Sulfur Isotope Reconnaissance of Porphyry Copper and Manto-Type Deposits in Chile and the Philippines

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Abstract: Sulfur isotopes of porphyry copper and manto-type mineralization and the host granitoids in Chile and the Philippines follow the trend characteristic of the magnetite-series granitoid regime. Isotopic fractionation between the rock- and ore sulfur, $\Delta\delta^{34}S_{(rock-ore)}$, is found to be 8 ± 1 permil on the average. This is larger than the value, 3 ± 1 for the skarn and vein-type deposits from Japanese granitic terrains and suggests that the relatively high fo_2 conditions have prevailed in the mineralizations concerned.

Introduction

Recent isotopic study on rock sulfur of Japanese granitic rocks (Sasaki and Ishihara, 1979) revealed that the two series of granitoids (magnetite-series and ilmenite-series) have different isotopic trends; positive $\delta^{34}S$ (CDT) values for the magnetite-series and negative values for the ilmenite-series in general. The sulfur of ilmenite-series granitoids appears to be largely of continental crust origin while that of magnetite-series rocks is most likely of upper mantle or lower crust origin with or without the incorporation of isotopically heavy sulfur of probably marine origin, which may have been supplied by subducting plate motion. It was further established that the ore sulfur of granitic affinity shows the isotopic trends in parallel with the host granitoid sulfur, indicating that both sulfurs are cognate as to their origin (Sasaki and Ishihara, 1980).

Porphyry-type copper and/or molybdenum mineralizations are said to be associated al-

most exclusively with the magnetite-series granitoid (Ishihara, 1977). Then the question may arise whether the sulfur related to porphyry-type mineralization follows the isotopic trend characteristic of the magnetite-series regime mentioned above. This paper presents a result of our preliminary investigation on this subject, examining some materials from Chile and the Philippines. The Chilean porphyry-copper deposits examined include the Paleogene Chuquicamata and El Salvador and the Miocene Rio Blanco and El Teniente. In the Philippines the samples are taken from the Miocene St. Niño, St. Thomas (Philex), Ino and Marcopper deposits and from the Paleocene Sipalay, Basay (Southern Star) and Atlas deposits (Motegi, 1977; Takenouchi, 1981). Also included in this reconnaissance are the "manto-type" copper ores from the Mesozoic granitoid terrain of the Chilean Pacific coast, which are hosted in Jurassic (Buena Esperanza and Susana) and lower Cretaceous (Mantos Blancos, Cerro Iman(Fe) and El Salado) andesitic rocks associated closely with small intrusions of similar age and composition.

Samples and Isotope Analysis

In order to figure out the average isotopic

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trend of ore sulfur, we have analyzed either the mill material or composite specimen anticipating them to represent each individual mineralization. The usefulness and validity of this approach has been demonstrated in our previous work on Japanese samples (SASAKI and ISHIHARA, 1980). Mill concentrates of porphyry-type ores may commonly contain supergene sulfides and this will bring some obscurity in our discussion

which is concerned about the isotopic behavior of hypogene sulfur. The isotopic fractionation involved in secondary enrichment processes of sulfide, however, is expected to be rather small (see *e.g.* the data by FIELD and GUSTAFSON, 1976), and may safely be ignored in this reconnaissance.

Rock sulfur of the host granitoid was examined for some major ore occurrences. Care has been taken to avoid any specimen of

Table 1 $\delta^{34}S$ data of porphyry copper and manto-type deposits and related granitoids from Chile.

No.	Sample No.	Locality	Material analyzed	$S(\%)$	$\delta^{34}S$ (‰) rock	ore	$\Delta\delta^{34}S$ (rock-ore)
Porphyry copper deposits							
1	79CHU8	Chuquicamata	Copper concentrate (Nov. 23, 1979)			−4.7	
2	79CHU3,5	West of Chuquicamata pit	Fortuna granodiorite	0.074	+4.0		8.7
3		El Salvador	Average of hypogene sulfides, after FIELD & GUSTAFSON (1979)			−3.0	
4	79PT–L	*ditto*, Inca adit, Dr. 8532N, 3956m W	"L" porphyry (biotite tonalite)	0.2	+5.9		8.9
5		Rio Blanco	Copper concentrate (Mar. 14, 1979)			−1.4	
6		*ditto*	Mill head (Mar. 14, 1979)			−1.3	
7	79031402	*ditto*	Biotite-hornblende granodiorite	0.002	+6.1		7.5
8		El Teniente	Copper concentrate (Nov., 1980)			−3.1	
9		*ditto*	Mill head (Dec. 13, 1979)			−2.1	
10	79SA11	Romeral, East of Santiago	Fine-grained granodiorite	0.004	+3.3		6.4
Manto-type deposits							
11	79BE10	Buena Esperanza	Copper concentrate (Nov. 19, 1979)			−0.3	
12	79TC13	Tocopilla	Hornblende diorite, slightly altered	0.010	+9.1		9.4
13		Susana, Carolina Michilla	Copper concentrate (Jun., 1982)			−2.1	
14	79MB1	Mantos Blancos, Sapresa East, 888L, xc 20	Composite ore sample, andesite host			−0.1	
15	79MB4	*ditto*, 843L, Dr. 29	Chalcopyrite-pyrite diorite (mineralized)			−1.5	
16		Cerro Iman	Magnetite concentrate (Dec. 7, 1979)			−0.1	
17	79CH15	*ditto*	Biotite-hornblende tonalite	0.002	+4.2		4.3
18	79ES5	El Salado, outcrop	Bornite-chalcocite ore			−1.3	
19	79SA9	*ditto*, 40m below orebody	Coarse-grained diorite, slightly altered	0.003	+5.0		6.3
20	79SA8	*ditto*, 1.5km from the mine	Fine-grained granodiorite, slightly altered	0.002	+2.2		

Table 2 $\delta^{34}S$ data of porphyry copper deposits and related granitoids from the Philippines.

Locality	S (%)	$\delta^{34}S$ (‰)	$\Delta\delta^{34}S$ (rock-ore)
St. Niño, Luzon			
Copper concentrate		+1.7	
Granitoid (SN–1)	0.005	+9.5	7.8
St. Thomas (Philex), Luzon			
Copper concentrate		+3.5	
Ino, Marinduque			
Copper concentrate		+2.0	
Marcopper, Marinduque			
Copper concentrate		+0.1	
Sipalay, Negros			
Copper concentrate		−3.7	
Granitoid (altered)	0.07	−1.4	2.3
Basay (Southern Star), Negros			
Composite ore (BY–1, 5 & 7)		+5.0	
Atlas, Cebu			
Composite ore (AT–3, 7, 8, 11 & 15)		−0.5	
Granitoid (AT–1)	0.09	+8.2	8.7

possible contamination by ore sulfur. But this was not quite realized in some cases.

Extraction of sulfur for isotope analysis is done by the Kiba-reagent method (SASAKI et al., 1979). Copper-rich concentrates are mainly treated with a mixture of HI, HCl and H_3PO_2 (THODE et al., 1961). The extracted sulfur is then converted to SO_2 for the isotopic analysis following the method by ROBINSON and KUSAKABE (1975). A McKINNEY-type mass spectrometer (Hitachi RMU–6, modified type) is used for the analysis and the result is expressed in conventional $\delta^{34}S$ (CDT) permil notation. Overall experimental reproducibility in our routine analyses is estimated to be ± 0.2 permil (1σ) and this will apply also to the present work.

The isotopic results are summarized in Tables 1 and 2.

Results and Discussion

Rock sulfur

All but one examined rock samples returned positive $\delta^{34}S$ (CDT) values. As seen in Fig. 1, the trend is in accord with what has been observed for the magnetite-series granitoids in Japan (SASAKI and ISHIHARA, 1979). Eight specimens of the Chilean granitoids have the value ranging from +2.2 to +9.1 with an apparent concentration around +4 to +6. No clear distinction can be seen between the Mesozoic and Cenozoic terrains. Two Philippine rocks have higher δ values, +8.2 and +9.5. A negative value, −1.4, of an altered granitoid from Sipalay may indicate contamination with ore sulfur.

Among Japanese granitoids of the magnetite-series, relatively high δ values averaging +5 permil are specific to the terrains where the generation of magma seems to be related with subducting plate motion. A similar tectonic setting may be envisaged for the genesis of both the Chilean and Philippine granitoids concerned. If the positive $\delta^{34}S$ trend of magnetite-series granitoids implies that the magma has been influenced by isotopically heavy sulfur of marine origin (SASAKI and ISHIHARA, 1979), the more positive trend of Philippine rocks might indicate a higher contribution of marine sulfur in the magma genesis as compared with the case of Japanese and Chilean granitoids.
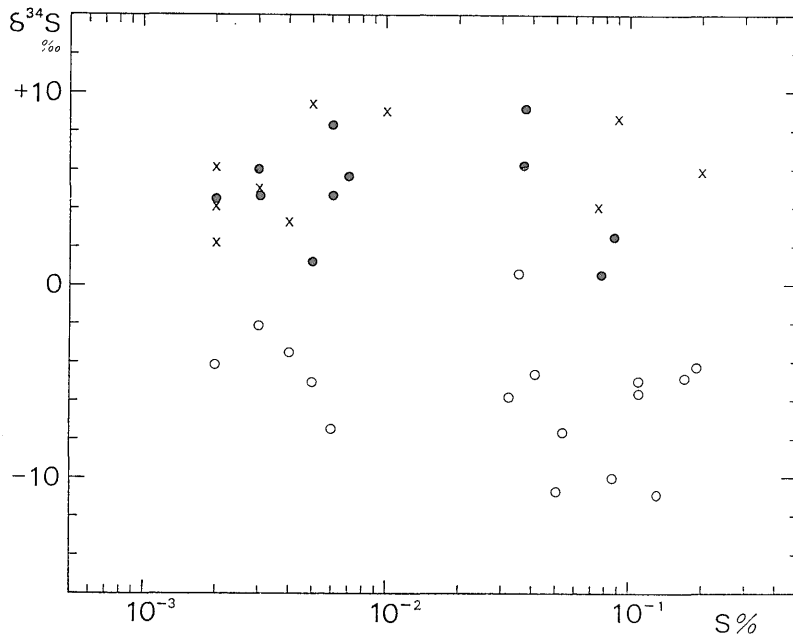
Fig. 1   Sulfur content and $\delta^{34}S$ of granitic rocks. Cross represents granitoids related with porphyry copper and manto-type deposits from Chile and the Philippines. Solid and open circles are, respectively, magnetite-series and ilmenite-series granitoids of Japan (SASAKI and ISHIHARA, 1979).
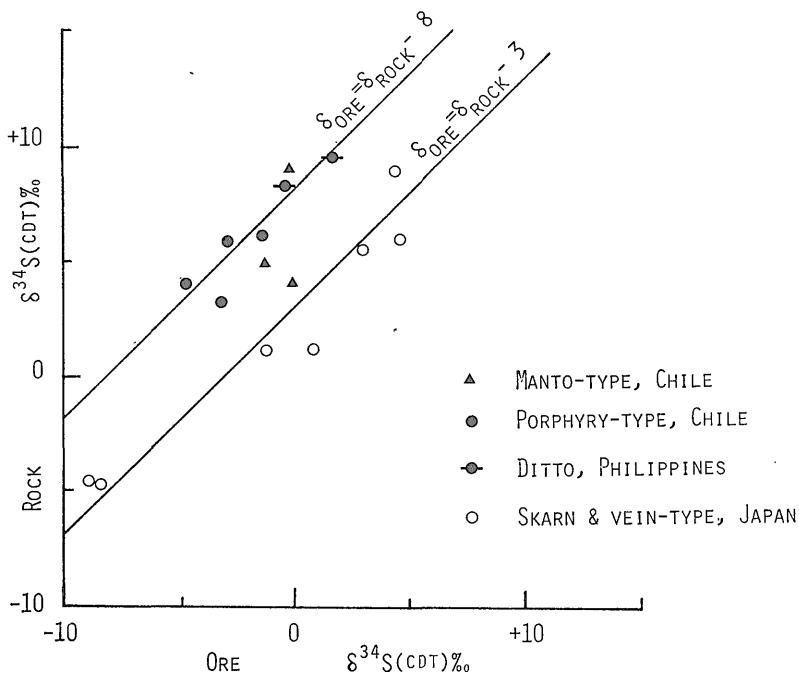

Fig. 2   Sulfur isotope relation between granitoids and associated ores.

Ore sulfur

In comparison with the rock sulfur, the sulfur in ores is remarkably enriched in the lighter isotope, ^{32}S, giving $\delta^{34}S$ (CDT) near zero or of even slightly negative trends. This relationship of the rock- and ore sulfur, $\delta^{34}S_{rock} > \delta^{34}S_{ore}$, is also similar to the trend observed for the Japanese specimens (SASAKI and ISHIHARA, 1980). These authors interpreted the observation as the result of isotopic partitioning between oxidized- and reduced sulfur species in the magma–ore-fluid system and subsequent deposition of the reduced species as sulfide ores. $\Delta\delta^{34}S_{(rock-ore)}$ values for the Japanese samples which are from the skarn and vein-type deposits cluster around 3 ± 1 permil, while in the porphyry and manto-type deposits of Chile and the Philippines the value of 8 ± 1 seems to be most common (Fig. 2).

Provided that a similar formative temperature prevails, larger Δ values would mean higher fo_2 conditions in the mineralization and, thus, more sulfur would have gone into the oxidized sulfur species *i.e.* sulfates through the mineralization. This seems consistent with the observation that hypogene sulfate minerals are quite common in most of the porphyry-type mineralizations, while Japanese deposits of granitic affinity are known to be nearly free of such minerals.

H_2S/SO_4^{-2} ratio in ore-fluid

As a first approximation it may reasonably be assumed that the sulfur in the magma–ore-fluid system concerned is distributed among H_2S and SO_4^{2-}, the most representative, reduced and oxidized, sulfur species. Then the partitioning of sulfur isotopes in the system is:

$$\delta^{34}S_{\Sigma S} = X\delta^{34}S_{H_2S} + (1-X)\,\delta^{34}S_{SO_4^{2-}} \cdots (1)$$

where ΣS represents the total sulfur and X denotes the mole fraction of H_2S. When equilibrium isotope exchange is attained δ values of the two sulfur species are related one another:

$$\delta^{34}S_{SO_4^{2-}} = \delta^{34}S_{H_2S} + \Delta\delta_{(SO_4^{2-}-H_2S)} \cdots (2)$$

where $\Delta\delta_{(SO_4^{2-}-H_2S)}$ is the equilibrium fractionation factor between SO_4^{2-} and H_2S, which is solely dependent on temperature. Formative temperatures of 400–600°C would be a reasonable assumption for the deposits of granitic affiliation, particularly for the porphyry-type mineralization (ROEDDER, 1979; FIELD and GUSTAFSON, 1976; OHMOTO and RYE, 1979). $\Delta\delta_{(SO_4^{2-}-H_2S)}$ for this temperature range may be estimated as 17 to 10 permil (OHMOTO and RYE, 1979).

Based on the above reasoning and further assuming the isotopic data for ore and rock sulfur given in Tables 1 and 2 to approximate $\delta^{34}S_{H_2S}$ and $\delta^{34}S_{\Sigma S}$ in the equation (2), respectively, X and (1–X) in the equation (1), namely H_2S/SO_4^{2-} ratio in ore-fluid, can be estimated for the mineralizations concerned (Table 3). In the table also included are the estimates for some Japanese mineralizations.

Table 3 Estimated ratio of H_2S/SO_4^{2-} of ore-fluid.

Deposit	(H_2S/SO_4^{2-}) I	(H_2S/SO_4^{2-}) II	Deposit	(H_2S/SO_4^{2-}) I	(H_2S/SO_4^{2-}) II
Porphyry copper deposits (Chile)			Manto-type deposits (Chile)		
Chuquicamata	50/50	15/85	Buena Esperanza	45/55	5/95
El Salvador	50/50	20/80	Cerro Iman	75/25	55/45
Rio Blanco	55/45	25/75	El Salado	65/35	35/65
El Teniente	60/40	35/65	Japanese deposits		
Porphyry copper deposits (Philippines)			Nippo (Fe-Cu skarn)	85/15	75/25
St. Niño	55/45	20/80	Kamaishi (*ditto*)	100/0	95/5
Atlas	50/50	15/85	Otani (Sn-W vein)	80/20	60/40

Figures are rounded to 5 % intervals.
Equilibrium temperature is taken to be 400°C (I), and 600°C (II).
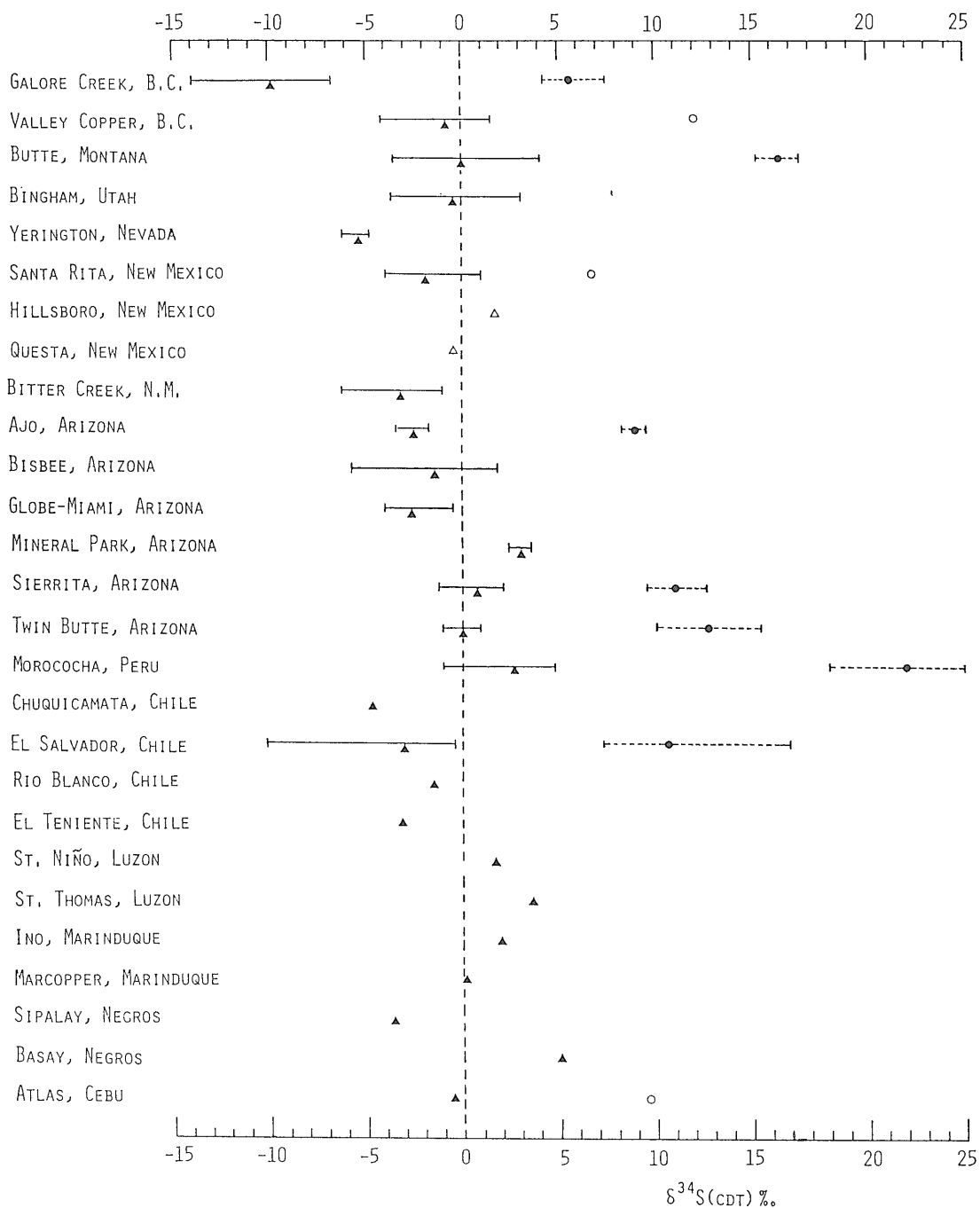
Fig. 3 Range and mean of δ³⁴S values of porphyry-type deposits. Triangle and circle represent sulfide and sulfate, respectively. Solid symbol is the mean value or the value for a mean sample. Open symbol stands for a single specimen. Compiled from FIELD (1966), FIELD and GUSTAFSON (1976), JENSEN (1971) OHMOTO and RYE (1979). A. SASAKI (unpublished data) and the present study.

As compared with the Japanese deposits, much higher concentrations of oxidized sulfur species in the ore-fluids of porphyry copper and manto-type deposits would be realized.

Data of other porphyry deposits

In Fig. 3, available isotope data of other porphyry-type mineralizations from the North and South American continents are summarized together with our results on the Chilean and Philippine examples. Most of the previous data were obtained for ore sulfides and in some deposits hypogene sulfates were also analyzed, whereas no data have been reported for rock sulfur to date.

It is seen that the $\delta^{34}S_{ore}$ of porphyry-type deposits from both the American continents shows a fairly consistent trend, indicating probably a common provenance in them. Our data on the Philippine deposits may suggest a slightly heavier ore sulfur here as compared to the American Cordillera. However, similar values do exist in some American deposits (*e.g.* Mineral Park), while other Philippine ores (*e.g.* Sipalay) are rather close to the Cordilleran trend. Thus, at the moment, what appears to be more intriguing is their similarity rather than dissimilarity.

Remarkably consistent, near zero $\delta^{34}S$ values of most of the Cordilleran ores have been thought to be a positive evidence for a simple magmatic origin of, or perhaps the mantle-derived, sulfur (*e.g.* JENSEN, 1971). The present investigation suggests, however, that the source sulfur would be better represented by the host granitoid sulfur which is much heavier than the ore sulfur, having an average $\delta^{34}S$ of around $+5$.

Concluding Remarks

A reconnaissance of rock- and ore sulfur isotopes of some porphyry copper deposits in Chile and the Philippines confirms that the systematics established for the granitoids and related ore deposits in Japan also applies to this group of mineralizations.

The Chilean granitoids of Mesozoic to Cenozoic times show $\delta^{34}S$ averaging $+5$ while two Philippine rocks return somewhat heavier values, $+8$ to $+9$, implying larger con-

tributions of marine sulfur in the magma genesis of the latter.

Ore sulfurs are always depleted in ^{34}S relative to the sulfur of source granitoid rocks. Average $\Delta\delta^{34}S_{(rock-ore)}$ is 8 ± 1 permil, being larger than the value for the Japanese ore deposits of granitic affinity, 3 ± 1, and indicates higher fo_2 conditions in the mineralization concerned. This is consistent with the occurrence of abundant hypogene sulfates in porphyry-type deposits.

In terms of sulfur isotopes there is a close similarity between porphyry copper and manto-type deposits.

Isotopic consistency in ore sulfurs of the North and South American porphyry-type deposits is a strong evidence for a common provenance and common formative mechanism in them.

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チリおよびフィリピンの斑岩銅鉱床・マント型鉱床の硫黄同位体比予察

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要　　旨

斑岩銅鉱床の硫黄同位体組成を関連花崗岩類のそれとの比較で検討した．日本の花崗岩類と関連鉱床の研究から明らかにされた規則性 (SASAKI and ISHIHARA, 1979; 1980) はこの場合にも成立ち，磁鉄鉱系花崗岩の硫黄に特有な同位体的諸傾向が確認された．チリの中生代花崗岩地域に多いマント型の銅（鉄）鉱床も硫黄同位体的には類似の傾向を示す．

花崗岩硫黄と鉱石（硫化物）硫黄間の同位体分別，$\Delta\delta^{34}S$（岩石－鉱石），はほぼ 8 ± 1 パミルとなり，スカルン型や鉱脈型鉱床で代表される日本の花崗岩系鉱化作用で見い出されている値，3 ± 1，より明らかに大きい．これは鉱化時の fo_2 がより高かったことを示唆するが，事実，斑岩銅鉱床には初生の硫酸塩鉱物を豊富に含むものが少なくない．

岩石硫黄から推定される鉱化系の全硫黄同位体比はチリの諸鉱床で $+5$ パミル前後，フィリピンではこれよりやや重く $+8\sim+9$ パミルとなる．