mine, Taiwan. *Acta Geol. Taiwanica*, no. 19, 1–12.
- Ichikuni, M. (1972) *Inorganic Geochemistry*. Baifukan, Tokyo,



- 148 p. (in Japanese).
- Imai, H. (1943) The copper ores from the Mankayan mine, Luzon, Philippine Islands, with special reference to enargite and luzonite problems. *Jour. Geol. Soc. Japan*, 50, 253–261 (in Japanese).
- Imai, H. (1978) Problem of enargite, luzonite and famatinite. *in Geological Studies of Mineral Deposits in Japan and East Asia* (Imai, H., ed), Univ. of Tokyo Press, 143–161.
- Imai, H. (1986) Mineralization and paragenesis of the Huanzala mine, Peru, A reply. *Econ. Geol.*, 81, 196–199.
- Imai, H., Adachi, M., Takahashi, M., Yamaguchi, M. and Yashiro, K. (1988) Sulfide mineralization in Oku-Aizu geothermal field, with genetical relation to epithermal gold deposits. *Mining Geol.*, 38, 291–301 (in Japanese with English abstr.).
- Imai, H., Kawasaki, M., Yamaguchi, M. and Takahashi, M. (1985) Mineralization and paragenesis of the Huanzala mine, central Peru. *Econ. Geol.*, 80, 461–478.
- Imai, H., Takahashi, M. and Yamaguchi, M. (1996) Relation between volcanic-hosted precious- and base-metal deposits and geothermal systems. *Resource Geol.*, 46, 73–94.
- Iwasaki, I., Ozawa, T., Yoshida, M., Katsura, T., Iwasaki, B. and Kamada, M. (1966) Differentiation of magmatic emanation. *Bull. Tokyo Inst. Technol.*, no. 74, 57 p.
- Japan Mining Industry Association (1968) Ore Deposits in Japan. 869–903 (in Japanese).
- Kaneda, H., Shoji, T. and Takenouchi, S. (1980) Sulfide mineralization of the Shinyama ore deposit Kamaishi mine, Iwate Prefecture. *Mining Geol.*, 30, 169–182 (in Japanese with English abstr.).
- Kharaka, Y. K. and Barnes, I. (1973) SOLMNEO, solution-mineral equilibrium computation. *U. S. Geol. Surv. Computer Contr.*, 82 p.
- Krauskopf, K. B. (1957) The heavy metal content of magmatic vapor at 600°C. *Econ. Geol.*, 52, 786–807.
- Krauskopf, K. B. (1964) The possible role of volatile metal compounds in ore genesis. *Econ. Geol.*, 59, 22–45.
- Krauskopf, K. B. (1965) The use of thermochemical data in defining conditions of high-temperature ore formation. *Symp. Problems of Postmagmatic Ore Deposition*, 2, 332–355, Prague.
- Lovering, T. S. (1949) Rock alteration as a guide to ore, east Tintic district. *Econ. Geol. Monograph*, 1, 64 p.
- Matsukuma, T. and Horikoshi, E. (1970) Kuroko deposits in Japan, A review. *in Volcanism and Ore Genesis* (Tatsumi, T., ed.), 153–179, Univ. of Tokyo Press.
- Meyer, C., Shea, E. P. and Goddard, C. C. (1968) Ore deposits at Butte, Montana. *in Ore Deposits of the United States, 1933–1967* (Ridge, J. D., ed.) A.I.M.E., 1373–1416.
- Muntean, J. L., Kesler, S. E., Russel, N. and Polanko, J. (1990) Evolution of the Monte Negro acid-sulfate Au-Ag deposit, Pueblo Viejo, Dominican Republic, important factors in grade development. *Econ. Geol.*, 85, 1738–1416.
- Oki, Y. (1983) Geology and hydrothermal system of Hakone volcano and Tanzawa mountains. *Bull. Hot Spring Research Inst.*, 15, Spec. Issue, Kanagawa, 68 p.
- Ozawa, T. and Nagashima, S. (1975) Geochemical studies of geothermal activity on Onikobe Basin. *Jour. Japan. Geotherm. Energy Assoc.* 12, 35–38 (in Japanese with English abstr.).
- Robie, R. A., Hemingway, R. S. and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298 K and 1 bar pressure and at high temperatures. *U. S. Geol. Surv., Bull.* 1452, 456 p.
- Sales, R. H. (1948) Wall rock alteration at Butte, Montana. *Trans. A.I.M.E.*, 178, 9–35.
- Scott, S. D. and Barnes, H. L. (1972) Sphalerite-wurtzite equilibria and stoichiometry. *Geochim. Cosmochim. Acta*, 36, 1275–1295.
- Sillitoe, R. H. (1991) Gold metallogeny of Chile- An introduction. *Econ. Geol.*, 86, 1187–1205.
- Slack, J. F. (1980) Multistage vein ores of the Lake City district, western San Juan Mountains, Colorado. *Econ. Geol.*, 75, 963–991.
- Soler, P., Carrascal, R. and Saez, T. (1986) Mineralization and paragenesis of the Huanzala mine, central Peru—A discussion. *Econ. Geol.*, 81, 195–196.
- Spycher, N. F. and Reed, H. (1989) Evolution of a Broadlands-type epithermal ore fluid along alternative P-T paths. Implications for the transport and deposition of base, precious, and volatile metals. *Econ. Geol.*, 84, 328–359.
- Stoffregen, R. (1987) Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado. *Econ. Geol.*, 82, 1575–1591.
- Sugimoto, R. (1952) On the geology of the Teine mine, with some remarks on the mineral composition and paragenesis of the Mitsuyama and Koganezawa ore deposits. *Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, 36, 72–84 (in Japanese).
- Truesdell, A. H. and White, D. E. (1973) Production of superheated steam from vapor-dominated geothermal reservoirs. *Geothermics*, 2, 154–173.
- Utada, M. (1980) Hydrothermal alterations related to igneous activities in Cretaceous and Neogene formations of Japan. *Mining Geol. Spec. Issue*, no 8, 67–83.
- Wang, Y. (1973) Wall rock alteration of Late Cenozoic mineral deposits in Taiwan. *Mineralogical and physicochemical aspects. Acta Geol. Taiwanica*, no. 16, 1–30.
- Watanabe, M. (1940) Some observations in Chiufen and Chinkuashih deposits, Taiwan. *Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, 23, 263–284; 24, 83–90 (in Japanese).
- Watanabe, M. (1943) Modes of occurrence of luzonite at the Hokuetsu and Kinkaseki mines. *Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, 30, 52–73 (in Japanese).
- Watanabe, M. (1951) Luzonite from Japan and Formosa. *Sci. Rept. Tohoku Univ. Ser. III*, 4, 33–44.
- Watanabe, T. (1936) Study of the reflection microscope of the gold-silver-telluride minerals from the Teine mine. *Jour. Geol. Soc. Japan*, 43, 787–799 (in Japanese).
- Watanabe, T. (1943a) Mode of occurrence of minerals of the enargite group from the Teine mine. *Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, 30, 80–90 (in Japanese).
- Watanabe, T. (1943b) Teine mine. *Guide Book of the Excursion at 50th Ann. Meet., Geol. Soc. Japan*. 15 p. (in Japanese).
- Watanabe, T. (1944) Mineral paragenesis at the Teine mine. *Jour. Geol. Soc. Japan*, 51, 27–28, (in Japanese).
- White, D. E., Muffler, L. J. P. and Truesdell, A. H. (1971) Vapor-dominated hydrothermal system compared with

hot-water systems. *Econ. Geol.*, 66, 75–97.

Yen, C. C. (1976) Trapping temperature and pressure of the fluid inclusions in the gangue minerals of gold-silver-copper deposits at Chinkuashih mine, Taiwan. *Geol. Soc. China, Proc.*, no 19, 127–133.

Yen, T. P. (1941) Geology and ore deposit in the Chiufen

mine. Private publication, 37 p. (in Japanese).

Yoshida, Y. (1991) Geochemistry of the Nigorikawa geothermal system, southwest Hokkaido, Japan. *Geochem. Jour.*, 25, 203–222.

(Editorial handling : Hidehiko SHIMAZAKI)