

## Oxygen and Sulfur Isotopic Compositions of Quartz, Anhydrite and Sulfide Minerals from the El Teniente and Rio Blanco Porphyry Copper Deposits, Chile

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**Abstract:** Oxygen and sulfur isotopic compositions are reported for quartz, anhydrite and sulfide minerals from the El Teniente and Rio Blanco porphyry copper deposits where primary (hypogene) mineralization-alteration is well preserved. The primary mineralization-alteration at the El Teniente deposit is divided into 4 stages; stage I of typical potassic alteration (K-feldspar and biotite) developed around a dacite porphyry intrusion, stages II and III of phyllic alteration characterized by quartz-anhydrite veins with quartz-sericite halo, and stage IV of the latest mineralization in the adjacent breccia pipe. The alteration at the Rio Blanco deposit is zoned as K-zone (potassic alteration), K-propylitic transitional zone and quartz-sericite zone (phyllic alteration).

At El Teniente, anhydrite has consistently lower  $\delta^{18}\text{O}$  values than quartz, and the average  $\delta^{18}\text{O}$  value of each mineral is lowest in the stage I, increasing gradually through the stages II and III with a marked increase in the stage IV. This isotopic behavior suggests that the minerals were precipitated from a common fluid in oxygen isotopic equilibrium. The anhydrite-chalcopyrite sulfur isotope geothermometer indicates that the mineralization temperature decreases from 460°C at the stage I through 420-410°C at the stages II and III down to 360°C at the stage IV. A lower temperature of 300°C is indicated for the stage IV by the chalcopyrite-galena geothermometer. With these temperatures and oxygen isotopic data of quartz and anhydrite, the  $\delta^{18}\text{O}$  value of the hydrothermal fluids is calculated to be virtually constant at 6‰ for all the stages, suggesting that magmatic fluids or fluids of meteoric origin which had extensively interacted with wall rocks might have been repeatedly incorporated during the primary mineralization-alteration processes. Participation of the similar fluids is indicated for mineralization at Rio Blanco because of the isotopic resemblance between the two deposits, although mineralization-alteration at Rio Blanco is not so clearly divided into different stages as was done at El Teniente.

Provided that anhydrite and sulfide minerals were precipitated from the fluid of a closed system containing  $\text{SO}_4$  and  $\text{H}_2\text{S}$  as main sulfur species, the  $\delta^{34}\text{S}$  values of total sulfur in the fluid are computed to be +4.5‰ and +7.6‰ for the El Teniente and Rio Blanco deposits, respectively, based on a material balance calculation using the observed  $\delta^{34}\text{S}$  values of the minerals. These values calculated above are in good harmony with the reported  $\delta^{34}\text{S}$  values of rock sulfur in non-mineralized granitoids that are associated

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with the porphyry copper deposits of the area. This may indicate that during cooling of the magmatic fluid rich in  $\text{SO}_2$ ,  $\text{SO}_4$  and  $\text{H}_2\text{S}$  are produced by the disproportionation reaction of  $\text{SO}_2$  with  $\text{H}_2\text{O}$ .

### Introduction

Copper is produced from a variety of sources such as vein type deposits, skarn deposits, massive volcanogenic sulfide deposits, stratiform sulfide deposits of sedimentary origin, and porphyry copper deposits. Among those, porphyry copper deposits are taking the largest share of the world copper production because of the world-wide distribution with relatively low metal content but a large volume of ores and low mining cost (SKINNER, 1976). Statistics show that about 40% of copper ores (including mined and reserve ores) of the well-known circum-Pacific porphyry copper province comes from Chile (TITLEY and BEANES, 1981). Of the large porphyry copper deposits in Chile, i.e., Chuquibambilla, El Salvador, El Teniente and Rio Blanco, the primary mineralization-alteration is relatively well preserved at El Teniente and Rio Blanco, whereas Chuquibambilla is characterized by development of secondary enriched zone.

The Geological Survey of Japan carried out a geological and geochemical research program on base metal mineralization in Chile as one of the Research and Development Cooperation ITIT Projects during the period of 1979 to 1983. In this program an isotope geochemical study of the El Teniente and Rio Blanco porphyry copper deposits was undertaken in order to clarify the origin of hydrothermal fluids responsible for the primary mineralization-alteration of these deposits. Oxygen isotopic compositions of alteration minerals may reflect the origin and temperatures of the hydrothermal fluids during alteration-mineralization, and sulfur isotopic compositions of ore and gangue minerals may indicate the source of sulfur in the system as well as geochemical parameters of the fluids in relation to the

precipitation of the minerals.

The primary mineralization of porphyry copper deposits is in general associated with hydrothermal alteration developed within fracture systems produced by intrusion of intermediate to acidic magmas. It is a matter of interest whether the hydrothermal fluids responsible for the primary mineralization-alteration are mainly of magmatic origin liberated from the magmas during the final consolidation, or mostly of extraneous origin such as meteoric groundwaters which could take up various materials from wall rocks during circulation through the fracture systems following a convection pattern produced by the magmatic heat source. It has been shown that the stable isotopic investigation of alteration minerals including sulfate and sulfide minerals commonly associated with the porphyry copper environs is highly useful to solve the above mentioned problems (e.g., SHEPPARD *et al.*, 1971; SHEPPARD and GUSTAFSON, 1976; FIELD and GUSTAFSON, 1976; SHELTON and RYE, 1982; EASTOE, 1983). Their studies suggest a coupling of the activity of magmatic waters in the earlier stages and the later circulation of heated meteoric groundwaters in the porphyry copper environs. In the present paper oxygen and sulfur isotopic data are reported for quartz, anhydrite, chalcopyrite, pyrite and galena separated from the drill cores and hand specimens from the El Teniente and Rio Blanco deposits. Special emphasis is placed on comparison of interpretation of the isotopic data from El Teniente and Rio Blanco with those from other deposits reported in the literatures.

### Geological Settings and Alteration Stages

#### El Teniente

Figure 1 shows a simplified geological map of central Chile (after SERNAGEOMIN, 1982).

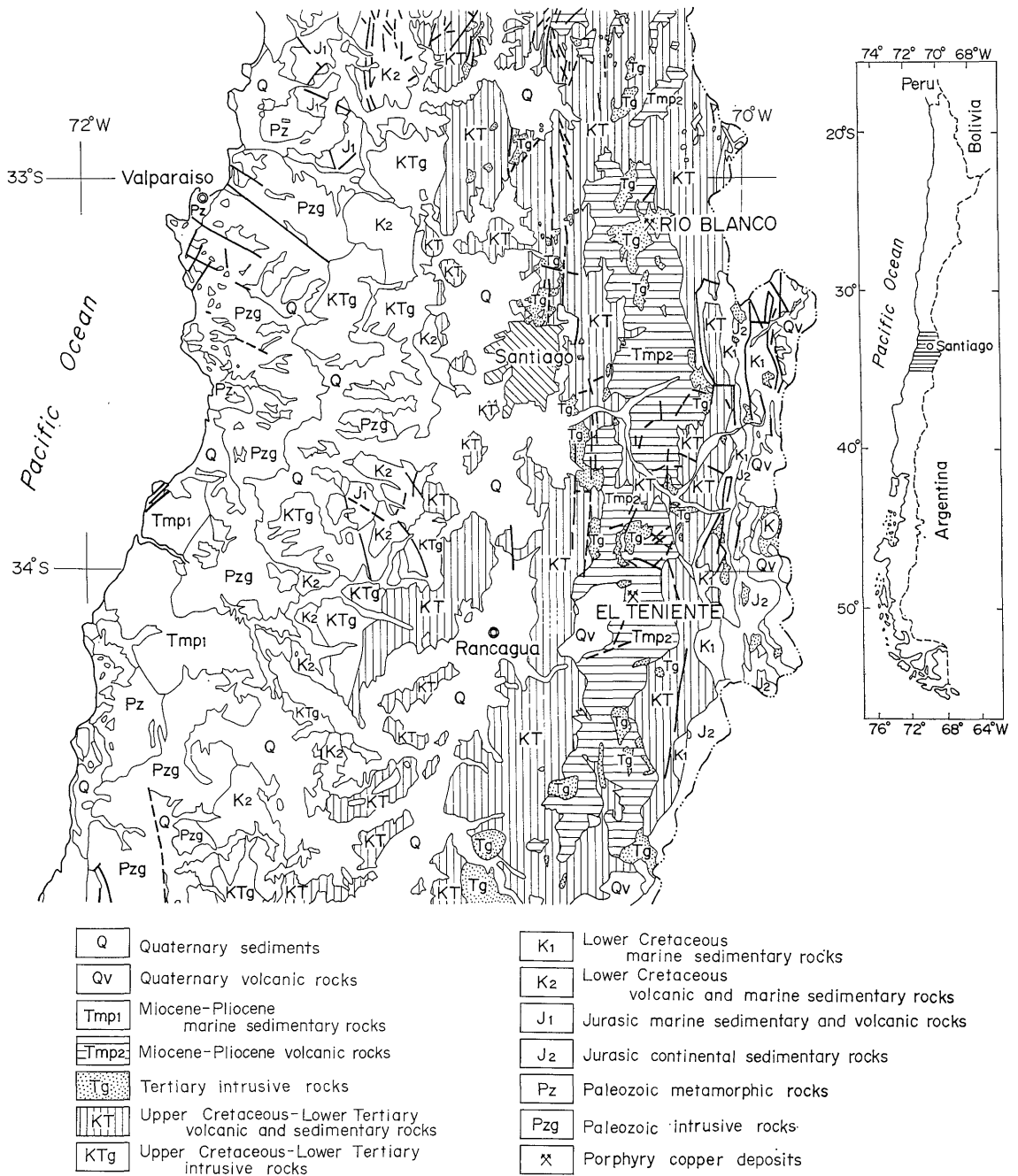


Fig. 1 Geological map of central Chile, and localities of the El Teniente and Rio Blanco porphyry copper deposits (after SERNAGEOMIN, 1982).

The El Teniente porphyry copper deposit is located in the midst of the thick Tertiary volcanic terrane of the Farellones formation (2700 m in total thickness) which extends from north to south along the western flank of the Andes (Tmp2 in Fig. 1). The Farellones formation, composed mostly of andesitic lavas and pyroclastics, is intruded by several small-size Tertiary granitoids, some of which are intimately related to formation of porphyry copper deposits. According to CAMUS (1975) who described the geology and wall-rock alteration of the El Teniente area, quartz diorite (tonalite) and dacite porphyry intruded into andesites of the lower Farellones formation which constitutes the main wall rocks of the mineralization and alteration. Figure 2A shows the geological plan at T-5 level of the mine. Dacite porphyry which caused the principal mineralization and alteration extends about 1300 m to NNW direction along the strike, becoming thinner towards the surface (300 m across at the lowest known level to 50 m across at the surface). The dacite porphyry is strongly altered and characterized by phenocrysts of quartz, K-feldspar, plagioclase of albite-oligoclase composition, and idiomorphic biotite "books" in aplitic groundmass. The Braden formation, a peculiar circular shape in Fig. 2A, is a typical breccia pipe often associated with porphyry copper environs. The pipe has a funnel-shape structure (800 m in diameter at T-5 level), consisting of tourmaline breccias with fragments of surrounding rocks, i.e., andesite, quartz diorite and dacite por-

phyry. The formation of this pipe is considered to be later than the main mineralization stage, since the fragments of breccias have been subject to similar alteration and mineralization.

According to the well-cited generalization by LOWELL and GUILBERT (1970), the alteration of porphyry copper deposits is zoned from potassic (K-feldspar and biotite) at the core, being located within and around a porphyry intrusion, outward through phyllic (quartz-sericite-pyrite), argillic (quartz-kaolinite-montmorillonite), and propylitic (epidote-calcite-chlorite). Paragenesis of sulfide minerals also changes from chalcopyrite-pyrite-molybdenite through pyrite-chalcopyrite to pyrite-galena-sphalerite in response to the above mentioned zonal alteration. Occurrence of a large amount of anhydrite gives an additional feature to the porphyry copper mineralization.

Figure 2B shows distribution of the alteration zones of the earliest stages around the dacite porphyry intrusion at El Teniente. The alteration pattern at El Teniente, however, is slightly different from the above generalization in that the alteration zones are not concentrically distributed but overlapping of alteration of different stages is recognized. For example, potassic alteration caused by early hydrothermal fluids is cut by fine veins characterizing later phyllic alteration. The primary (hypogene) alteration and mineralization at El Teniente is categorized into 4 stages based on mineral assemblages and occurrence of veins (Table 1). The stage

Table 1 Primary (hypogene) alteration and mineralization in the El Teniente porphyry copper deposit.

Stage	Alteration	Vein	Sulfides	Remarks
I Late Magmatic	K-feld, Biotite (Potassic)	Qz, Anh	Cp, Bo, Py, Mo	Potassic alteration affects 70% of the host rocks
II Principal Hydrothermal	Qz, Sericite, Chlorite	Qz, Anh	Cp, Py, Mo	Veinlets with Qz-sericite halo
III Late Hydrothermal	Qz, Sericite, Chlorite	Anh, Qz, Tour, Epid	Cp, Py, Bo, Mo	Tourmalinization related to the Braden pipe
IV Latest		Anh, Gyp, Siderite	Cp, Py, Gn, Sph, Tenn	In the Braden pipe

Abbreviations : K-feld=potassium feldspar, Qz=quartz, Tour=tourmaline, Epid=epidote, Anh=Anhydrite, Gyp=gypsum, Cp=chalcopyrite, Bo=bornite, Py=pyrite, Mo=molybdenite, Gn=galena, Sph=sphalerite, Tenn=tennantite

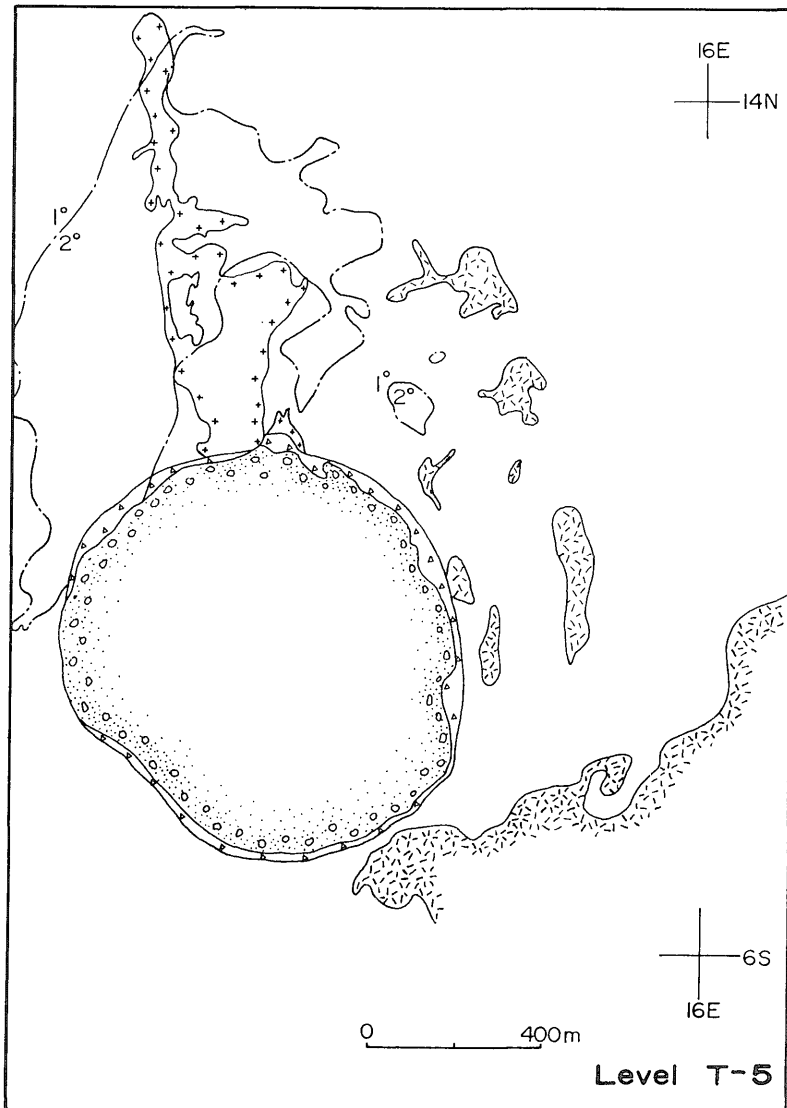


FIG. 2A

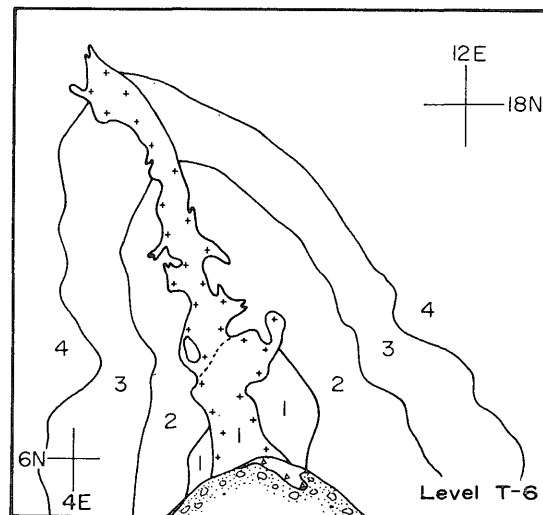


FIG. 2B

GEOLOGY

- Braden formation (pipe)
- Marginal breccia
- Dacite porphyry
- Quartz diorite
- Farellones formation (andesite)
- Secondary enrichment

LATE MAGMATIC ALTERATION DISTRIBUTION

- 1 Potassic alteration
- 2 Highly biotitized zone
- 3 Biotitized zone
- 4 Propylitic zone

Fig. 2A Geological map at the T-5 level of the E1 Teniente porphyry copper deposit.

Fig. 2B A diagram showing distribution of the stage I alteration zones developed around the dacite porphyry intrusion (T-6 level). 1: potassic alteration zone, 2: highly biotitized zone, 3: biotitized zone, and 4: propylitic zone.

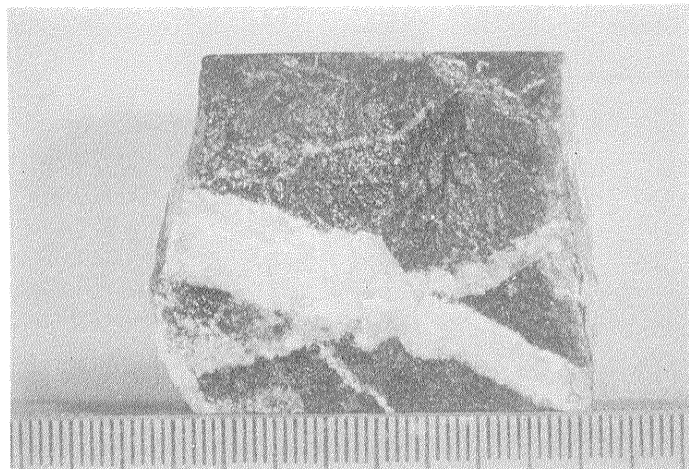


Fig. 3 Stage I quartz-anhydrite vein with a clear boundary cutting through highly biotitized andesite (Sec. 98, DDH 709, 720 ft). The smallest reading of the scale is 1 mm.

I or late magmatic stage is of typical potassic alteration with mineral assemblages of K-feldspar, biotite and chlorite in the wall rocks, quartz and anhydrite in the veins, and sulfide minerals of chalcopyrite, bornite, pyrite and molybdenite. The quartz-anhydrite veins of this stage cut the wall rocks very clearly as shown in Fig. 3. Sulfide minerals occur either in the veins or in the wall rocks in the disseminated form. The veins develop widely in the andesites, while the dissemination is dominant in the intrusives.

The stage II or principal hydrothermal stage is of phyllic alteration. Veins of this stage consisting of quartz and anhydrite have characteristically quartz-sericite halo extending into the wall rocks (Fig. 4). The stage II alteration often overlaps the stage I alteration; the stage I veins in the biotitized zone are cut by the stage II veins characterized by quartz-sericite halo. Figure 5 shows schematic distribution of the stages II and III alteration which overlaps the stage I alteration near the Braden pipe. To the north, the stage

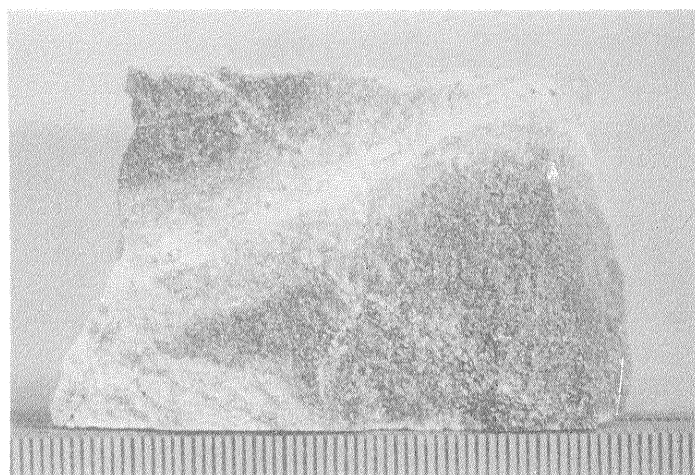


Fig. 4 Stage II quartz-anhydrite vein (4 mm wide in the middle) characterized by development of quartz-sericite halo (Sec. 87, DDH 1064, 36 ft). Dark background represents biotitized andesite. Scale is the same as in Fig. 3.

II veins are more widely distributed around the dacite porphyry intrusion, and the population of the veins of this stage decreases with depth, indicating that the hydrothermal fluids might have migrated downward following a flow pattern which enveloped the dacite porphyry intrusion. The stage III or late hydrothermal stage is also of phyllic alteration and is very similar to the stage II alteration in mineralogy except that tourma-

line and epidote are sometimes recognized in the veins. A lot of chlorite is also recognized in the sericite halos. The stage III veins consisting of anhydrite and tourmaline with minor quartz, gypsum and calcite are distributed spatially in accord with the Braden breccia pipe. These veins are likely to have formed at the time of intrusion of the Braden breccia pipe. The mineralization of this stage consists of bornite, tennantite, chalcopyrite,

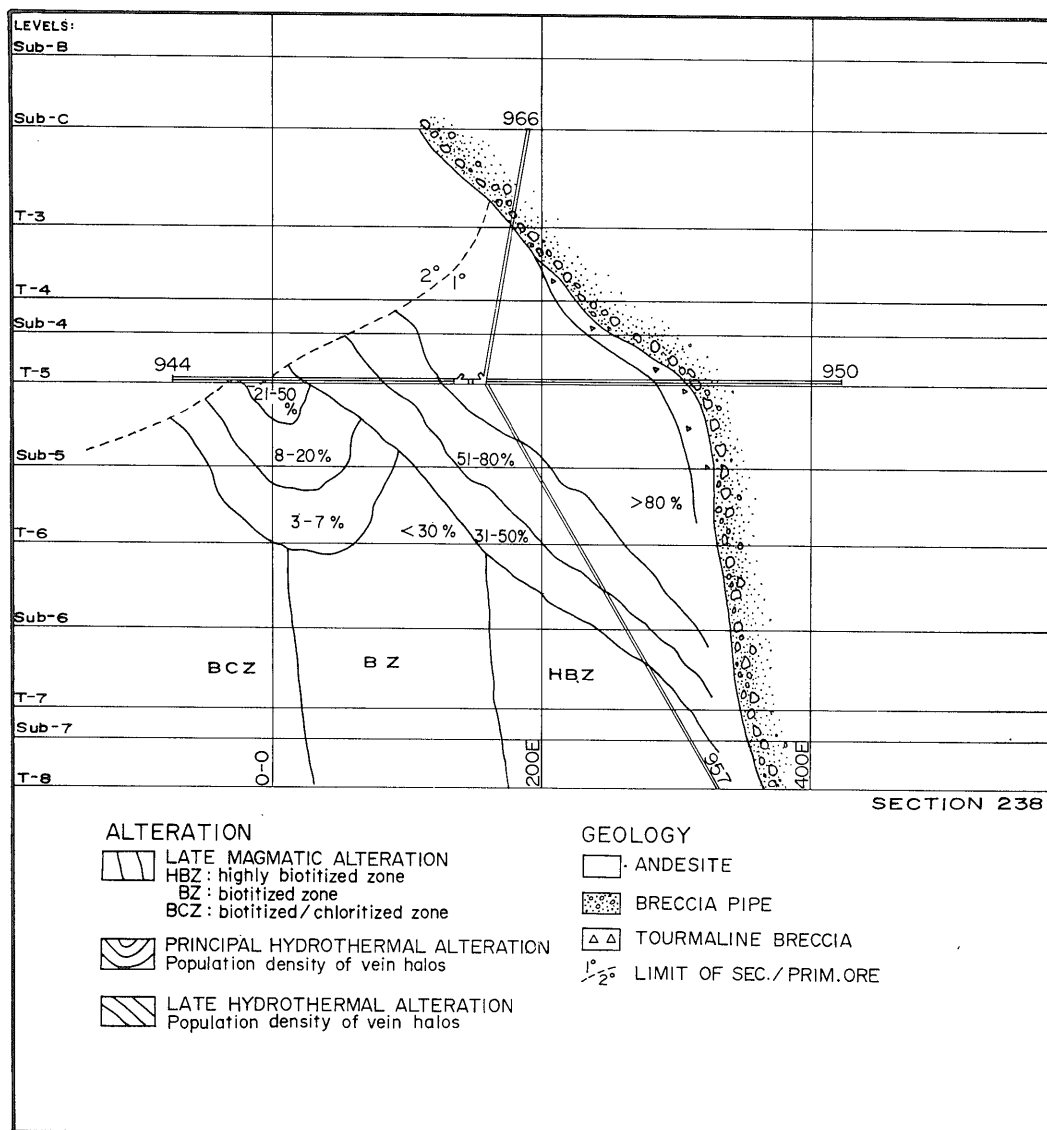


Fig. 5 A schematic diagram showing overlapping of different stages of alteration at the western edge of the Braden breccia pipe. Population density of veins is given in percentage.

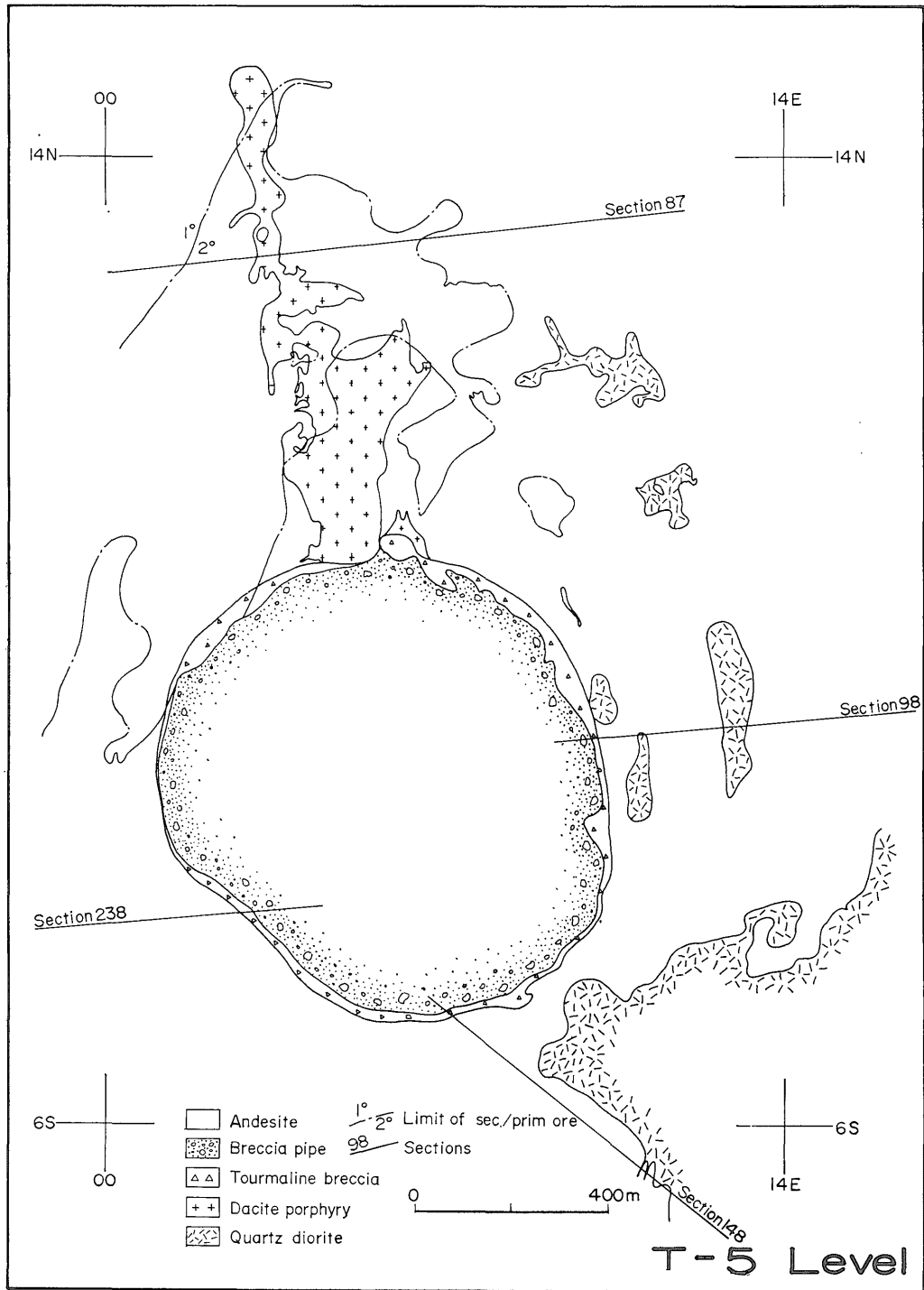


Fig. 6 Distribution of Sections 87, 98, 148 and 238 along which diamond drill hole (DDH) samples were taken, projected onto the T-5 level of the El Teniente deposit.



pyrite and molybdenite occurring as a filling of veinlets and in matrix of the breccias. Finally, the stage IV or latest hydrothermal mineralization occurs within the Braden pipe. The veins of this stage consisting of anhydrite, siderite, gypsum, galena and sphalerite fill the openings of the breccia pipe.

**Rio Blanco**

The Rio Blanco deposit is also located on the western flank of the Andes about 150 km north of El Teniente at an elevation of about 4000 m above sea level (Fig. 1). Geology of the Rio Blanco deposit is essentially similar to that of the El Teniente deposit (STAMBUK et al., 1982). At Rio Blanco, the Farellones formation of Miocene age was successively intruded by the Rio Blanco-San Francisco granodiorite (the Rio Blanco-San Francisco batholith) (7 to 14 Ma), quartz monzonite

and quartz monzodiorite porphyry complex (ca. 5 Ma), and dacite porphyry and rhyolite pipe (ca. 4 Ma) (STAMBUK et al., 1982). Among these, the intrusion of quartz monzonite porphyry complex seems to be responsible for the principal mineralization-alteration. The quartz monzonite porphyry, which is about 200 m across at the N-19 level (600 m below the surface), occurs as a small dike 1 to 2 m wide at the surface outcrop. The Rio Blanco-San Francisco granodiorite extends widely underground, and constitutes the main wall rocks of the mineralization-alteration.

During the late magmatic stage of the porphyry intrusion, an intense fracturing resulted in development of a stockwork of quartz and K-feldspar veining along with pervasive biotitization of the rocks. The alteration is zoned

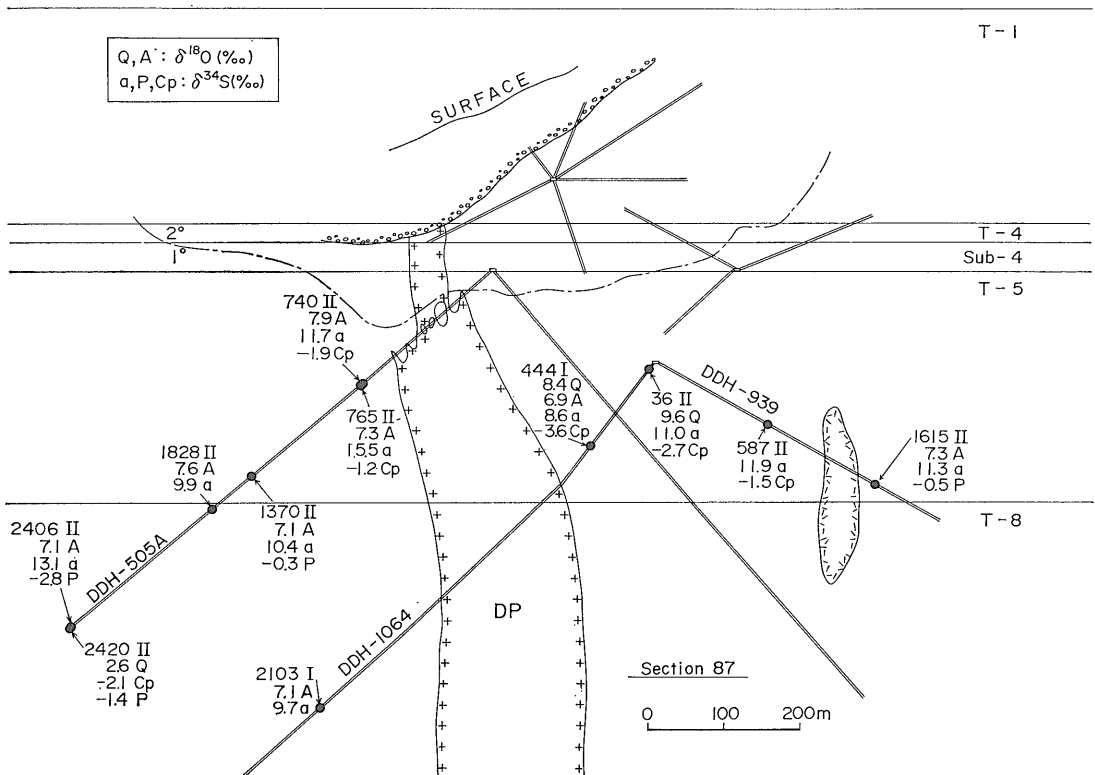


Fig. 7 Localities of DDH-505A, -939, and -1064 along the Section 87 at El Teniente. Sample localities (●) are also shown together with the alteration stages (I, II or III) and isotopic results. Q stands for  $\delta^{18}\text{O}_{\text{quartz}}$ , A for  $\delta^{18}\text{O}_{\text{anhydrite}}$ , a for  $\delta^{34}\text{S}_{\text{anhydrite}}$ , cp for  $\delta^{34}\text{S}_{\text{chalcopyrite}}$  and p for  $\delta^{34}\text{S}_{\text{pyrite}}$ .

around the quartz monzonite porphyry. That is, the potassic zone (K-zone) characterized by K-feldspar and biotite develops within and on western side of the quartz monzonite porphyry, and transitionally transfers to the propylitic zone outward as chlorite and epi-

dote prevail. The quartz-sericite zone of the succeeding hydrothermal stage overlaps in space with the above two zones, occurring as veins with quartz-sericite halo cutting the earlier alteration. Tourmaline breccia pipes develop near the surface, and transfer to

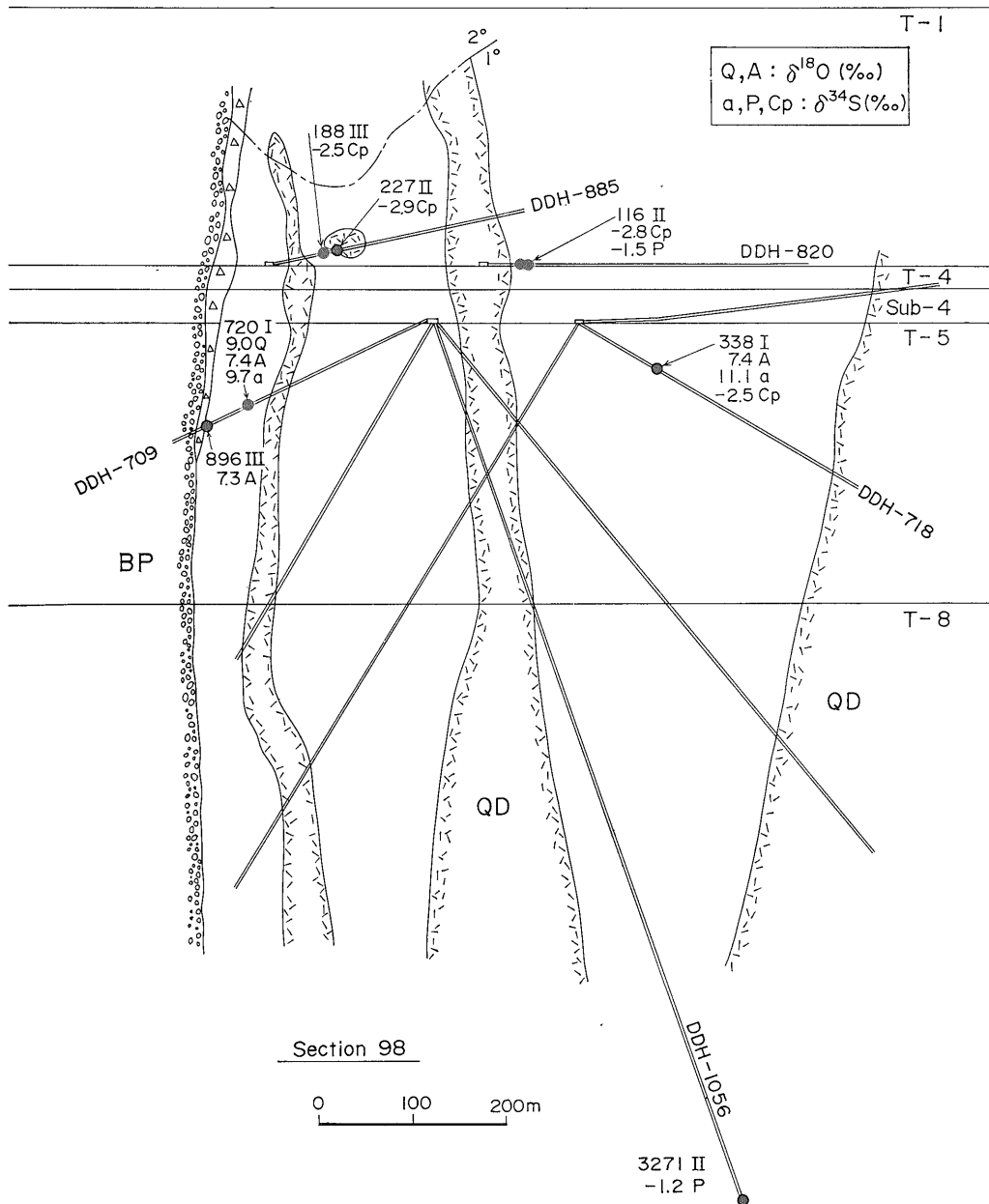


Fig. 8 Localities of DDH-709, -718, -820, -885 and -1059 along the Section 98 at El Teniente. Sample localities (●) are shown together with the alteration stages (I, II or III) and isotopic results. Abbreviations for the isotopic results are the same as in Fig. 7.

brecciated granodiorite and quartz monzonite porphyry at lower levels. The vuggy breccias and tourmaline breccias are extensively altered to quartz-sericite assemblage.

The mineralization in the potassic zone is characterized by abundant chalcopyrite. The relative amount of chalcopyrite to pyrite decreases outward toward the propylitic zone. A subsequent active erosion precluded the development of a significant supergene enrichment zone.

The dacite porphyry of the latest intrusion was strongly sericitized in a hydrothermal stage which was later than the main stages of the principal mineralization-alteration. This late hydrothermal stage was accompanied with mineralization of anhydrite, siderite, pyrite, sphalerite and galena. Relic quartz phenocryst is abundant in the dacite porphyry,

occurring as "rounded quartz eyes".

### Sample Description and Isotope Analyses

Brief description of the samples used in the present study is given in Appendices A and B. One of the purposes of the present study is to see if there was any difference in isotopic compositions of hydrothermal fluids at different alteration stages. In order to meet this requirement, the samples were mostly selected from drill cores of the diamond drill holes (DDH) which penetrated through different alteration zones. Figure 6 shows distribution of sections, projected onto the T-5 level of El Teniente, from which the DDH samples were taken. Sample localities are indicated on Figs. 7 through 10, each cor-

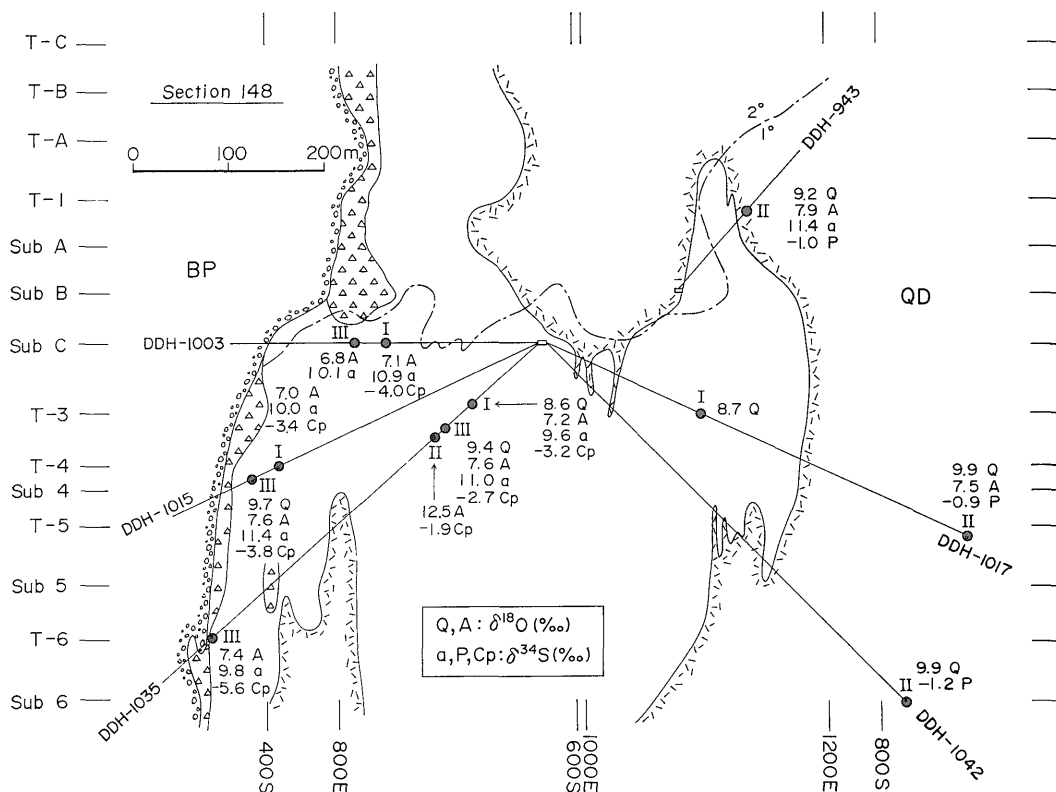


Fig. 9 Localities of DDH-1003, -1015, -1017, -1035 and -1042 along the Section 148. Sample localities (●) are shown together with the alteration stages (I, II or III) and isotopic results. Abbreviations for the isotopic results are the same as in Fig. 7.

responding to the Sections 87, 98, 148 and 238, respectively. Some hand specimens were also collected from the mine (Mine-4, 5, 6, 9 and 10) (Fig. 11). Distribution of the DDH's and sample localities of the Rio Blanco deposit are given in Fig. 12.

Sulfides are mostly dominated by chalcopyrite and lesser proportion of pyrite. Other sulfides such as molybdenite, bornite and tennantite were recognized to occur in a minor quantity. Galena and sphalerite were found only in the samples Mine-9 and -10 which represent the latest and possibly the lowest temperature hydrothermal mineralization. The sulfides occur abundantly within the quartz-anhydrite veins as small but independent crystal aggregates. At the same time, however, the sulfides also occur outside the veins in a disseminated form, finely mixed

with the wall rock silicate minerals.

Mineral separations were carried out using the standard techniques; large crystals were separated from samples by hand-picking under a binocular microscope when necessary. For fine sulfide crystals intimately mixed with silicate and/or anhydrite, a heavy liquid was used to concentrate the sulfide fraction, which was then treated with an isodynamic separator to concentrate chalcopyrite from non-magnetic pyrite. The purity of all the concentrates was examined to be better than 95% by X-ray diffractometry which had been calibrated with artificial mixtures of known composition. Anhydrite was dissolved in dilute hydrochloric acid, and the resulting  $\text{SO}_4$  was purified by an ion-exchange technique and finally converted to  $\text{BaSO}_4$ . In case of mixtures of fine grained quartz and anhydrite,

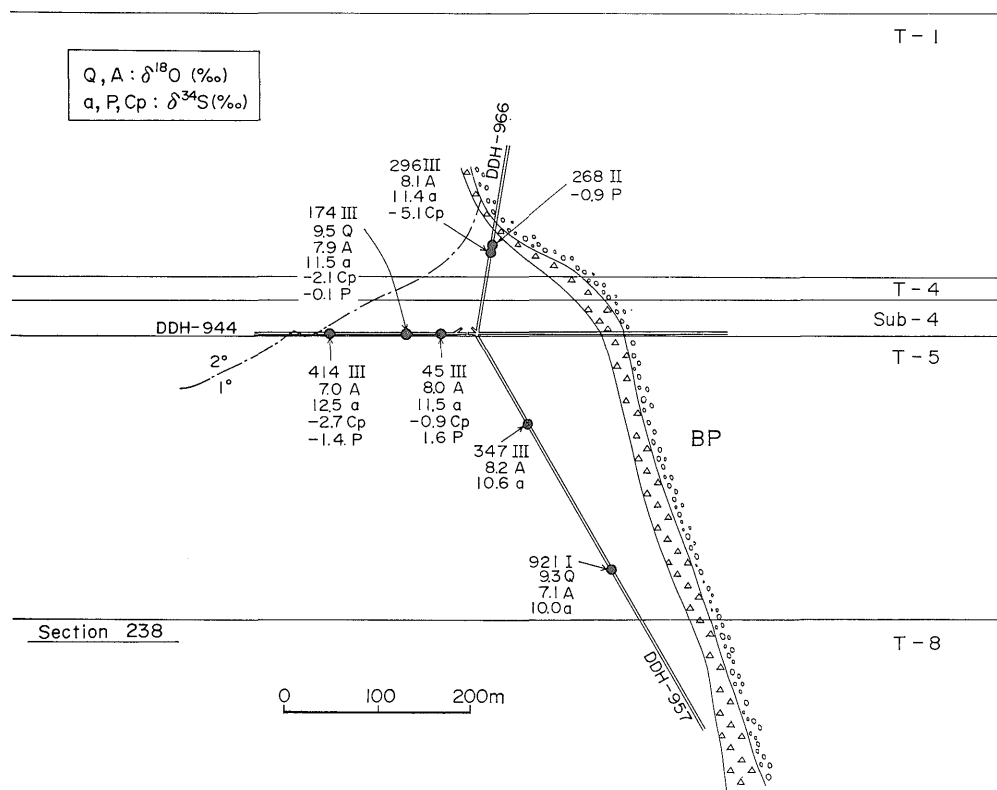


Fig. 10 Localities of DDH-944, -957 and -966 along the Section 238 at El Teniente. Sample localities (●) are shown together with the alteration stages (I, II or III) and isotopic results. Abbreviations for the isotopic results are the same as in Fig. 7.

*Oxygen and Sulfur Isotopic Compositions (Kusakabe et al.)*

the samples were treated with hot 1N hydrochloric acid to remove anhydrite. After the treatment, the purity of quartz and the removal of anhydrite were assured by X-ray diffractometry.

The oxygen and sulfur isotopic analyses were carried out using the standard methods. Quantitative extraction of oxygen from quartz was followed by the  $\text{BrF}_5$  technique (CLAYTON and MAYEDA, 1963), and that from anhydrite by the carbon reduction method (MIZUTANI, 1971). The resulting  $\text{CO}_2$  was measured mass spectrometrically for oxygen isotopic determination. Pyrite-sulfur was extracted by use of the "Kiba" solution (SASAKI *et al.*, 1979) in the form of  $\text{H}_2\text{S}$

which was eventually converted to  $\text{Ag}_2\text{S}$ . The  $\text{BaSO}_4$  converted from anhydrite was carbon-reduced (RAFTER, 1957) to  $\text{BaS}$  which was again converted to  $\text{Ag}_2\text{S}$ . The  $\text{Ag}_2\text{S}$  thus prepared was oxidized to  $\text{SO}_2$  with the  $\text{Cu}_2\text{O}$  technique (ROBINSON and KUSAKABE, 1975) for sulfur isotopic measurement. Chalcopyrite was directly burnt to  $\text{SO}_2$  with  $\text{Cu}_2\text{O}$ .

The isotopic data are given in terms of a conventional  $\delta$ -expression (in ‰ unit) which is defined as follows;

$$\delta = \left[ \frac{R_x}{R_{\text{std}}} - 1 \right] \times 1000$$

where  $R_x$  and  $R_{\text{std}}$  represent the isotopic

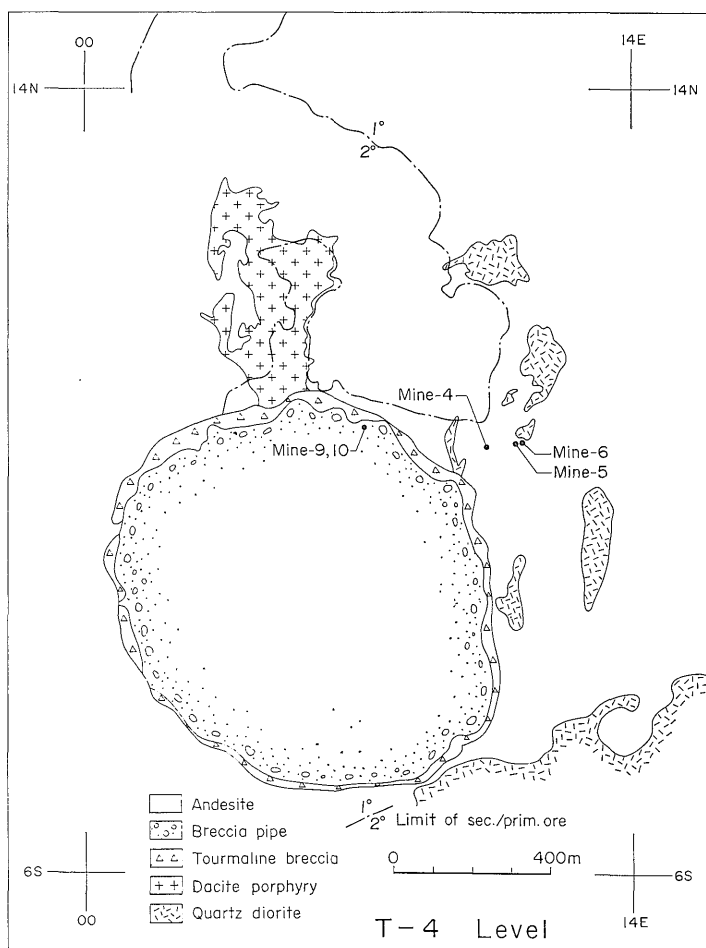


Fig. 11 Localities of the mine samples collected from the T-4 level of the El Teniente deposit.

ratios ( $^{18}\text{O}/^{16}\text{O}$  or  $^{34}\text{S}/^{32}\text{S}$ ) of the sample and standard, respectively. The  $\delta^{18}\text{O}$  values are given relative to the standard SMOW (Standard Mean Ocean Water), and the  $\delta^{34}\text{S}$  values to the standard CDT (Troilite from the Canyon Diablo meteorite). Analytical accuracy is estimated to be  $\pm 0.1\text{‰}$  for quartz,  $\pm 0.2\text{‰}$  for anhydrite oxygen and  $\pm 0.2\text{‰}$  for all the sulfur determinations.

Results

In Tables 2 and 3 are given the oxygen

and sulfur isotopic data of the samples from the El Teniente and Rio Blanco porphyry copper deposits, respectively. The El Teniente samples include 16 quartz, 31 anhydrite, 26 chalcopyrite, 14 pyrite and 2 galena samples. Among the sulfur-bearing minerals, anhydrite and chalcopyrite are found to coexist in 20 specimens, anhydrite and pyrite in 7 specimens, and anhydrite-chalcopyrite-pyrite assemblage is found in only 3 samples. The Rio Blanco samples include 4 quartz, 14 anhydrite, 17 chalcopyrite and 9 pyrite samples. Anhydrite and chalcopyrite coexist in

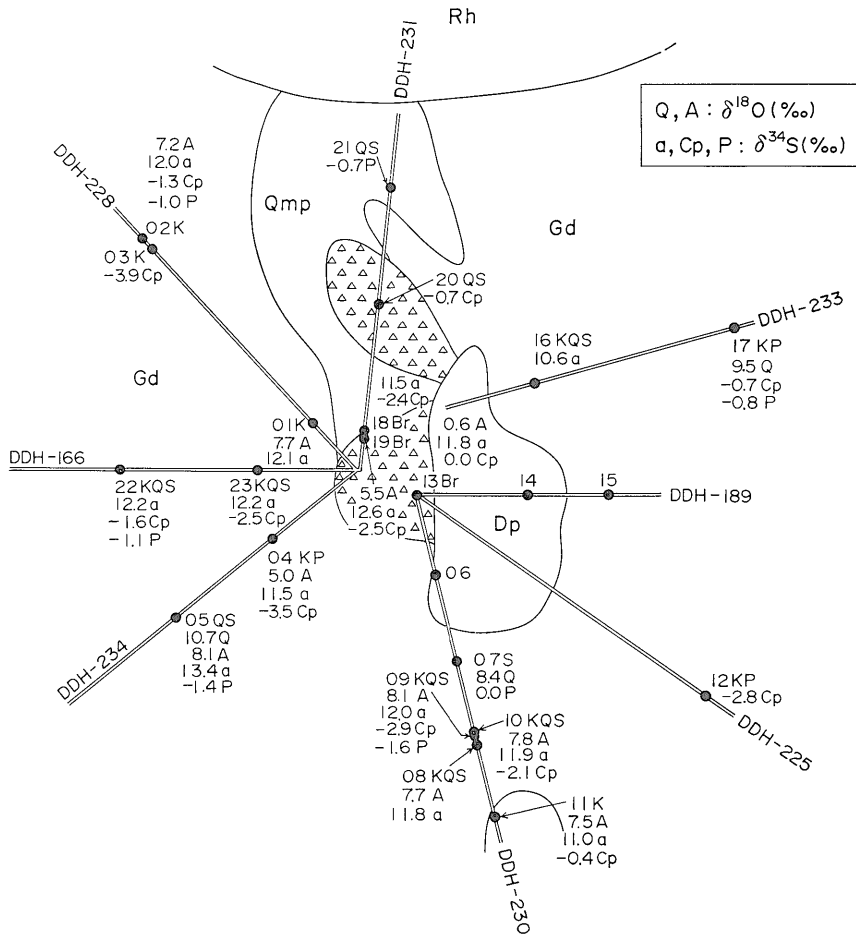


Fig. 12 Distribution of DDH-166, -189, -225, -228, -230 and -231, projected onto the N-19 level of the Rio Blanco deposit. Sample localities (●), alteration zones and isotopic results are shown. Abbreviations for the isotopic results are the same as in Fig. 7. For alteration zones, K stands for K-zone, KP for K-propylitic transitional zone, KQS for K-zone with quartz-sericite alteration, QS for quartz-sericite zone, S for sericite alteration restricted in dacite porphyry (DP). Rh : rhyolite pipe, Qmp : quartz monzonite porphyry, Gd : granodiorite, and Br : brecciated zone.

Oxygen and Sulfur Isotopic Compositions (Kusakabe et al.)

Table 2 Oxygen and sulfur isotopic analyses of minerals from the El Teniente porphyry copper deposit, Chile.

Sample Number			$\delta^{18}\text{O}$ (‰)			$\delta^{34}\text{S}$ (‰)		
Sec.	DDH	Site (ft)	Stage	Qz	Anh	Anh	Cpy	Py
87	1064	444	I	8.4	6.9	8.6	-3.6	
		2103	I	8.7	7.1	9.7		
98	709	720	I	9.0	7.4	9.7		
	718	338	I		7.4	11.1	-2.5	
148	1003	557	I		7.1	10.9	-4.0	
	1015	1006 B	I		7.0	10.0	-3.4	
	1035	366	I	8.6	7.2	9.6	-3.2	
238	957	921	I	9.3	7.1	10.0		
Mine 5			I	9.2	7.2	9.0	-1.6	
Mine 6			I		6.8	8.9	-4.0	
		<i>Average</i>		8.9	7.1	9.8	-3.2	
		<i>One sigma</i>		0.4	0.2	0.8	0.9	
87	505 A	740	II		7.9	11.7	-1.9	
		765	II		7.3	15.5	-1.2	
		1370	II		7.1	10.4		-0.3
		1828	II		7.6	9.9		
		2406	II		7.1	13.1		-2.8
		2420	II	2.6*			-2.1	-1.4
		939	587	II			11.9	-1.5
	1615	II		7.3	11.3		-0.5	
98	1064	36	II	9.6		11.0	-2.7	
	820	116	II				-2.8	-1.5
	885	227	II				-2.9	
148	1056	3271	II					-1.2
	943	351A,B	II	9.2	7.9	11.4		-1.0
	1017	1551	II	9.9	7.5			-0.9
	1035	421	II			12.5	-1.9	
	1042	1749	II	9.9				-1.2
227	1068	1717	II	9.9				-1.2
238	966	268	II					-0.9
		<i>Average</i>		9.7	7.5	11.9	-2.1	-1.2
		<i>One sigma</i>		0.3	0.3	1.6	0.5	0.6
98	709	896	III		7.3			
	885	188	III				-2.5	
148	1003	589 B	III		6.8	10.1		
	1015	1045A,B	III	9.7	7.7	11.4	-3.8	
	1035	404A,B	III	9.4	7.6	11.0	-2.7	
		1508	III		7.4	9.8	-5.6	
238	944	45	III		8.0	11.5	-0.9	1.6
		174	III	9.5	7.9	11.5	-2.1	-0.1
		414	III		7.0	12.5	-2.7	-1.4
	957	347	III		8.2	10.6		
	966	296	III		8.1	11.4	-5.1	

Table 2 (continued)

Sample Number			$\delta^{18}\text{O}$ (‰)		$\delta^{34}\text{S}$ (‰)		
Sec.	DDH	Site (ft)	Qz	Anh	Anh	Cpy	Py
Mine 4					11.5		
		<i>Average</i>	9.5	7.6	11.1	-3.2	0.0
		<i>One sigma</i>	0.2	0.5	0.8	1.6	1.5
Mine 9			13.4	10.6	11.4	-5.4	
						-5.1	
						-4.8	
						-6.5*(galena)	
						-6.9*(galena)	
Mine 10			11.6				
		<i>Average</i>	12.5	10.6	11.4	-5.1	
		<i>One sigma</i>	1.3			0.3	

\* Excluded from the average.

Table 3 Oxygen and sulfur isotopic analyses of minerals from the Rio Blanco porphyry copper deposit, Chile.

Sample Number			$\delta^{18}\text{O}$ (‰)		$\delta^{34}\text{S}$ (‰)		
No.	DDH	Site (m)	Qz	Anh	Anh	Cpy	Py
K-zone							
01	228	99.85		7.7	12.1		
02		478.05		7.2	12.0	-1.3	-1.0
03		467.16				-3.9	
11	230	502.5		7.5	11.0	-0.4	
K-propylitic transitional zone							
04	234	161.0		5.0	11.5	-3.5	
12	225	499.4				-2.8	
17	233	450.1	9.5			-0.7	-0.8
K-zone with quartz-sericite alteration							
08	230	387.0		7.7	11.8	-2.1	
09		375.1		8.1	12.0	-2.9	-1.6
10		371.9		7.8	11.9	-2.1	
16	233	129.4			10.6	-2.1	
22	166A	361.2			12.2	-1.6	-1.1
23		150.1		8.5	12.2	-2.5	
Quartz-sericite alteration zone							
05	234	353.2	10.7	8.1	13.4		-1.4
20	231	251.2				-0.7	
21		433.1					-0.7
Brecciated zone							
13	189	9.9		0.6	11.8	0.0	
18	231	59.6			11.5	-2.4	
19		54.4		5.5	12.6	-2.5	
45	—	—	9.9(Euhedral Qz)				
Sericite zone in dacite porphyry							
07	230	257.6	8.4(Qz-eye)				



Oxygen and Sulfur Isotopic Compositions (Kusakabe et al.)

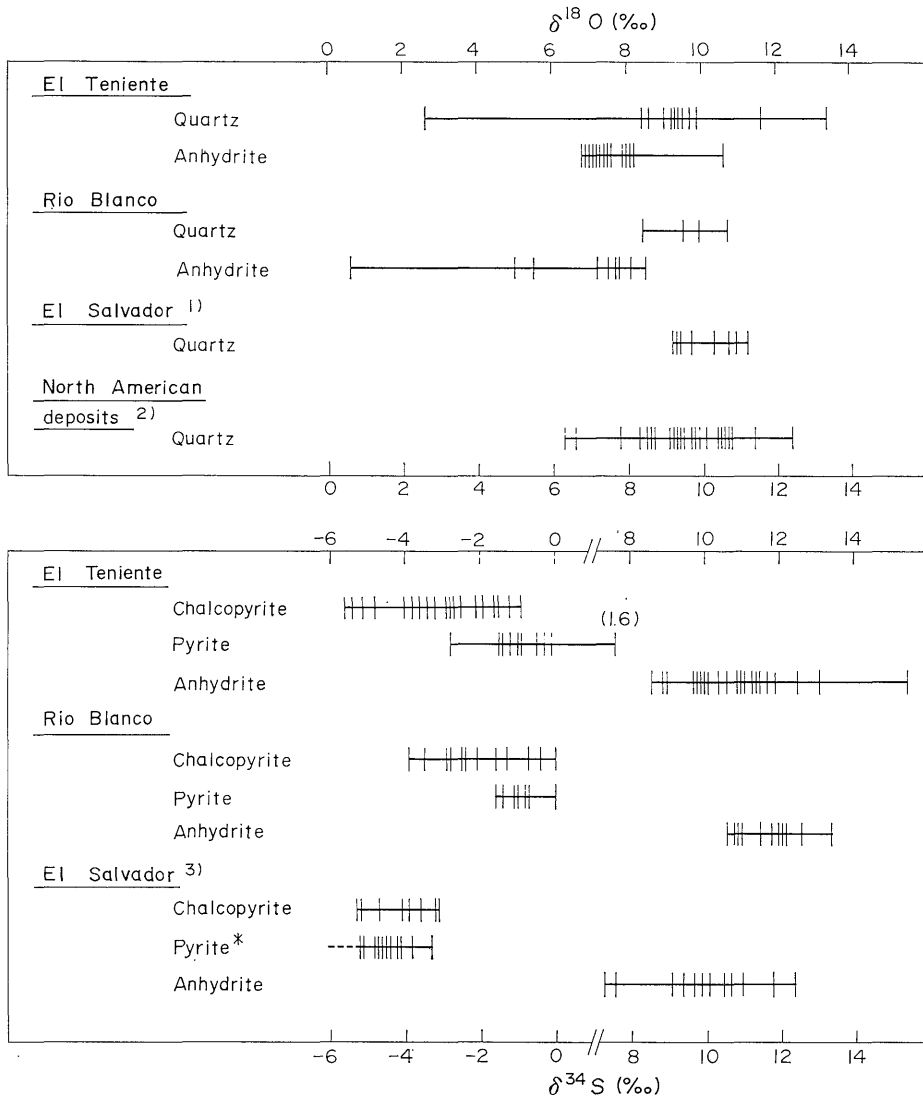


Fig. 13 Comparison of the  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values of minerals from El Teniente and Rio Blanco with those from other porphyry copper deposits. 1) SHEPPARD and GUSTAFSON (1976), 2) SHEPPARD *et al.* (1971), 3) FIELD and GUSTAFSON (1976). \*Corrected according to FIELD and GUSTAFSON (1976).

13 specimens, anhydrite and pyrite in 3 specimens, and anhydrite-chalcopyrite-pyrite in 2 specimens.

The isotopic data in Tables 2 and 3 are graphically shown in Fig. 13. On the diagram the isotopic data for the El Salvador, Chile, and North American porphyry copper deposits are given for comparison (FIELD and

GUSTAFSON, 1976; SHEPPARD and GUSTAFSON, 1976; SHEPPARD *et al.*, 1971). It is noted that (1) the  $\delta^{18}\text{O}$  values for quartz from El Teniente and Rio Blanco (+8.4 to +10.7‰ except for one low value of +2.6‰ and higher values of the stage IV quartz from El Teniente) are similar to those from El Salvador which are in the range of

plutonic quartz, (2) anhydrite from the El Teniente and Rio Blanco deposits have  $\delta^{18}\text{O}$  values (+6.8 to +8.5‰ mostly) similar to each other (with few exceptions), and they are lower than those of quartz, (3) in accordance with the general trend,  $\delta^{34}\text{S}$  values of anhydrite (+8.6 to +15.5‰) are distinctly higher than those of sulfide minerals (-5.4 to +1.6‰ except for galena), (4)  $\delta^{34}\text{S}$  values of chalcopyrite are lower than those of pyrite, although substantial overlapping is recognized, (5) a distribution pattern of sulfur isotopic data between different minerals is, roughly speaking, very similar between the three deposits. The data of  $\delta^{18}\text{O}$  values of anhydrite given in the present study are the first ones for porphyry copper anhydrites. The average and standard deviation of the  $\delta$  values of minerals in each alteration-mineralization stage at El Teniente are also listed in Table 2. The average  $\delta^{18}\text{O}$  values of quartz and anhydrite, and the average  $\delta^{34}\text{S}$  value of anhydrite are lower in the stage I than in the other stages, whereas the  $\delta^{34}\text{S}$  values of sulfides do not show such a trend but are variable through all the stages.

Although the Rio Blanco samples are not so well classified into different alteration stages as at El Teniente, a rough comparison of the isotopic data between the corresponding alteration zones is possible (Table 3). Anhydrite has lower  $\delta^{18}\text{O}$  values in K-zone than in K-zone with quartz-sericite alteration which may correspond to El Teniente's stage I, and stages II and III, respectively. The  $\delta^{34}\text{S}$  values of anhydrite and sulfide minerals do not change appreciably with the mode of occurrence from the K-zone through Brecciated zone.

Spatial variation of isotopic compositions is examined for the Sections 87, 98, 148 and 238 of the El Teniente deposit, which is shown on Figs. 7 through 10. In these Figures no distinctively systematic variation of  $\delta$  values is observed within a stage. For instance, the stage I quartz has identical  $\delta^{18}\text{O}$  values at 200 m and 480 m distance from the edge of the Braden pipe, and the

stage II and III quartz has similar values crossing the Section 148 (Fig. 9). Anhydrite has relatively uniform  $\delta^{18}\text{O}$  values. These observations suggest that the hydrothermal fluids fairly uniform in isotopic composition and temperature may have prevailed in each mineralization-alteration stage.

#### Isotopic Fractionation and Temperature of Mineralization

Isotopic composition of a mineral is, in general, determined by a number of factors such as (1) temperature of deposition, (2) isotopic composition of the hydrothermal fluid from which the mineral is deposited, (3) relative amount of the mineral deposited to the fluid, (4) chemical composition of the fluid including pH,  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  at the time of mineralization, (5) cationic and anionic composition of the precipitating mineral, and so on. However, enrichment of an isotope in a mineral relative to another phase which could be either a different mineral or fluid is solely a function of temperature. This enrichment is called isotopic fractionation  $\Delta_{\text{A-B}}$ , which is approximated by the difference of isotopic compositions between the two phases A and B, i.e.,  $\delta_{\text{A}} - \delta_{\text{B}}$ .

Table 4 lists the observed oxygen and sulfur isotopic fractionations between coexisting quartz-anhydrite and anhydrite-chalcopyrite pairs in the veins of different alteration stages at the El Teniente and Rio Blanco porphyry copper deposits. Oxygen isotopic fractionation between quartz and anhydrite is about 2‰ and virtually constant for at least the first three stages, and possibly for the stage IV as well. The magnitude of the above isotopic fractionations is very close to the equilibrium values of 2.3 to 2.6‰ (in the range from 300 to 500°C) which are calculated from the experimentally determined fractionations for quartz-water system (MATSUHIRA *et al.*, 1979) and anhydrite-water system (CHIBA *et al.*, 1981). Therefore it is most likely that the two minerals were precipitated from a common hydrothermal fluid in (or close to) iso-

Oxygen and Sulfur Isotopic Compositions (Kusakabe et al.)

topic equilibrium. Unfortunately, however, it is difficult to calculate equilibrium temperatures for the pair based on the observed fractionation, because temperature dependence of the equilibrium fractionation between quartz and anhydrite is very small. The majority of the  $\delta^{18}\text{O}$  values of anhydrite and quartz from the Rio Blanco deposit falls in ranges of +7 to +8‰ and +9.5 to +10.7‰, respectively, almost identical to those of El Teniente, suggesting an oxygen isotopic similarity of the hydrothermal fluids between the two deposits.

Sulfur isotopic fractionation between sul-

fates and sulfides from several porphyry copper deposits is summarized in OHMOTO and RYE (1979). They showed that the  $\delta^{34}\text{S}$  values of sulfides are nearly 0‰ or slightly lower and those of sulfates between +8 and +15‰, indicating the fractionations to be fairly uniform regardless of large geographical distribution of the deposits reviewed. It is said that the general agreement of isotopic temperatures based on the observed fractionations with other geological temperature estimates may suggest establishment of isotopic equilibrium among the oxidized and the reduced sulfur species in the hydrothermal

Table 4 Oxygen and sulfur isotope fractionation between mineral pairs and sulfur isotope temperatures for the El Teniente and Rio Blanco porphyry copper deposits, Chile.

Alteration Stage or Zone	Sample Number			$\Delta^{18}\text{O}^*$	$\Delta^{34}\text{S}^*$	Sulfur Isotope Temp. (°C)	
	Sec.	DDH	Site (ft)	Qz-Anh	Anh-Cpy		
<u>EL TENIENTE</u>							
Stage I	87	1064	444	1.5	12.2	475	
		98	709	720	1.6		
	148		718	338		13.6	433
			1003	557		14.9	401
			1015	1006B		13.4	439
	238		1035	366	1.4	12.8	456
			957	921	2.2		
	Mine 5			2.0	10.6	532	
	Mine 6				12.9	453	
				<i>Average</i>	$1.7 \pm 0.3$	$12.8 \pm 1.4$	$456 \pm 41$
Stage II	87	505A	740		13.6	433	
			765		16.7	362	
			939	587	13.4	439	
	148		1064	36		13.7	431
			943	351A,B	1.3		
			1017	1551	2.4		
		1035	421		14.4	413	
			<i>Average</i>	$1.9 \pm 0.8$	$14.4 \pm 1.4$	$416 \pm 31$	
Stage III	148	1015	1045A,B	2.1	15.2	394	
			1035	404A,B	1.8	13.7	431
	238	944		1508		15.4	389
				45		12.4	468
				174	1.6	13.6	433
				414		15.2	394
				966	296		16.5
			<i>Average</i>	$1.8 \pm 0.3$	$14.6 \pm 1.4$	$411 \pm 35$	
Stage IV	Mine 9			2.8	16.8	360	

Table 4 (continued)

Alteration Stage or Zone	Sample Number		$\Delta^{18}\text{O}^*$ Qz-Anh	$\Delta^{34}\text{S}^*$ Anh-Cpy	Sulfur Isotope Temp. ( $^{\circ}\text{C}$ )
	No.	DDH			
<u>RIO BLANCO</u>					
K-zone	02	228	99.85	13.3	442
	11	230	502.5	11.3	505
			<i>Average</i>	$12.3 \pm 1.4$	$473 \pm 45$
K-propylitic transitional zone					
	04	234	161.0	15.0	398
K-zone with quartz-sericite alteration					
	08	230	387.0	13.9	425
	09	230	375.1	14.9	401
	10		371.5	14.0	423
	16	233	129.4	12.7	459
	22	166A	361.2	13.8	428
	23		150.1	14.6	408
			<i>Average</i>	$14.0 \pm 0.9$	$424 \pm 22$
Quartz-sericite zone					
	05	234	353.2	2.6	

\*  $\Delta_{A-B} = \delta_A - \delta_B$ 

fluids as well as in minerals.

Sulfur isotopic fractionations between anhydrite and chalcopyrite from the El Teniente and Rio Blanco deposits given in Table 4 agree well with the generalization mentioned above. A closer look at Table 4 reveals that the fractionation varies with alteration stages or zones. At El Teniente, the average fractionation is found to be smallest in the stage I ( $\Delta_{\text{Anh-Cpy}} = 12.8$ ), with a gradual increase as the stage progresses, reaching  $\Delta_{\text{Anh-Cpy}} = 16.8$  in the stage IV, although overlapping of the individual fractionation is fairly substantial. The fractionations are almost identical with those at Rio Blanco, where the smallest one is again found in K-zone with an increase towards the K-propylitic transitional zone and quartz-sericite zone. This may imply decrease in temperature as an alteration stage progresses.

Sulfur isotopic equilibrium temperatures listed in Table 4 were calculated for coexisting anhydrite-chalcopyrite pairs based on the sulfur isotopic temperature scale recently modified by OHMOTO and LASAGA (1982). The highest temperature of  $456 \pm 41^{\circ}\text{C}$  was

obtained for the stage I at El Teniente. The average equilibrium temperature then decreases to  $416 \pm 31^{\circ}\text{C}$  at the stage II, staying at almost the same temperature of  $411 \pm 35^{\circ}\text{C}$  at the stage III. The lowest temperature of  $360^{\circ}\text{C}$  is calculated for the stage IV, but this temperature may be somewhat too high as compared with that expected for the latest stage mineral assemblage. It should be noted that the temperature for the stage IV was calculated from a single pair of anhydrite and chalcopyrite. In a stage IV sample (Mine 9, El Teniente) galena was found completely embraced by chalcopyrite. If these two sulfides were in isotopic equilibrium the temperature is calculated to be  $300^{\circ}\text{C}$  (OHMOTO and RYE, 1979), some  $60^{\circ}\text{C}$  lower than the anhydrite-chalcopyrite temperature. At Rio Blanco the highest temperature of  $473^{\circ}\text{C}$  was calculated for anhydrite-chalcopyrite pairs from the K-zone which corresponds to the stage I of El Teniente. The equilibrium temperatures become lower if we go into the K-zone with quartz-sericite alteration ( $424^{\circ}\text{C}$ ) and the K-propylitic transitional zone ( $398^{\circ}\text{C}$ ). These temperatures again

show an excellent agreement with those obtained for the stages II and III alteration at El Teniente. These agreements probably suggest that the hydrothermal fluids characterized by similar isotopic and chemical compositions prevailed at early to late mineralization-alteration stages at both deposits. Agreement in  $\delta^{18}\text{O}$  values of anhydrites from the corresponding alteration stages of the two deposits supplies further supporting evidence to this suggestion.

The sulfur isotopic temperatures calculated from the coexisting anhydrite-pyrite and pyrite-chalcopyrite pairs are more variable than those from the anhydrite-chalcopyrite pairs especially at El Teniente. This may be due to failure to attain equilibria in systems containing pyrite, and hence the anhydrite-pyrite temperatures are not included in this paper. Relatively large variability in sulfur isotopic fractionation and in  $\delta^{18}\text{O}$  values of anhydrite, found in the Brecciated zone of Rio Blanco, is not understood.

If the following assumptions are made that the temperatures calculated above are correct and that oxygen isotopic equilibrium between minerals and fluids was attained at the same time when sulfur isotopes reached equilibrium, oxygen isotopic compositions of the fluids can be calculated using the temperature data in Table 4, the average  $\delta^{18}\text{O}$  values of quartz and anhydrite in Table 2, and oxygen isotopic fractionation factors for the quartz-water system (MATSUHISA *et al.*, 1979) and for the anhydrite-water system (CHIBA *et al.*, 1981). Figure 14 shows the variation in the calculated  $\delta^{18}\text{O}_{\text{fluid}}$  with alteration stages together with the  $\delta^{18}\text{O}$  values of quartz and anhydrite, and the temperature estimates for the El Teniente porphyry copper deposit.

The  $\delta^{18}\text{O}_{\text{fluid}}$  values calculated from  $\delta^{18}\text{O}_{\text{qz}}$  values agree quite well with those from  $\delta^{18}\text{O}_{\text{anh}}$  values at all stages, suggesting the two minerals were precipitated in equilibrium with the fluid. The  $\delta^{18}\text{O}_{\text{fluid}}$  values are about +6‰ and virtually constant from the stage I through IV of El Teniente if the uncertainties in estimation ( $\pm 0.8\%$ ) are taken

into account. The values of +5 to +7‰ are calculated for Rio Blanco (excluding the Brecciated zone) which are essentially the same as at El Teniente. The value of +6‰ is in the lower limit of the range for "primary magmatic water" (TAYLOR, 1979), and may be interpreted to have resulted from thorough equilibration of fluids with igneous rocks at temperatures higher than 500°C. This interpretation is consistent with the generally accepted porphyry copper environments.

The present results suggest that the hydrothermal fluids responsible for primary mineralization-alteration processes might be of magmatic origin through various phases of alteration at least at El Teniente and Rio Blanco. This interpretation is in striking contrast with the hypothesis that although potassic alteration with strong biotitization was caused by reaction with magmatic hydrothermal fluids derived from the porphyry stocks, the later alteration characterized by quartz-sericite assemblage was produced by invasion of heated groundwaters of meteoric origin (SHEPPARD *et al.*, 1971; TAYLOR, 1974). It should be kept in mind that the hydrothermal fluids with  $\delta^{18}\text{O}$  value of +6‰ calculated for the major alteration-mineralization stages of El Teniente and Rio Blanco could be produced by oxygen isotopic exchange of local meteoric water with porphyry stocks and/or surrounding wall rocks at temperatures higher than, say, 500°C. The water to rock ratios involved in the exchange have to be smaller than 0.1 (i.e., 10% or less of water in the whole system) if the initial rock has  $\delta^{18}\text{O}$  of +7‰, and the initial meteoric water has  $\delta^{18}\text{O}$  of -8‰ or less. Considering relatively high solubility of water in granitic magmas, it may not be necessary that meteoric water occupies a large fraction of the hydrothermal fluids. In any event,  $\delta^{18}\text{O}$  values of fluids are not diagnostic for discrimination of the ultimate origin of the hydrothermal fluids. Determination of hydrogen isotope ratios of alteration minerals would give a more useful clue to this problem.

SHEPPARD and GUSTAFSON (1976) esti-

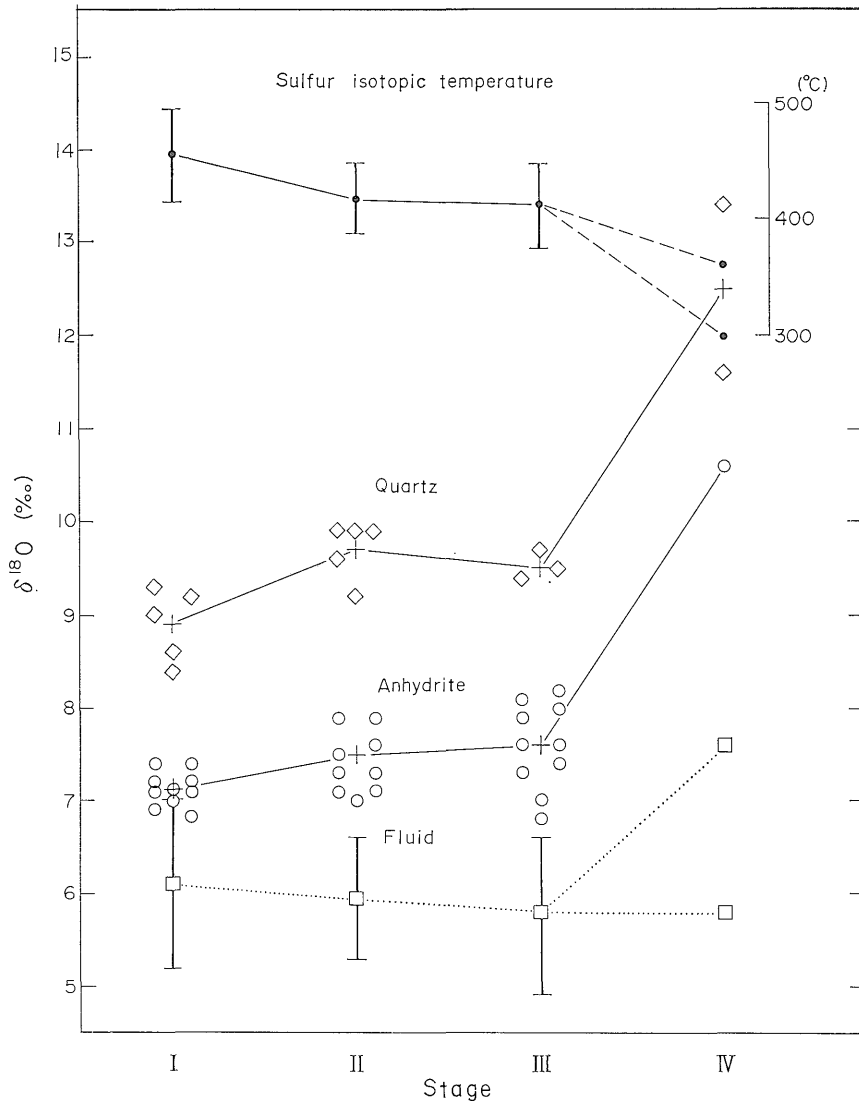


Fig. 14 Variations in  $\delta^{18}\text{O}$  values of quartz ( $\diamond$ ), anhydrite ( $\circ$ ) and hydrothermal fluids ( $\square$ ), and sulfur isotopic equilibrium temperatures ( $\bullet$ ) with alteration stages at El Teniente. The average values of each item (+) at different stages are connected by tie-lines. The fractionation factor of 1.0407 between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  is used in calculation of  $\delta^{18}\text{O}_{\text{fluid}}$  values.

mated the  $\delta^{18}\text{O}$  values of fluids responsible for the alteration at the El Salvador deposit. For "L" porphyry with minimum alteration and the potassic alteration zone, the values of +6.6 to +8.2‰ are calculated, which are in the typical magmatic range and are comparable to the value of +6 to +7‰

for the K-alteration stages of El Teniente and Rio Blanco. However, SHEPPARD and GUSTAFSON's estimates of 0 to +6‰ for the later quartz-sericite alteration are much lower and scattered as compared with the corresponding stages of the present study. It should be noticed that the  $\delta^{18}\text{O}$  values of

+9 to +12‰ reported for vein quartz from El Salvador are identical to the present results for El Teniente and Rio Blanco. Therefore difference in the calculated fluid compositions between the two studies depends solely on temperature estimates; SHEPPARD and GUSTAFSON used the temperature estimates for the later alteration based on sulfate-sulfide sulfur isotope fractionations (for their Transitional "B" vein quartz), fluid inclusion measurements (Transitional "B" vein and "D" vein quartz) and "geological intuition". Our temperature estimates depend completely on sulfur isotope temperatures calculated from coexisting anhydrite-chalcopyrite pairs as discussed previously. Preliminary results on filling temperatures of primary fluid inclusions in quartz from El Teniente (KUSAKABE, unpublished data) indicate that the stage I experienced the highest temperatures, the stages II and III slightly lower and the stage IV the lowest, and that good agreement is obtained between the fluid inclusion and sulfur isotope temperatures if pressure correction is made for the assumed emplacement of porphyry stocks at depth of 2 to 3 km in the crust. Similar results have been obtained for Rio Blanco.

A low  $\delta^{18}\text{O}$  value of +2.6‰ was obtained for a stage II quartz from El Teniente (87-505A-2420). This sample was collected from a vein at the northwestern edge of the alteration-mineralization zones (Figs. 6 and 7). The low  $\delta^{18}\text{O}$  value might suggest that the quartz precipitated from a heated meteoric groundwater which came into the system at the marginal zone. However, more data of low  $\delta^{18}\text{O}$  values are needed to confirm this assumption.

A quartz "eye" from the sericitized dacite porphyry of Rio Blanco (No. 07) has a  $\delta^{18}\text{O}$  value of +8.4‰. This value is on the lower limit of the compositional range for the hydrothermal quartz from the El Teniente deposit. It is more likely, however, that this value represents that of primary igneous quartz which remained as "eyes", being resistant to the alteration.

### Choice of Sulfur Isotope Fractionation Factor Between Sulfate and Sulfide

Since a discrepancy exists in the published sulfur isotope fractionation factors between aqueous sulfate and sulfide, choice of one fractionation factor out of several possibilities at a given temperature could lead to a different geological interpretation even though the same set of data is used. OHMOTO and RYE (1979) summarized sulfur isotope fractionation factors for various sulfur-bearing systems. As far as the aqueous sulfate-sulfide system is concerned, OHMOTO and RYE put emphasis on SAKAI (1968)'s theoretical curve at high temperatures coupled with ROBINSON (1973)'s experimental curve at lower temperatures. Recently, OHMOTO and LASAGA (1982) have proposed modified fractionation factors which are significantly lower than OHMOTO and RYE (1979)'s compilation, especially at temperatures higher than 250°C. OHMOTO and LASAGA gave special weight to later experimental works by SAKAI and DICKSON (1978) and IGUMNOV (1978), and on possible retrograde re-equilibration during quenching of hydrothermal runs of the previous experiments. The modification is as much as 2.5‰ at 350°C or higher, which corresponds to temperature lowering of some 70°C for fractionation of 15‰ typically encountered in porphyry copper sulfate-sulfide pairs. It is this "latest version" given by OHMOTO and LASAGA (1982) that we have chosen in the present study.

If the modified fractionation is applied to sulfur isotopic data of El Salvador given by FIELD and GUSTAFSON (1976), a picture very similar to that for El Teniente and Rio Blanco is drawn, and hence similar geological interpretation comes out (the  $\delta^{34}\text{S}$  values of pyrite have been corrected according to the statement on p. 1544 of their paper).

### Chemical Conditions of Hydrothermal Fluids and Source of Sulfur

Mineral assemblage of alteration is con-

trolled by chemical conditions of fluids and temperature. Chemical conditions of fluids are modified by reactions with wall rocks at the same time. Stability field of K-feldspar and sericite (approximated by muscovite) in the presence of quartz is defined by temperature and concentration ratio of KCl/HCl in solution (MONTROYA and HEMLEY, 1975). K-feldspar moves into the muscovite field with a temperature decrease from 500°C to 400°C, provided that the KCl/HCl molal ratio of the fluids is between 2 and 3 in logarithmic unit. This implies that alteration sequence of K-feldspar to sericite could be produced by simple cooling of early stage hydrothermal fluids without incorporation of significant amount of groundwater.

FIELD and GUSTAFSON (1976) used a plot

of  $\delta^{34}\text{S}$  versus  $\Delta^{34}\text{S}$  for pairs of coexisting sulfates and sulfides from El Salvador. Use of this plot necessarily involves the assumptions that (1) the hydrothermal fluids were in a closed system during mineralization, (2) the ratio of sulfate to sulfide in the fluids were kept constant, and (3) isotopic composition of total sulfur in the fluids,  $\delta^{34}\text{S}_{\Sigma\text{S}}$ , was kept constant. If the assumptions were fulfilled and the sulfates and sulfides were coprecipitated, then the  $\delta^{34}\text{S}$  vs.  $\Delta^{34}\text{S}$  diagram would show covariance of sulfur isotopic composition of one mineral with another; as the  $\delta^{34}\text{S}_{\text{sulfate}}$  values become more positive, the corresponding  $\delta^{34}\text{S}_{\text{sulfide}}$  values become more negative. The intersection of the two covarying lines indicates the  $\delta^{34}\text{S}_{\Sigma\text{S}}$  value of the system.

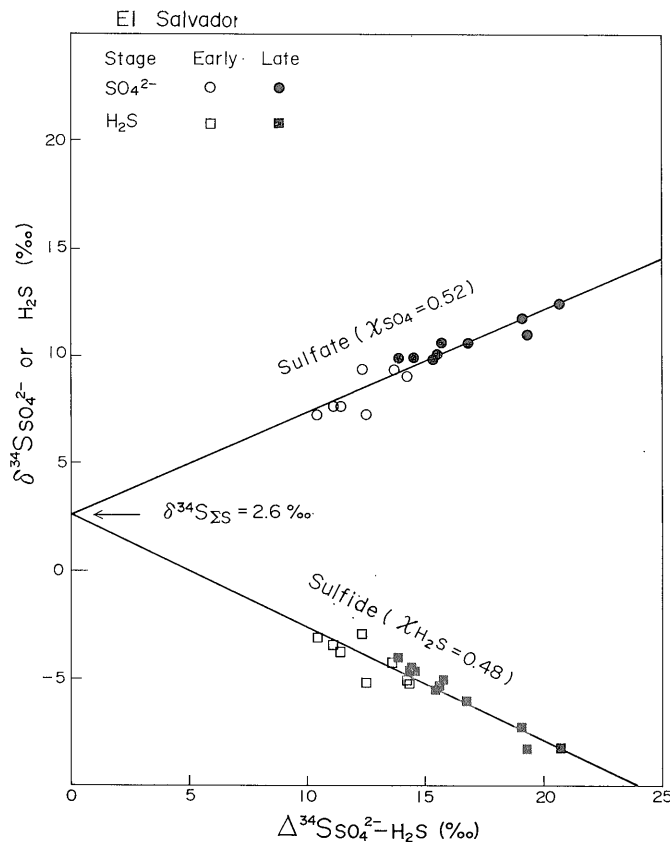


Fig. 15 A plot of  $\delta^{34}\text{S}$  values of  $\text{SO}_4$  and  $\text{H}_2\text{S}$  in fluids as a function of  $\Delta^{34}\text{S}_{\text{SO}_4-\text{H}_2\text{S}}$  for El Salvador. The values are calculated from the corrected mineral isotopic data given by FIELD and GUSTAFSON (1976).



Figure 15 shows such a diagram for El Salvador (data taken from FIELD and GUSTAFSON (1976). In Fig. 15 and in Figs. 16 and 17 that follow, the  $\delta^{34}\text{S}$  values of sulfate and sulfide minerals have been respectively converted to those of dissolved sulfate and sulfide in hydrothermal fluids using the appropriate fractionation factors summarized by OHMOTO and RYE (1979), and hence the  $\delta^{34}\text{S}$  and  $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$  values are given on the  $\text{SO}_4\text{-H}_2\text{S}$  basis. Since FIELD and GUSTAFSON'S  $\delta^{34}\text{S}$  data for pyrite have been corrected as mentioned previously, Fig. 15 looks quite different from their original Fig. 4. The data points are discriminated into two groups, Early K-silicate background + Early "A" vein, and Late sericite-chlorite background + Late "D"

vein. They nicely lie on a single set of lines. This suggests that the sulfates and sulfides were coprecipitated from the fluids characterized by a relatively constant sulfate/sulfide ratio of about 1/1 and by a  $\delta^{34}\text{S}_{\Sigma\text{S}}$  value of +2.6‰. It would be fair to note that this is our interpretation based on their corrected data.

Figures 16 and 17 delineate the  $\delta^{34}\text{S}$  vs.  $\Delta^{34}\text{S}$  diagrams for El Teniente and Rio Blanco, respectively, constructed under the same line of thoughts as above. In these Figures, the data points for the early stages are shown separately from those for the later stages. The data points for El Teniente tend to make clusters between the  $\Delta$  values of 10 and 15‰. The lines are drawn through the clusters by

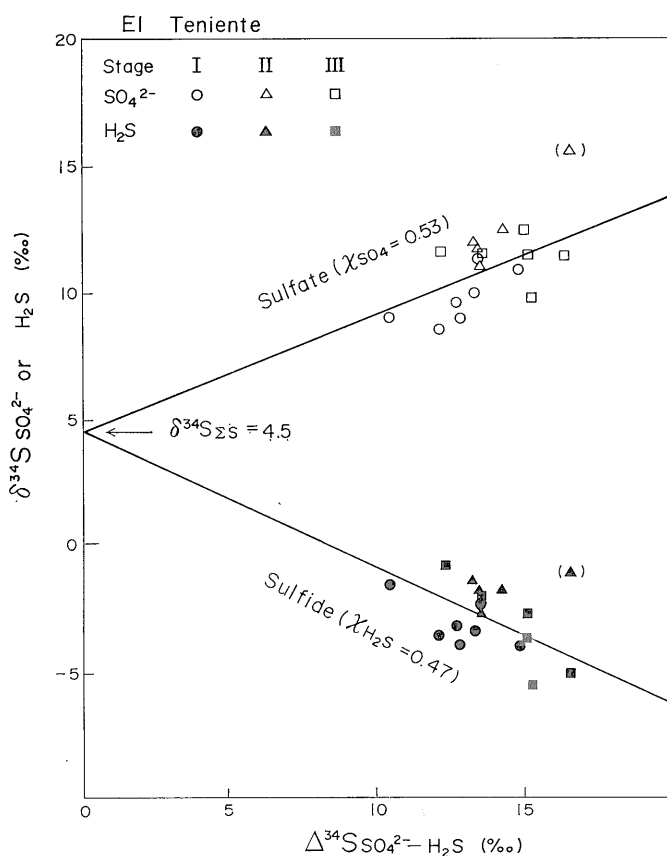


Fig. 16 A  $\delta^{34}\text{S}$  versus  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-H}_2\text{S}}$  diagram for the hydrothermal fluids at El Teniente. The data points are for the coexisting anhydrite-chalcopyrite pairs in stages I, II and III. A pair of data points in parentheses is excluded from the least square fitting.

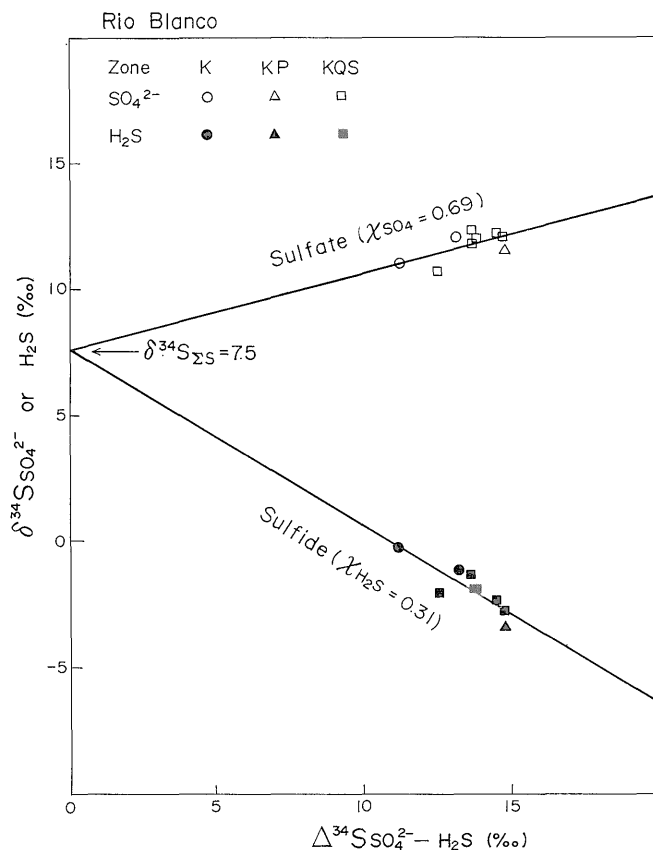


Fig. 17 A  $\delta^{34}\text{S}$  versus  $\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$  diagram for the hydrothermal fluids at Rio Blanco. The data points are obtained from the coexisting anhydrite-chalcopyrite pairs in K-zone (K), K-propylitic transitional zone (KP) and K-zone with quartz-sericite alteration (KQS).

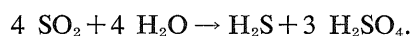
the least square fit, converging at  $\Delta=0$  to give a  $\delta^{34}\text{S}_{\Sigma\text{S}}$  value of  $+4.5\text{‰}$  (excluding a pair of data in the parentheses). Although samples from each stage seem to plot on a particular region in Fig. 16, it is difficult to draw a set of lines pertinent to a given stage. Since the  $\delta^{34}\text{S}_{\Sigma\text{S}}$  value obtained from relatively long extrapolation on the diagram depends strongly on a slope of the lines, it is even dangerous to draw a line using the data points divided into a smaller number (e.g., Fig. 32 in BEANE and TITLEY, 1981, Fig. 16 in SHELTON and RYE, 1982). Because oxygen isotopic data suggest isotopically uniform fluids prevailed at all stages, we assume that the fluids were also uniform with respect to sulfur isotopes. Thus, the isotopic

composition of total sulfur is estimated to be  $+4.5\text{‰}$  and  $+7.5\text{‰}$  at the El Teniente and Rio Blanco porphyry copper deposits, respectively.

SASAKI *et al.* (1984) measured  $\delta^{34}\text{S}$  values of total sulfur in fresh Andean granitoids that are regarded as unmineralized equivalents of porphyritic rocks of the mining areas. The  $\delta^{34}\text{S}$  values of  $+5.9\text{‰}$ ,  $+3.3\text{‰}$  and  $+6.1\text{‰}$  are given for the rocks collected in the proximity of the El Salvador, El Teniente and Rio Blanco porphyry copper deposits, respectively. These values are surprisingly in good harmony with the isotopic compositions of total sulfur of the El Teniente and Rio Blanco porphyry copper systems estimated in the present study, suggesting that the sul-

fate-sulfur as well as sulfide-sulfur of these deposits were derived almost entirely from a magmatic source.

The slopes of the lines in Figs. 16 and 17 indicate that mineralization took place with the fluid sulfate/sulfide ratio of 1 to 2, being excess of sulfate over sulfide. According to HOLLAND (1965),  $\text{SO}_2$  is the dominant sulfur species in fluid at  $600^\circ\text{C}$  and  $f_{\text{H}_2\text{O}} = 750$  atm in the system where magnetite, hematite and pyrite coexist. The mineral assemblage in granitoids related to porphyry copper deposits typically satisfies the requirement. With decreasing temperature,  $\text{SO}_2$  reacts with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  according to the following disproportionation reaction;



Sulfuric acid thus formed would have been combined with calcium from wall rocks to precipitate anhydrite (HOLLAND, 1979). The water participated in the reaction was magmatic one or a thoroughly interacted product in porphyry copper environments if any incorporation of groundwater did occur.

SHELTON and RYE (1982) have developed completely different interpretation of the  $\delta^{34}\text{S}$  vs.  $\Delta^{34}\text{S}$  diagram using their detailed sulfur isotopic data of Mines Gaspé, Quebec. They classified the sulfate-sulfide mineral pairs into two groups, (1) non-coprecipitated and (2) coprecipitated. The group (1) tends to show a  $\delta^{34}\text{S}$  vs.  $\Delta^{34}\text{S}$  plot that is featured by a line with a slope near zero for one of the paired minerals and the variation is caused only by the isotopic composition of another. From this type of diagram, such an interpretation may be derived that a hydrothermal fluid very much enriched in either sulfate or sulfide having a self-induced  $\delta^{34}\text{S}_{\Sigma\text{S}}$  value was responsible for mineralization. The group (2) typically shows a sympathetic variation in the  $\delta^{34}\text{S}$  vs.  $\Delta^{34}\text{S}$  diagram, as illustrated by Fig. 17, for example. According to SHELTON and RYE (1982), isotopic distribution of this type can be produced by the disequilibrium or partial equilibrium processes in which an initial

disequilibrium pair changes their isotopic compositions toward the equilibrium fractionation at a constant temperature. Such an example has been demonstrated for anhydrite-sulfide pairs from Mines Gaspé, where the initial disequilibrium pair has a  $\Delta^{34}\text{S}$  value as low as 7‰. This fractionation corresponds to isotopic temperature of  $770^\circ\text{C}$  which is unrealistically high as compared with the observed fluid inclusion temperatures of  $350$  to  $425^\circ\text{C}$ . SHELTON and RYE have also stated that the El Salvador deposit is most likely not in sulfur isotope equilibrium but be a better example representing disequilibrium, judging from disagreement of sulfur isotopic temperatures with fluid inclusion data. This is completely contradictory situation to ours. The contradiction clearly arises from choice of sulfur isotopic fractionation factor.

Thus it is urgently needed to accumulate experimental data on sulfur isotope fractionation between sulfate and sulfide at hydrothermal temperatures. Furthermore, when treating the problems like those discussed in the present paper, it is very important to obtain means or methods by which attainment of equilibrium can be examined in addition to the conventional comparison between isotopic and fluid inclusion data. In this respect determination of oxygen isotopic compositions of vein minerals such as quartz and anhydrite from various stages in a single porphyry copper deposit may afford an additional useful information.

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Appenix A Brief description of samples from the El Teniente porphyry copper deposit, Chile.

Sec.	Sample Number		Alteration Stage	Description Mineral assemblage of vein; Wall rock alteration
	DDH	Site(ft)		
87	1046	3212	I	Qz-Anh vein; Bi "books" in Dp
	1064	444	I	Qz-Anh-Cpy vein; K-feld and Bi in And wall rock, Cpy disseminated
		2103	I	Qz-Anh vein; Bi in And wall rock
98	709	720	I	Qz-Anh vein; Bi in And wall rock
	718	338	I	Qz-Anh-Cpy vein; Bi and Chl in And wall rock
148	1003	557	I	Anh-Cpy-Py vein; Qz, Bi and Chl in And wall rock
	1015	1006B	I	Qz-Anh vein; Bi in And, Cpy disseminated
	1035	366	I	Qz-Anh-Chl-Cpy vein; Bi in And wall rock
238	957	921	I	Qz vein, Qz-Anh vein; Bi in And wall rock
	Mine 5 T-4 XC-6AN/1R-BD*		I	Cpy-Py-Qz-Anh vein; Bi in And wall rock
	Mine 6 T-4 XC-6AN/1-2L*		I	Anh-Cpy-Bo vein; Bi in And wall rock

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Appendix A (continued)

Sec.	Sample Number		Alteration Stage	Description Mineral assemblage of vein; Wall rock alteration		
	DDH	Site (ft)				
87	505A	740	II	Anh-Cpy vein; Qz-Ser-Chl halo, Bi in And wall rock		
		765	II	Qz-Anh-Cpy-Py vein; Qz-Ser-Chl halo in And wall rock		
		1370	II	Qz-Anh-Py-Tour vein; Qz-Ser halo, Tour, Cpy and Py disseminated in halo		
		1828	II	Qz-Anh-Cpy-Mo vein; Qz-Ser-Chl halo, Cpy and Mo disseminated in halo, Bi in And wall rock		
		2406	II	Qz-Anh vein; Qz-Ser halo in And wall rock, Cpy and Py disseminated in halo		
		2420	II	Qz-Cpy-Py-Chl vein; Qz-Ser halo in And wall rock, Cpy and Py disseminated in halo		
		939	587	II	Qz-Anh-Cpy vein; Qz-Ser-Chl halo, Bi in And wall rock	
		1615	II	Qz-Anh-Chl-Py vein; Qz-Ser halo in And wall rock		
		1064	36	II	Qz-Anh-Cpy vein; Qz-Ser halo in And wall rock, Cpy disseminated in halo	
		98	820	116	II	Qz-Anh-Py-Cpy vein; Qz-Ser-Chl halo in And wall rock, Py and Cpy disseminated
		885	227	II	Qz-Anh-Cpy vein; Qz-Ser halo in And wall rock, Cpy disseminated in halo	
		1056	3271	II	Qz-Py vein; Qz-Ser halo in chloritized Qd wall rock	
		148	943	351A, B	II	Qz vein, Anh-Py vein; Qz-Ser halo in Qd wall rock
		1017	1551	II	Qz-Anh-Py vein; Qd wall rock	
		1035	421	II	Anh-Cpy vein; Qz-Ser halo, Bi in And wall rock	
		1042	1749	II	Qz-Py vein; Qz-Ser halo in Qd wall rock	
227	1068	1717	II	Qz vein; Py disseminated in Latite porphyry		
238	966	268	II	Py vein; Qz-Ser-Chl halo, Bi in And wall rock		
98	709	896	III	Qz-Anh-Bo vein; Qz-Ser-Chl halo in And wall rock		
		885	188	III	Qz-Cpy-Tour vein; Ser-Chl halo in And wall rock	
148	1003	589B	III	Anh-Tour-Mo vein; Qz-Ser halo in And wall rock		
		1015	1045A, B	III	Qz-Bo-Cpy-Mo vein, Anh-Bo-Cpy-Mo vein; Qz-Ser halo in And wall rock	
		1035	404A, B	III	Qz-Tour-Cpy vein, Anh-Cpy vein; irregular veins in And wall rock	
		1508	III	Anh-Cpy vein; brecciated And wall rock		
		238	944	45	III	Anh-Cpy-Py vein with Tour; Qz-Ser-Chl halo in And wall rock
		174	III	Qz-Anh-Cpy-Py-Mo vein; Qz-Ser-Ep halo in And wall rock		
		414	III	Anh-Cpy-Py-Tour vein; Ser-Ep halo, Bi in And wall rock		
		957	347	III	Anh-Cpy-Mo vein; Qz-Ser halo in and wall rock, Cpy disseminated	
		966	296	III	Anh-Cpy-Tour vein; irregular vein with Qz-Ser-Chl halo in And	
Mine 4	T-4	XC-6AN/6-5R*	III	Gyp-Bo-Anh-Sid-Tenn vein; And wall rock		
Mine 9	T-4	HWDR/XC-14AN*	IV	Anh-Qz-Gn-Sph-Cpy-Gyp-Sid vein; druse in Braden breccia pipe		
Mine 10		ditto	IV	ditto ; ditto		

\* Mine 4, 5, 6, 9 and 10 samples were collected at the T-4 level of the El Teniente mine.  
For abbreviations, see the footnotes of Appendix B.

*Oxygen and Sulfur Isotopic Compositions (Kusakabe et al.)*

Appendix B Brief description of samples from the Rio Blanco porphyry copper deposit, Chile.

No.	Sample Number		Description Mineral assemblage of vein; Wall rock alteration
	DDH	Site (m)	
<b>K-zone</b>			
01	228	99.85	Anh vein; K-feld and partly chloritized Bi in Gd wall rock, Cpy disseminated
02		478.05	Anh-Cpy-Py vein; Bi "books" in Gd wall rock
03		467.16	Anh-Cpy vein; K-feld, Bi and magnetite in Gd wall rock
11	230	502.5	Anh-Qz-Cpy vein; Bi and magnetite in Qmp wall rock, Cpy disseminated
<b>K-propylitic transitional zone</b>			
04	234	161.0	Anh-Cpy vein with Chl, Qz vein; K-feld, Bi, Chl and Ep in Gd wall rock, Hm and Cpy disseminated
12	225	449.4	K-feld, Bi and chloritized Pl in Gd wall rock, Hm and Cpy disseminated
17	233	450.1	Qz-Cpy-Py-Hm vein; Chloritized Gd wall rock
<b>K-zone with quartz-sericite alteration</b>			
08	230	387.0	Anh vein; K-feld and Bi in Gd wall rock, Pl partly sericitized, Hm and Cpy disseminated
09		375.1	Anh-Cpy vein, Qz-Cpy vein; K-feld remained in sericitized Gd wall rock, Cpy disseminated
10		371.9	Anh-Cpy vein; Bi remained in sericitized Gd, Cpy and Bo disseminated
16	233	129.4	Anh-Cpy vein, Qz-Ser-Cpy vein; Bi and K-feld in Gd wall rock, Cpy disseminated
22	166A	361.2	Qz-Cpy-Py vein with Qz-Ser halo; Qz, K-feld, Bi, Chl and Ep in Gd wall rock
23		150.1	Anh-Cpy vein with Qz-Ser halo; K-feld, Qz, Bi and Hm in Gd wall rock
<b>Quartz-sericite zone</b>			
05	234	353.2	Qz-Anh-Py vein with Qz-Ser halo; Chloritized Gd wall rock
20	231	251.2	Qz vein with Qz-Ser halo, Gyp vein; Chl and Ser in Qmp wall rock, Cpy disseminated
21		433.1	Qz-Py vein with Qz-Ser halo; Chl and Ser in Qmp wall rock, Py disseminated
<b>Brecciated zone</b>			
13	189	9.9	Anh-Sid-Hm-Cpy irregular vein; Qmp breccia
18	231	59.6	Qz-Anh-Cpy-Hm vein; Chloritized Bi in Gd wall rock
19		54.4	Anh-Sid-Cpy-Hm vein with Chl; Chloritized Gd breccia
45	—	—	Euhedral quartz crystal in druse of tourmaline breccia
<b>Sericite zone in dacite porphyry</b>			
07	230	251.2	Py veinlet; Qz "eye" in sericitized Dp

The following abbreviations are used in Appendices A and B.

*Minerals.* Anh: anhydrite, Bi: biotite, Bo: bornite, Chl: chlorite, Cpy: chalcopyrite, Ep: epidote, Gn: galena, Gyp: gypsum, Hm: hematite, K-feld: K-feldspar, Mo: molybdenite, Pl: plagioclase, Py: pyrite, Qz: quartz, Ser: sericite, Sid: siderite, Sph: sphalerite, Tenn: tennantite, Tour: tourmaline.

*Rocks.* And: andesite, Dp: dacite porphyry, Gd: granodiorite, Qd: quartz diorite, Qmp: quartz monzoporphyry.

酸素および硫黄同位体比による El Teniente および Rio Blanco  
斑岩銅鉱床 (チリ) の初生鉱化作用・変質作用の研究

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要 旨

南米チリの El Teniente および Rio Blanco 斑岩銅鉱床の初生鉱化作用・変質作用の各鉱化ステージ・変質帯に産する石英、硬石膏および硫化鉱物について、酸素と硫黄同位体比を測定し、鉱化温度、鉱液の起源ならびにその化学的性質について検討を行った。

El Teniente 鉱床の鉱化・変質作用は、鉱物組合せや脈の産状から、ステージ I (カリウム変質)、ステージ II・III (フィリック変質) およびステージ IV (末期熱水変質) に分けることができる。Rio Blanco 鉱床では El Teniente 鉱床ほど明瞭にステージを区別できないが、変質はカリウム変質帯、カリウム-プロピライト変質漸移帯、フィリック変質帯に分帯される。

El Teniente 鉱床では鉱化・変質ステージが進むにつれて、石英と硬石膏の  $\delta^{18}\text{O}$  値が共に増加する。また両者の差はほぼ一定で、石英が約 2‰ ほど高い値を持つ。共存する硬石膏-硫化鉱物系の硫黄同位体平衡温度は 450-300°C の範囲にあり、各ステージ毎の平均値はステージが進むにつれて低下する。この平均温度と石英および硬石膏の各ステージ毎の  $\delta^{18}\text{O}$  平均値とから計算される鉱液の  $\delta^{18}\text{O}$  値は、ステージによらず一定で、ほぼ +6‰ となる。このことは鉱液の起源がマグマ水か、天水起源としても高温の岩石と十分に反応した熱水が、繰り返し鉱化・変質作用に関与したことを示す。Rio Blanco 鉱床においても類似の熱水の存在が推定される。

鉱液中の  $\text{SO}_4^{2-}$  と  $\text{H}_2\text{S}$  とが、ある共通の閉鎖系から温度の低下に伴って、それぞれ硬石膏および硫化鉱物として沈殿したとすると、鉱液中の全硫黄の  $\delta^{34}\text{S}$  値は El Teniente で +4.5‰, Rio Blanco で 7.6‰ と推定される。この値は両地域の花崗岩類の全岩硫黄の  $\delta^{34}\text{S}$  値 (El Teniente +3.3‰, Rio Blanco +6.1‰, SASAKI *et al.*, 1984) とよく一致している。また鉱液中の  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  比はそれぞれ 1 および 2 と見積もられる。これらのことは、磁鉄鉱系の高い  $f\text{O}_2$  を持つ花崗岩質マグマに付随する  $\text{SO}_2$  に富んだマグマ性流体の冷却の過程で、 $\text{SO}_2$  と  $\text{H}_2\text{O}$  の反応により  $\text{SO}_4^{2-}$  と  $\text{H}_2\text{S}$  とが生じたとする説 (HOLLAND, 1965) と調和的である。

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