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# DISTRIBUTION OF SELENIUM IN HIGH-TEMPERATURE HYDROTHERMAL SULFIDE DEPOSITS AT 13° NORTH, EAST PACIFIC RISE*

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## ABSTRACT

"Black smoker" chimneys and Fe–Cu-rich massive sulfides are found on the axial graben and off-axis seamounts, respectively, of the East Pacific Rise at 13°N. The trace element selenium substitutes for sulfur in solid solution in all sulfide minerals. Electron-microprobe analyses were performed under optimal conditions to obtain a minimum detection-limit (MDL) of 30 ppm for selenium in chalcopyrite, with a calculated precision of 30 ppm. The Se content of the sulfides depends on the physicochemical parameters of the ore solutions during precipitation. High Se values occur in high-temperature mineral assemblages. The highest selenium contents are found in chalcopyrite ($\approx$ 2500 ppm) and in euhedral pyrite ($\approx$ 1500 ppm). For selected samples, the lowest mean concentration of Se in chalcopyrite is 645 ppm. These minerals precipitate in chimneys and in the middle part of the deposit, in equilibrium with the unmixed hydrothermal waters. On active vents, the inferred characteristics of the fluid are: $f(O_2)$ $10^{-35}$ atm, pH 3-4, $f(S_2)$ $10^{-10}$ atm, T 335°C. The lowest Se values occur in the outer part of the sulfide deposits, where mixing of pure hydrothermal waters and seawater [$f(O_2)$ $10^{-.64}$ atm, pH 7.8, T 2°C] is at a maximum. The mean S/Se value is in good agreement with that expected for hydrothermal or volcanic ores, but the range is much wider (250 to >50,000) and depends on physicochemical conditions of precipitation. This wide range of variation overlaps the S/Se values of massive sulfides considered characteristic of volcanic and sedimentary environments, respectively. This overlap suggests reconsideration of previous inferences made for these deposits on the basis of the S/Se value.

*Keywords:* selenium, East Pacific Rise, 13° North, massive-sulfide deposit, black smoker, S/Se value, high temperature, paragenesis, hydrothermal, chalcopyrite, pyrite.

## SOMMAIRE

Dans les cheminées de type «fumeurs noirs» et les sulfures massifs riches en fer et cuivre de la dorsale Est Pacifique à 13° Nord, respectivement à l'axe et sur les volcans sous-marins situés hors de l'axe, le sélénium remplace le soufre pour former des solutions solides dans tous les sulfures. Les analyses à la microsonde électronique ont été réalisées dans des conditions optimales (30 kV, 300 nA et 300 s) et ont permis d'atteindre un seuil de détection limite (MDL) de 30 ppm de Se dans la chalcopyrite. La précision calculée dans ces conditions est égale à 30 ppm. Les plus fortes concentrations de Se ont été rencontrées dans la chalcopyrite ($\approx$ 2500 ppm) et, à moindre teneur, dans la pyrite automorphe ($\approx$ 1500 ppm). La teneur moyenne la plus faible obtenue dans la chalcopyrite de certains échantillons atteint 645 ppm. Ces minéraux précipitent à l'équilibre avec les eaux hydrothermales dans les cheminées et au coeur des dépôts. Les caractéristiques du fluide mesurées sur les évents actifs sont: $f(O_2)$ $10^{-35}$ atm, pH 3-4, $f(S_2)$ $10^{-10}$ atm, T 335°C. Les faibles valeurs de sélénium sont localisées dans les parties externes des dépôts, où le mélange de l'eau hydrothermale pure et de l'eau de mer [$f(O_2)$ $10^{-.64}$ atm, pH 7.8, T 2°C] est maximal. La moyenne du rapport S/Se est en accord avec une origine hydrothermale et volcanique du dépôt. Cependant l'intervalle de variation est plus étendu (250 à >50 000) et est fonction des conditions chimiques de précipitation. Cette grande variation conduit à un recouvrement des valeurs entre les gisements de sulfures massifs associés à des basaltes et ceux qui sont associés à des sédiments. Ces observations remettent en cause les implications génétiques fondées sur la valeur du rapport S/Se.

*Mots-clés:* sélénium, ride Est Pacifique à 13° Nord, dépôt de sulfures massifs, fumeur noir, rapport S/Se, haute température, paragenèse, hydrothermal, chalcopyrite, pyrite.

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## INTRODUCTION

Since 1978 numerous hydrothermal sulfide deposits have been discovered along the East Pacific Rise and elsewhere in the eastern Pacific (Edmond *et al.* 1979, Hekinian *et al.* 1980, 1983a, b, Lonsdale *et al.* 1980, Koski *et al.* 1984, Renard *et al.* 1985, Bäcker *et al.* 1985, Hannington 1986). Mineralogical and geochemical studies indicate that most of these deposits have similar mineral assemblages (Oudin 1981, Février 1981, Koski *et al.* 1985, Hekinian & Fouquet 1985, Hannington 1986). The proportion of the different mineral assemblages depends on the maturity of deposits (Hekinian & Fouquet 1985). We have attempted to characterize differences among East Pacific Rise deposits by looking at variations in the trace-element content in different assemblages depending on stage of maturity, both in the bulk samples by XRF analyses (Fouquet *et al.*, in prep.) and by electron-microprobe studies of the individual sulfide minerals. We present here results concerning the selenium content of high-temperature sulfide minerals that occur in chimneys (black smokers) and mature copper-rich massive sulfides from 13°N.

## METHOD OF ELECTRON-MICROPROBE ANALYSIS

The Cameca electron microprobe (wavelength dispersion) was used to obtain our analyses. Bulk concentrations of selenium had previously been obtained for high-temperature hydrothermal deposits at 13°N (Hekinian & Fouquet 1985, Fouquet *et al.*, in prep.). The selenium concentration of the bulk samples (XRF) ranges from 100 to 1100 ppm. The absolute error is ± 5 ppm for values of Se ranging from 5 to 120 ppm. For greater values of Se, the estimated absolute error is extrapolated (P. Cambon, pers. comm.). This range was used to test the precision and minimum detection-limit (MDL) of the electron microprobe as a method of analysis for selenium in sulfides.

Analyses for Cu, Fe, Zn and S were performed at 30 kV, 15 nA and 6 s counting time. X-ray lines, crystals used and standards are listed in Table 1. A homogeneity test according to Buseck & Goldstein (1969) was carried out on the standards. A standard is homogeneous if $H$ is less than 1; $H$ is defined as $S/2s$, where $S$ is the standard deviation, and $s$ is the minimum standard deviation attained from the Poisson statistic. Table 2 gives values of $H$ for the different elements in the standards.

Analyses for Se were performed at 30 kV, with different values of the beam current (20–300 nA) and counting times (30–360 s) to select the optimal conditions and to test the resistance of the mineral to damage by the electron beam.

The Se$K\alpha_1$ X-ray line was measured with a LIF crystal. The background was determined on either side (sin$\alpha$ ± 0.00500) of the Se$K\alpha_1$ peak. X-ray lines of other major elements (Cu, Fe, Zn, S) and minor elements (Co, Ag, Mo, As, Pb, Cd, Au) are absent from the spectrum. The Se peak is absent from another standard (Strathcona chalcopyrite), which is known to contain less than 10 ppm Se (L.J. Cabri, pers. comm.).

### *Precision and minimum detection-limit (MDL)*

The minimum detection-limit (MDL) is defined as $\Gamma \geq 3^{*}\sqrt{B}/\sqrt{t}$, where $B$ is the number of background counts, and t the counting time. With the electron gun at 30 kV, a beam intensity of 300 nA and the counting time at 60 seconds, the minimum detection-limit for Se is 80 ppm. The highest precision was achieved for t = 300 seconds and reaches

TABLE 1. X-RAY LINES, CRYSTALS AND STANDARDS USED FOR ELECTRON-MICROPROBE ANALYSES

| | X-ray line | | | | |
|---|---|---|---|---|---|
| | Cu$K\alpha_1$ | Fe$K\alpha_1$ | S$K\alpha_1$ | Zn$K\alpha_1$ | Se$K\alpha_1$ |
| MINERAL | (LIF) | (LIF) | (PET) | (LIF) | (LIF) |
| Chalcopyrite | $CuFeS_2$(1) | $CuFeS_2$(1) | $CuFeS_2$(1) | ZnS(3) | CuFe(S-Se)(4) |
| Pyrite | $CuFeS_2$(1) | $FeS_2$(2) | " | " | " |
| Cubanite | $CuFe_2S_3$(5) | $CuFe_2S_3$(5) | " | " | " |

Standards weight fractions (1) Cu(34.62) Fe(30.43) S(34.94) ; (2) Fe(59.8)S(20.8) ; (3) Zn(67.09) S(32.90) ; (4) Cu(32.15)Fe(35.32) S(32.38) Se(0.15) ; (5) Cu(23.41) Fe(41.15) S(35.44).(1) Strathcona chalcopyrite ; (4) Synthetic standard (527) and (5) Natural cubanite was provided by L.J. Cabri.

TABLE 2. HOMOGENEITY VALUES (H) FROM STANDARDS USED FOR ELECTRON-MICROPROBE ANALYSES

| | STANDARDS | | |
|---|---|---|---|
| ELEMENTS | Cp. (1)* | S27 (4)* | Cb (5)* |
| Cu | 0.31 | 0.25 | 0.12 |
| Fe | 0.17 | 0.07 | 0.024 |
| S | 0.17 | 0.34 | 0.13 |
| Se | | 0.095 | |

* Standards weight fractions are given in Table 1.

30 ppm. Under these optimum conditions (300 nA, 30 kV, 300 s), the MDL reaches 30 ppm ± 30. For our samples, the lowest mean value was 645 ppm, and the analytical precision $\epsilon$ ($< 5\%$) is thus acceptable for this range of values. Two analytical methods are possible: 1) continuous counting for 300 seconds at one point or 2) ten 30-second analyses at the same point. The second option was preferred because it provided a test of the reproducibility of the analyses and a way to detect aberrant values. It also served as a test to monitor damage of the sample.

## LOCATION OF THE SAMPLES

The samples were collected during the Cyatherm (1982) and Geocyarise (1984) cruises to the hydrothermal area near 13°N on the East Pacific Rise (Hekinian *et al.* 1983a, b, Gente *et al.* 1984, 1986, Hekinian & Fouquet 1985) (Fig. 1). The results of bulk chemical analyses (XRF) of the different mineral assemblages collected at 13°N are given in Hekinian & Fouquet (1985) and Fouquet *et al.* (in prep.). We selected copper-rich samples, because of the high correlation-coefficient (0.84) calculated by the method of Davis (1973) between copper and selenium. Copper-rich samples are representative of a high-temperature association of Cu-rich sulfides from black smokers and Cu–Fe-rich massive sulfides.

In the axial graben, Cu-rich sulfides were recovered from active chimneys (Cy 82-21-2, Cy 84-13-1, Cy 84-29-7) at 2500 to 3000 metres below sea level. They correspond to the first stage of building a hydrothermal deposit. In this study, the three samples are selected in a collection of 16 Cu-rich chimneys. On those chimneys 10 measurements of temperature made by submersible indicate that the range of temperatures for the exiting hydrothermal fluid is 283 to 335°C. For sample Cy 84-13-1, a temperature of the hydrothermal fluid of 335°C, in equilibrium with inner chalcopyrite, was measured during Geocyarise dives (1984). The calculated temperature of the end-member fluid (Edmond *et al.* 1979) of this sample is 370°C. Temperatures of the exiting fluid for Cy 84-29-7 and Cy 82-21-2 samples were not measured.

Fe–Cu-rich massive sulfides were sampled on the top of the graben faults and on off-axis seamounts (Fig. 1). They correspond to a mature stage of development of a volcanogenic hydrothermal edifice (Cy 82-15, Cy 84-29-6, Cy 84-29-5) and were collected form a cross-section in the middle part of an extinct deposit. These mature and tectonized deposits form by a combination of hydrothermal precipitation and the accumulation of sulfides from the mechanical and chemical breakdown of unstable chimneys.

## STUDIES OF MINERALOGY AND PARAGENESIS

### *Active chimneys (Cy 82-21-2, Cy 84-13-1, Cy 84-29-7)*

The samples studied are cross-sections through three high-temperature black smoker chimneys; the axial conduit varies from 1 to 4 cm in diameter (Fig. 2b). They correspond to three different layers in a 50-cm-high theoretical chimney. Two zones are evident from the inner to the outer part of a section. 1) In the inner part of the conduit, chalcopyrite crystals are 0.5 cm in length and well formed. Crystal size decreases to 20 μm toward the outside. The width of this chalcopyrite zone is variable (Fig. 2b), from a few millimetres at the top of the chimney (Cy 82-21-2) to 2 cm in the third cross-section, 50 cm below (Cy 82-13-1). Observations using optical microscopy show that well-formed crystals of chalcopyrite grow inward in the conduit by crystal enlargement (zone 1, Fig. 2b), whereas porous microcrystalline crystals grow outward by replacement of anhydrite (zone 2, Fig. 2b). The lack of porosity in the inner part of the chimney allows for better insulation from seawater and the attainment of equilibrium of the Cu-sulfides with the hydrothermal fluid (Haymon 1983). 2) The outer part consists of anhydrite precipitated from heated seawater (Blount & Dickson 1969). The thickening of the chalcopyrite wall insulates progressively the outer part of the chimney from the hot hydrothermal fluid and results in dissolution of the anhydrite (Bischoff & Seyfried 1978). A consequence of this process is the oxidation of the outer part of chalcopyrite wall, producing bornite, digenite, covellite, hematite and magnetite. The outer layer of anhydrite is composed mainly of large crystals of anhydrite (200–300 μm). Sulfides, primarily represented by disseminated chalcopyrite spots (< 15 μm) and elongate crystals of pyrrhotite (~2 × 15 μm), are scarce in this layer (zone 3, Fig. 2b).

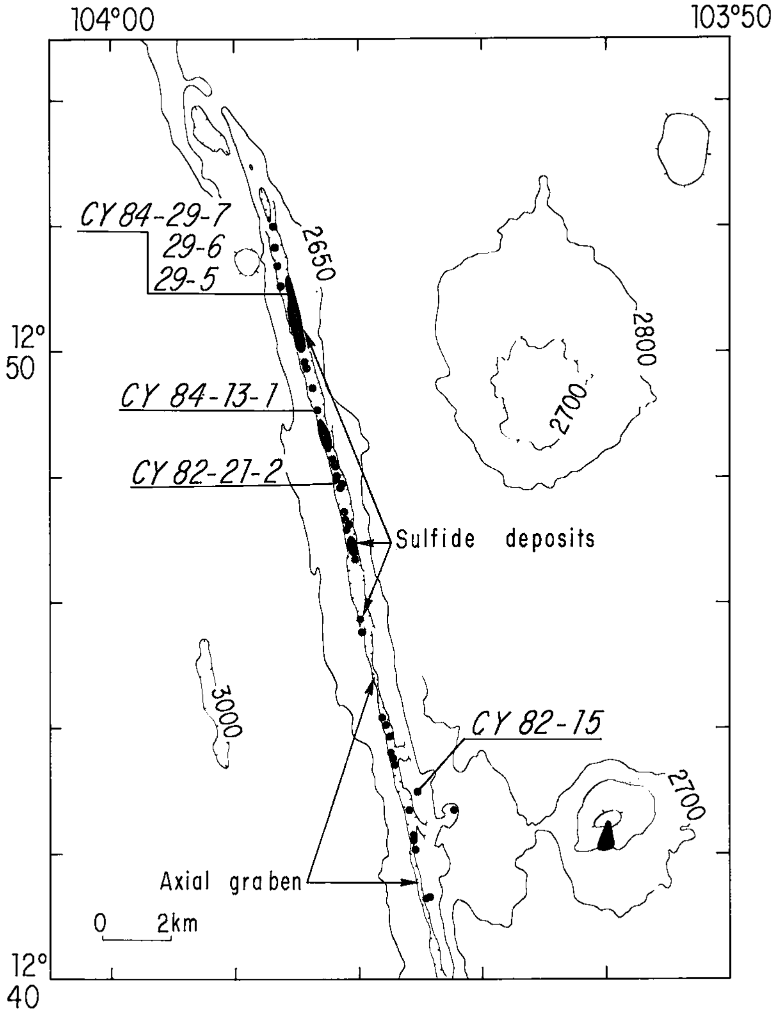

FIG. 1. Detailed bathymetric map at 12°50′N East Pacific Rise showing location of samples studied. This map was produced during the Clipperton cruise (1981) using a multibeam echo-sounder (SEABEAM). Samples were collected during Cyatherm (1982) and Geocyarise (1984) dives.

### *Fe-Cu-rich massive sulfides (Cy 82-15, Cy 84-29-6, Cy 84-29-5)*

No zonation was observed in these samples. During the maturation of the massive sulfides (Hekinian & Fouquet 1985, Fouquet *et al.*, in prep.), three successive associations of minerals occur. 1) Colloform layered and spherulitic pyrite is associated with microcrystalline marcasite and pyrite. Iron sulfate pseudomorphs after pyrrhotite are also encountered. This sequence occurs on top of sulfide mounds and corresponds to the early spongy stage in the maturation of the massive sulfides. 2) Idiomorphic pyrite develops in the open spaces, which leads progressively to less porous sulfides. Sphalerite microinclusions are encountered in euhedral pyrite. 3) In iron-rich samples, cavities can be filled by chalcopyrite, leading to mature copper-rich massive sulfides similar to those mined on land. Judging from temperatures of chalcopyrite crystallization in active chimneys, a temperature of more than 270°C is probable for this late stage of precipitation. This observation is consistent with the fact that samples were collected in the middle layer of hydrothermal deposits of massive sulfides. During the waning stage of hydrothermal activity, amorphous silica and marcasite are precipitated in the remaining cavities.

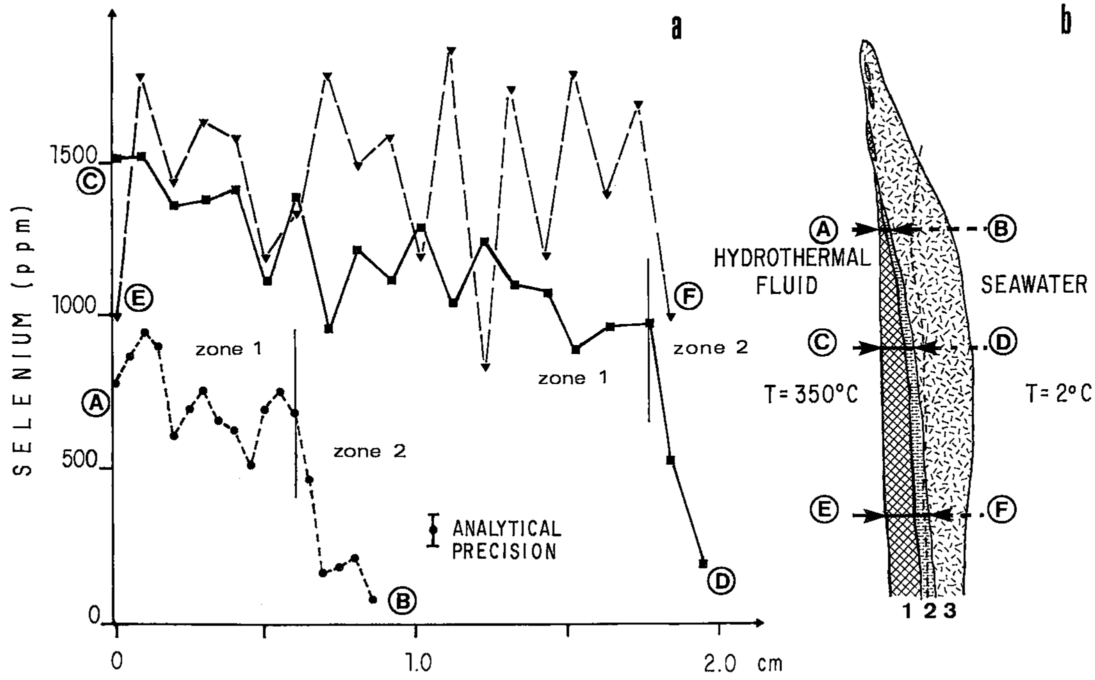

FIG. 2. a. Selenium concentrations (microprobe data) along 3 cross-sections in an idealized Cu-rich chimney. Location of the 3 sections are shown in Fig. 2b. Cross-sections A–B, C–D and E–F correspond, respectively, to Cy 82–21–2, Cy 84–29–7, Cy 84–13–1. Zone 1: chalcopyrite grows inward by crystal enlargement. Zone 2: chalcopyrite grows outward by replacement of anhydrite. Zone 3: large crystals of anhydrite and disseminated sulfides (chalcopyrite, pyrrhotite). Analyses were performed at 30 kV, 300 nA and 300 seconds. b. Half the longitudinal section of an idealized Cu-rich chimney. Dotted lines represent the oxidation front; 1, 2 and 3 refer to the Zones (Fig. 2a).

## DISTRIBUTION OF SELENIUM

### *Se in Cu sulfides from the black smokers*

In the three samples Cy 82–21–2, Cy 84–29–7 and Cy 84–13–1, bulk X-ray-fluorescence analyses yield, respectively, 470, 818 and 1095 ppm selenium. The Se content of primary (chalcopyrite) and secondary (bornite, digenite, covellite) Cu sulfides was measured by electron microprobe. The major Se concentration is localized in the primary Cu sulfides, such as the inner chalcopyrite; bornite, microcrystalline chalcopyrite and covellite have very low selenium contents ($< 30$ ppm). Chalcopyrite of the inner part (zone 1) of the black smokers has variable selenium contents, ranging from 100 to 2000 ppm. Figure 3a illustrates the distribution of selenium in chalcopyrite in the three analyzed samples. The mean Se-content reaches 645 ± 150 ppm in Cy 82-21-2, 1180 ± 280 in Cy 84-29-7 and 1375 ± 300 in Cy 84-13-1. Selenium content increases with maturation and thickening of the copper sulfide layer in the wall of the chimney. In two of the three samples reported in Figure 3a (Cy 82-21-2 and Cy 84-29-7), the Se content increases with the size of the chalcopyrite crystals. The extreme inner chalcopyrite, which is in equilibrium with the exiting hydrothermal fluid, has the greatest Se content (700, 1530 ppm) with respect to the outer chalcopyrite. The decrease in Se content with distance through the wall of the chimney (Fig. 2a) does not show the same slope for the three samples. The lack of selenium variation in the transverse section of sample Cy 84–13–1 is a consequence of the leaching of selenium during a stage of oxidation marked by the replacement of chalcopyrite by bornite, digenite and covellite and dissolution of anhydrite (Fig. 2a). The mean content of selenium increases with the thickness of the chalcopyrite layer.

### *Se in massive sulfides*

Trace concentrations of selenium were measured by XRF in the three Fe–Cu-rich samples Cy 82–15 (335 ppm), Cy 84–29–5 (450 ppm) and Cy 84–29–6 (627 ppm). Electron-microprobe analyses show that chalcopyrite has a greater Se-content than pyrite (Fig. 3b). Mean and ranges of Se in ppm in chalcopyrite are, respectively, 850 ± 500 (0–2500), 450 ± 350 (10–1000) and 780 ± 600 (160–1700). The respective values in ppm are lower for pyrite: 500 ± 500

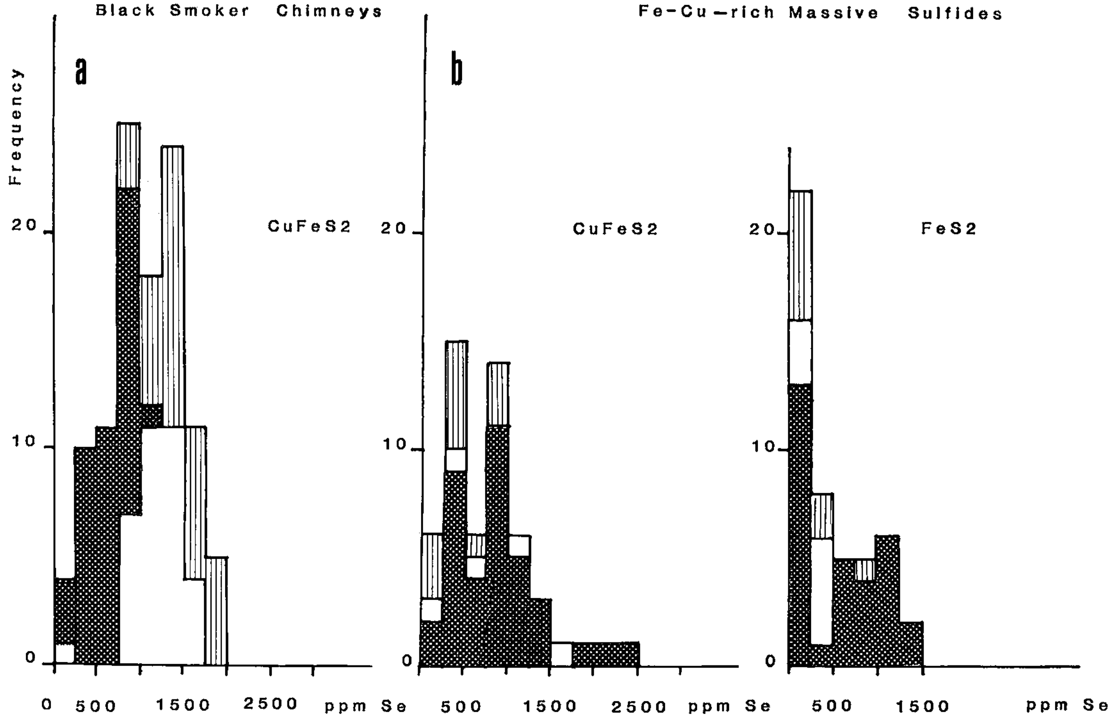

FIG. 3. a. Histogram illustrating distribution of selenium in Cu-rich chimneys. Dark pattern: sample Cy 82–21–2, vertical ruling: sample Cy 84–29–7, unpatterned: sample Cy 84–13–1. b. Histogram illustrating distribution of selenium in Fe-Cu-rich massive sulfides in colloform, euhedral pyrite and chalcopyrite. Dark pattern: sample Cy 82–15, vertical ruling: sample 84–29–5, unpatterned: sample Cy 84–29–6.

(0–1500), 240 ± 200 (0–870) and 260 ± 180 (0–480). In the three samples studied, euhedral pyrite has a higher Se content than colloform pyrite. Yudin (1964) also observed the highest concentrations of selenium in the well-formed sulfides. We do not observe any significant zonation of Se content within chalcopyrite or pyrite grains nor any variations in color or reflectivity between different crystals. Selenium distribution is homogeneous in a single grain.

In the hydrothermal edifice, the S/Se value ranges from 290 in the copper-rich inner zone to more than 50,000 in the iron-oxide outer zone (Fig. 4). In sulfide particles collected in vent fluids (Senant 1985) and in the stockwork mineralization, the S/Se value reaches 500 (440–730) and 5000 (1500– > 10,000), respectively. The range of S/Se values is large among individual minerals species. For example, in chalcopyrite the S/Se value is 230 to 300, and in Fe–Zn-rich sulfides (sphalerite or wurtzite), it can reach more than 50,000. The lowest S/Se values are encountered in active high-temperature chimneys. During the maturation of the deposit, Se content increases progressively from 5 ppm in the porous iron-rich outer part of the deposit (zone VI, Fig. 4) to 820 ppm in the massive copper-rich inner part (zone II, Fig. 4). This enrichment is related to a decrease in porosity that prevents mixing of hydrothermal fluid and seawater.

## DISCUSSION AND CONCLUSION

Previous studies on the geochemical behavior of Se in natural environments (Goldschmidt 1954, Hawley & Nichol 1959, Tischendorf 1966, Bethke & Barton 1971) reported that Se is a chalcophile trace element concentrated in high-temperature volcanic, magmatic or hydrothermal massive-sulfide ores. In these ores, galena and chalcopyrite are the usual hosts for Se. Under the same pressure–temperature conditions of crystallization, the S/Se value does not vary among sulfide minerals in equilibrium. Our detailed mineralogical studies, results of electron-microprobe analyses and a bibliographic compilation (*e.g.*, Hawley & Nichol 1959, Février 1981, Oudin 1981, 1983, Koski *et al.* 1984, 1985, Cabri *et al.* 1985, Hekinian & Fouquet 1985, Hannington 1986) show that there are no selenides in mid-ocean-ridge sulfides and that all the selenium is to be found in solid solution in chalcopyrite and pyrite.

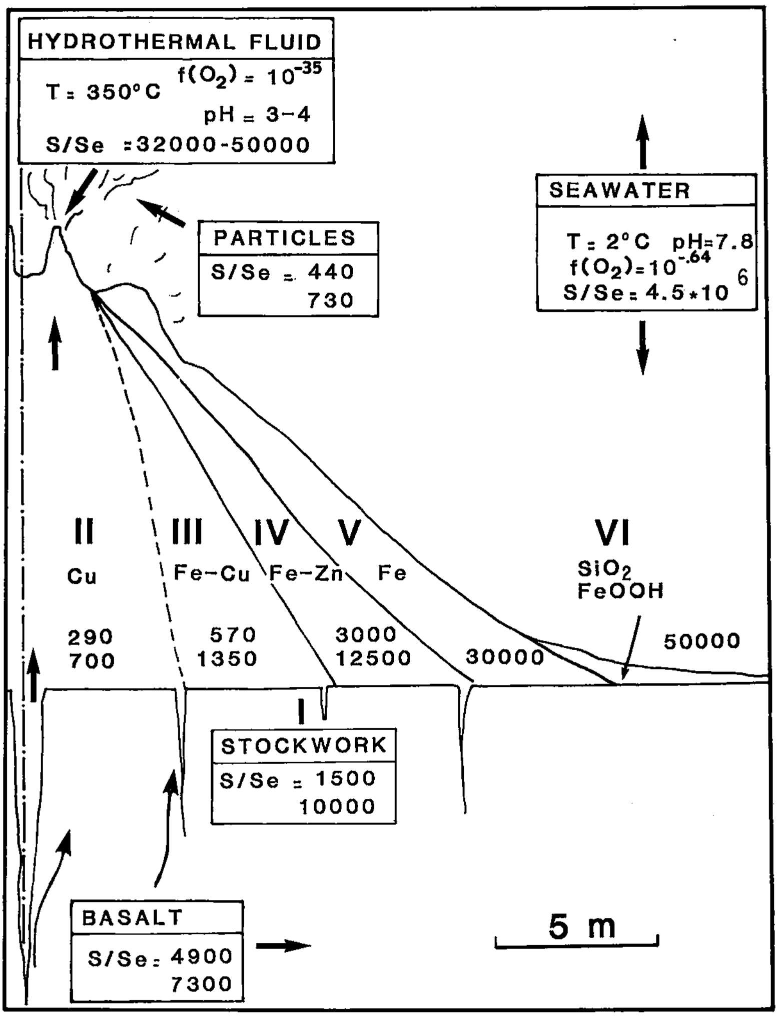

FIG. 4. Variation of S/Se ratio in present-day hydrothermal edifice, as proposed by Hekinian & Fouquet (1985). I Stockwork mineralization, II sulfides formed at high temperature during localized event of chimney formation, III high-temperature Fe–Cu-rich sulfides, IV intermediate-temperature Fe–Zn sulfides, V low-temperature porous Fe sulfides, and VI oxidized formation of primary sulfide phases and silica deposits.

The top of the chimney is largely composed of anhydrite and disseminated chalcopyrite. In this porous environment, chalcopyrite precipitation can be explained by two processes. 1) Replacement of anhydrite by chalcopyrite is produced by circulation of the hydrothermal fluid through the chimney wall. During this process, sulfur and selenium from anhydrite are incorporated in chalcopyrite. The Se content of anhydrite is low (<90 ppm), and the chalcopyrite resulting from this process has a high S/Se value (4000 ppm). 2) Chalcopyrite precipitation is produced by mixing of the hydrothermal exiting fluid with seawater. Chalcopyrite saturation is due to an increase in oxygen fugacity and pH and a decrease in temperature. The Se content of the chalcopyrite collected in the plume ranges from 460 to 800 ppm. This variation is due to mixing of hydrothermal fluid and seawater in different proportions.

The combination of these two processes produces the steep variation in Se content observed at the top of the chimney (Fig. 2, cross-section A-B). Lower in the chimney (Fig. 2, cross-sections C- D, E-F), this area, a few millimetres wide, corresponds to the outer zone of the chalcopyrite wall (zone 2, Fig. 2b). The later supergene oxidation of this zone produces Cu sulfides such as bornite, digenite and covellite.

In the lower part of the chimney, the progressive thickening of the chimney wall causes a sealing of the hydrothermal fluid in the conduit by inward growth of chalcopyrite (zone 1, Fig. 2b). Under these conditions, we do not expect large variations of the physicochemical parameters. The pH (3–4), $f(O_2)$ ($10^{-35}$ atm), $f(S_2)$ ($10^{-10}$ atm) do not vary greatly during crystallization of chalcopyrite (Oudin 1981, 1983, Zierenberg *et al.* 1984).

Conductive cooling is more efficient in a thin wall of chalcopyrite. Then, as the chalcopyrite grows inward, we can expect an increase of precipitation temperature. Janecky & Seyfried (1984) and Bowers *et al.* (1985) indicated that during conductive cooling, $f(O_2)$ does not change greatly, and pH decreases slightly. Yamamoto (1976) noted that at temperatures near 300°C, a change in pH by one unit does not produce a variation in log S/Se value of sulfide minerals. Therefore, at near-constant values of $f(O_2)$ ($10^{-35}$ atm) and pH (3–4), without native selenium in the ore solution, the inward increase of Se in chalcopyrite can only be explained by temperature increase of precipitation. Von Damm *et al.* (1985a) reported Se contents (70–80 nmol/g) in 21°N EPR vent fluids, which are exiting at 350°C, and no Se in NGS vent fluid, which is conductively cooled from 350 to 273°C. These data suggest that at higher temperature, more selenium can be incorporated into sulfides from the ore solution (Tischendorf 1966, Yamamoto 1976). The general trend of Se increase, observed in zone 1 (Fig. 2b), is consistent with thickening and better sealing, both of which progressively reduce conductive cooling.

In the massive sulfides, the Se enrichment observed from the outer zone to the inner part of the edifice is related to a decrease in porosity. This process leads to: 1) low temperature, high $f(O_2)$ and high pH for precipitation of the young porous outer part of the deposit (zone V, Fig. 4). As we concluded previously for the chimneys, we observe here that these conditions are not favorable to Se substitution in sulfides. 2) The progressive sealing of zone IV to zone III (Fig. 4) leads to high temperature, low $f(O_2)$ and low pH during precipitation of Zn-sulfides and chalcopyrite in the open spaces. These conditions are optimal for Se incorporation in the structure of sulfides. In zone

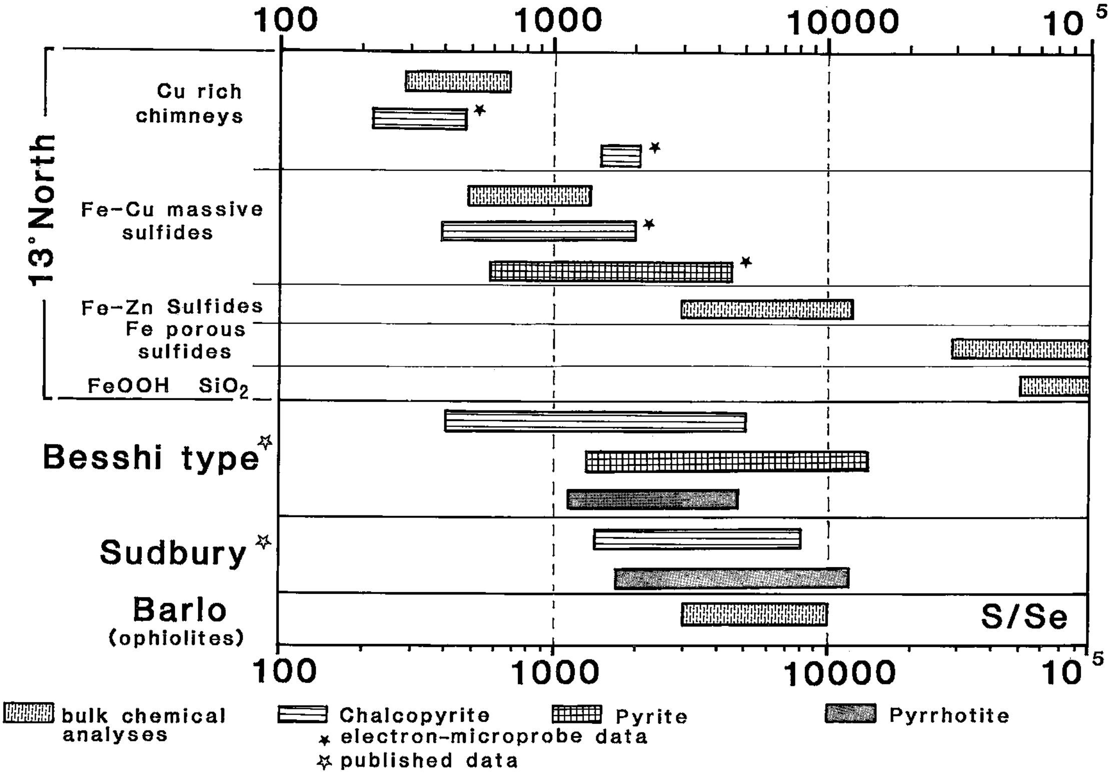

FIG. 5. S/Se values in different parageneses encountered in present-day hydrothermal deposits at 13°N EPR compared with fossil submarine hydrothermal massive sulfides such as in the Barlo deposits in the Zambales ophiolite (Boirat & Fouquet, in prep.), Besshi-type deposits (Yamamoto *et al.* 1984) and Subdury deposits (Cabri *et al.* 1984, 1985).

II (Fig. 4), chemical conditions are similar to those described for the lower part of the Cu-rich chimney.

Figure 4 shows the large range of S/Se values found in a typical hydrothermal edifice [such as the one described by Hekinian & Fouquet (1985)], in the basalt, in the exiting hydrothermal fluid and in seawater (Kay & Hubbard 1978, Rise Project Group 1980, Chaussidon & Sheppard 1986, von Damm *et al.* 1985a, b). Isotopic studies (Arnold & Sheppard 1981, Zierenberg *et al.* 1984) on $\delta^{34}S$ show that most (80–90%) of the sulfur come from the basalt. The S/Se value in oceanic basaltic rocks varies in a narrow range (4900–7300). The wide range of the S/Se values in our samples implies fractionation of Se with respect to S/Se ratio during leaching from the basalt, or mineral deposition (or both). Von Damm *et al.* (1985a) showed that S/Se in hydrothermal fluid from 21°N EPR is 32,000 to 50,000. This indicates a fractionation of Se during leaching.

In sedimentary rocks, S/Se varies very widely [10,000 in shales to >100,000 in other sedimentary rocks: Hem (1978), Leutwein (1978)]. If we assume that efficiency of extraction of the hydrothermal solution is similar in both environments, we may expect an overlap of S/Se values obtained in the basaltic hydrothermal sulfide ores and in the sedimentary hydrothermal ores. Thus it is difficult to make genetic inferences based on the values of the S/Se ratio in fossil deposits. At 13°N, the high Se-content of the exiting vent-fluid can explain the Se anomaly found in proximal hydrothermal sediments (A. Birolleau & J.L. Charlou, pers. comm.).

Very few data on S/Se values are available for fossil submarine volcanogenic hydrothermal deposits in ophiolitic terranes. S/Se values in iron–copper- and zinc-rich assemblages in the Barlo massive-sulfide deposit in the Zambales ophiolite, Philippines (Boirat & Fouquet, in prep.), range from 3,000 to 10,000, a very narrow interval compared to present-day seafloor deposits (Fig. 5). Some data are also available for massive sulfides in other environments. Values of the S/Se ratio in different minerals occurring in Besshi-type deposits (Yamamoto *et al.* 1984) and in Sudbury ores (Cabri *et al.* 1984, 1985) are also compared to present-day hydrothermal deposits at 13°N (Fig. 5). Pyrite and chalcopyrite of Besshi-type deposits have S/Se values similar to those encountered in pyrite and chalcopyrite of the Cu–Fe massive-sulfide samples at 13°N EPR, whereas in the Sudbury deposits, the S/Se values range only from 1200 to 12,000. Present-day hydrothermal sulfide deposits at 13°N appear to have a wider range of Se contents than other fossil hydrothermal, magmatic, or sedimentary ores. The mean value of the Se concentration in sulfides is also higher than in fossil deposits. Different depositional environments could also be an explanation for this discrepancy.

In conclusion, we can say that our data agree with the conclusions of Loftus-Hill & Solomon (1967) and Goldschmidt (1954), who indicated that a low S/Se value is characteristic of deposits of hydrothermal origin. Nevertheless, in the deposits studied in the present work, the value of S/Se ratio varies over a wide range and is related to chemical conditions of sulfide precipitation. Therefore, this wide variation in the S/Se ratio cannot be used to discriminate between volcanic and sedimentary massive-sulfide environments.

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