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A study of sulfur isotopes in the Outokumpu
ore deposit, Finland

by Markku Mäkelä



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A STUDY OF SULFUR ISOTOPES IN THE
OUTOKUMPU ORE DEPOSIT, FINLAND

BY

MARKKU MÄKELÄ

WITH 15 FIGURES AND ONE APPENDED TABLE

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In order to gain information on the genesis and post-depositional changes of the Outokumpu stratiform copper ore deposit, 258 sulfur isotope analyses from 13 systematically taken sample populations have been performed. The $\delta^{34}\text{S}$ values for sulfidic sulfur range from +5.8 to -19.2 permil, the arithmetic mean being -3.5 permil.

A sedimentary derivation is suggested and a submarine volcanic-exhalative mechanism is favored for generating the isotopic patterns characterizing three different stages during the ore deposition.

Profile data showing insignificant lateral $\delta^{34}\text{S}$ variation along the length axis of the main ore body are presented.

The relation between the pyritic ore and massive pyrrhotitic ore is studied in terms of sulfur isotope fractionation. Uncertainty remains, however, as to whether the pyrrhotitic ore is a result of primary deposition of monosulfides or an alteration product of the pyritic ore.

As an overall effect, a depletion of ^{34}S in remobilized sulfides by an average of 2.6 permil is observed, and solid-state diffusion is considered to be the main factor causing the depletion.

The delta values involving 59 pyrite-pyrrhotite pairs and 10 pyrite-sphalerite pairs are presented, and an equilibrium temperature of around 350°C is calculated.

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INTRODUCTION

Many attempts have been made to explain the genesis of the Outokumpu copper ore deposit. The discussion began ten years after the discovery, in 1920 when Mäkinen (1921) first described the geology of the Outokumpu ore deposit. Mäkinen suggested that the ore is epigenetic in origin and closely connected with the serpentinites, from which it had possibly been derived by means of differentiation.

Trüstedt (1921), the leader of the exploration activities, considers that the ore had originated from the Maarianvaara granite in the neighbourhood.

Väyrynen (1928) regards sulfides to have been original constituents of the sediments. The metamorphism caused by granitic intrusions has only concentrated these original sulfides forming the ore. Later on (1939) Väyrynen considered the whole of the Outokumpu complex as a nappe pushed over from the north-east with the ore intruding into it as a real ore magma.

Eskola (1933) thought that chrome-bearing minerals encountered in the deposit are hydrothermal in origin and closely related to the serpentinites of the region. In 1944 (p. 164—166) Eskola states that the Outokumpu ore is late magmatic i.e. pneumotectic in origin.

Disler (1953) holds the opinion that the ore had intruded the quartzite horizon which had opened up during the folding as one single phase. Not until later during metamorphism did the quartzitic country rock become mineralized. Thus, according to Disler, the banded pyritic ore type is younger than the massive inner parts of the ore.

Vähätalo (1953) considers the banded pyritic ore type to be older than the massive one since it occurs as fragments in the latter. According to him the metasediments in the complex were deposited in their present position and the ore melt intruded conformly into the quartzitic part of the complex. He also concludes that the ore is derived from a hypothetical dioritic or granodioritic primary magma. This is suggested by the average cobalt to nickel ratio in the ore being to 2 : 1.

Borchert (1954) makes a synthesis of the descriptions presented by Disler (*op.cit.*) and Vähätalo (*op.cit.*) and sees similarities between the Outokumpu ore deposit and the deposits of the Ergani-Meggen-Rammelsberg type. According to Borchert, submarine exhalations caused the original ore formation.

Saksela (1957) holds the opinion that the Outokumpu ore originates from the black schists and sulfide-bearing quartzites by the selective mobilization of sulfides.

The application of stable sulfur isotopes to the problems of ore genesis has provided additional information on the formation of numerous mineral deposits (Jensen, 1959; Stanton, 1960 a; Ault and Kulp, 1960; Gavelin *et al.*, 1960; Tatsumi, 1965; Anger *et al.*, 1966; Sakai, 1968; Grinenko *et al.*, 1969; Sangster, 1971; Ohmoto, 1972).

The aim of the present sulfur isotope study is thus to gain information on the genesis and post-depositional changes of the Outokumpu copper ore deposit. Outokumpu was selected for the first systematic sulfur isotope study on the Finnish Precambrium because of the immense amount of geologic information available for interpreting the sulfur isotope data.

BASIC CONCEPTS

The chemical properties of an element depend essentially on the number and configuration of the orbital electrons. The isotopes of each element slightly differ, however, in their rate of chemical behavior because of the slight differences in their thermodynamic properties. This fact forms the basis for isotope geochemistry.

Consequently, a molecule containing the light isotope differs in its thermal properties, such as internal energy, heat capacity, and entropy, from one containing the heavy isotope of the same element. These differences lead to the equilibrium fractionation of isotopes between coexisting phases. In addition to the equilibrium isotope effects, there are kinetic isotope effects linked with unidirectional chemical reactions. The isotope fractionation introduced is then a function of the rate constants for the isotopic substances. Variations in the isotope composition of the elements in natural materials result from both equilibrium and kinetic fractionations.

The geological utilization of sulfur isotope abundance ratios, i.e. sulfur isotope geochemistry, began in 1949 with the publication of Thode and his group (Thode *et al.*, 1949). In the same year the paper by Trofimotov was also published »Isotopenzusammensetzung des Schwefels in Meteoriten und irdischen Objekten» (Trofimotov 1949).

Vinogradov (1954) hoped to find information about ore-forming processes and on the original source of metals in rocks and ores by means of sulfur isotope studies. Although sulfur does not occur in abundance, it is widely distributed as a principal constituent of minerals that have formed throughout a broad spectrum of geologic environments, which in turn are representative of diverse physiochemical conditions. These conditions are reflected in the isotopic composition of sulfur. Thus, the use of stable sulfur isotopes is a significant and independent method for the investigation of modes of formation and post-depositional histories of mineral deposits and the earth's crust.

Four stable isotopes of sulfur occur in nature in the approximate abundances $^{32}\text{S} = 95.0\%$, $^{33}\text{S} = 0.76\%$, $^{34}\text{S} = 4.22\%$ and $^{36}\text{S} = 0.014\%$ (Bradt *et al.*, 1956).

Most sulfur isotope studies are generally concerned with the ratios of the two more abundant species, ^{32}S and ^{34}S . The results are reported as permil (‰) difference from a primary standard as follows:

$$\delta^{34}\text{S} \text{ ‰} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} - 1 \right] \times 1000$$

Sulfur from the Canyon Diablo meteorite troilite, with $^{34}\text{S}/^{32}\text{S} = 0.0450045$ (Jensen and Nakai, 1963), has been generally accepted as the standard and therefore has $\delta^{34}\text{S} = 0 \text{ ‰}$. Positive and negative permil values represent, respectively, enrichment and depletion of ^{34}S relative to this standard.

DESCRIPTION OF THE DEPOSIT

The Outokumpu copper ore deposit is situated in the western part of the Karelian schist formation (Fig. 1). It is connected with a long ribbon-like, 50° striking zone, the so-called Outokumpu complex, which is principally composed of quartzites, black schists, and serpentinites. The complex dipping to the south-east has been traced some 30 km, its average width being about half a kilometer. The Sotkuma gneiss granite dome in the north-east represents the basement of the Karelian schist formation. Only one acidic intrusive unit, the so-called Maarianvaara granite, occurs in the neighbourhood of the complex. Pegmatite dykes, thought to be connected with this granite, crosscut the Outokumpu complex in a few places.

According to the radiometric age determinations carried out on zircon using the U, Th—Pb method (Wetherill *et al.*, 1962), the Sotkuma gneiss granite dome exhibits an age of 2 470 m.y.. This should, however, be considered as a minimum for the basement, which generally has an age of 2 700—2 800 m.y..

The common lead determinations on Outokumpu galenas (Kouvo and Kulp, 1961) suggest an age of about 2 250 m.y. for the original ore-forming fluids. The only igneous rocks originating from the same event interval as the Outokumpu galenas are diabases resulting from the Early Karelian volcanic activity, which have radiometric ages of 2 150—2 160 m.y. (Sakko, 1971). Recently ages of 2 250 m.y. have been determined for Early Karelian diabases (Sakko, 1973, pers.comm.). These determinations were carried out on zircon and sphene by the U, Th—Pb method.

By using the Rb—Sr method muscovite from a pegmatite dyke crosscutting the ore has been shown to have an age of 1 845 m.y. (Kouvo, 1958). Using the same method on a phlogopite, an age of 1 820 m.y. has been determined (Kouvo and Tilton, 1966).

The mica schists and mica gneisses outside the Outokumpu complex represent originally pelitic sediments, graded bedding being the most typical primary structure in well preserved parts. They are quartz- and feldspar-bearing biotite schists which

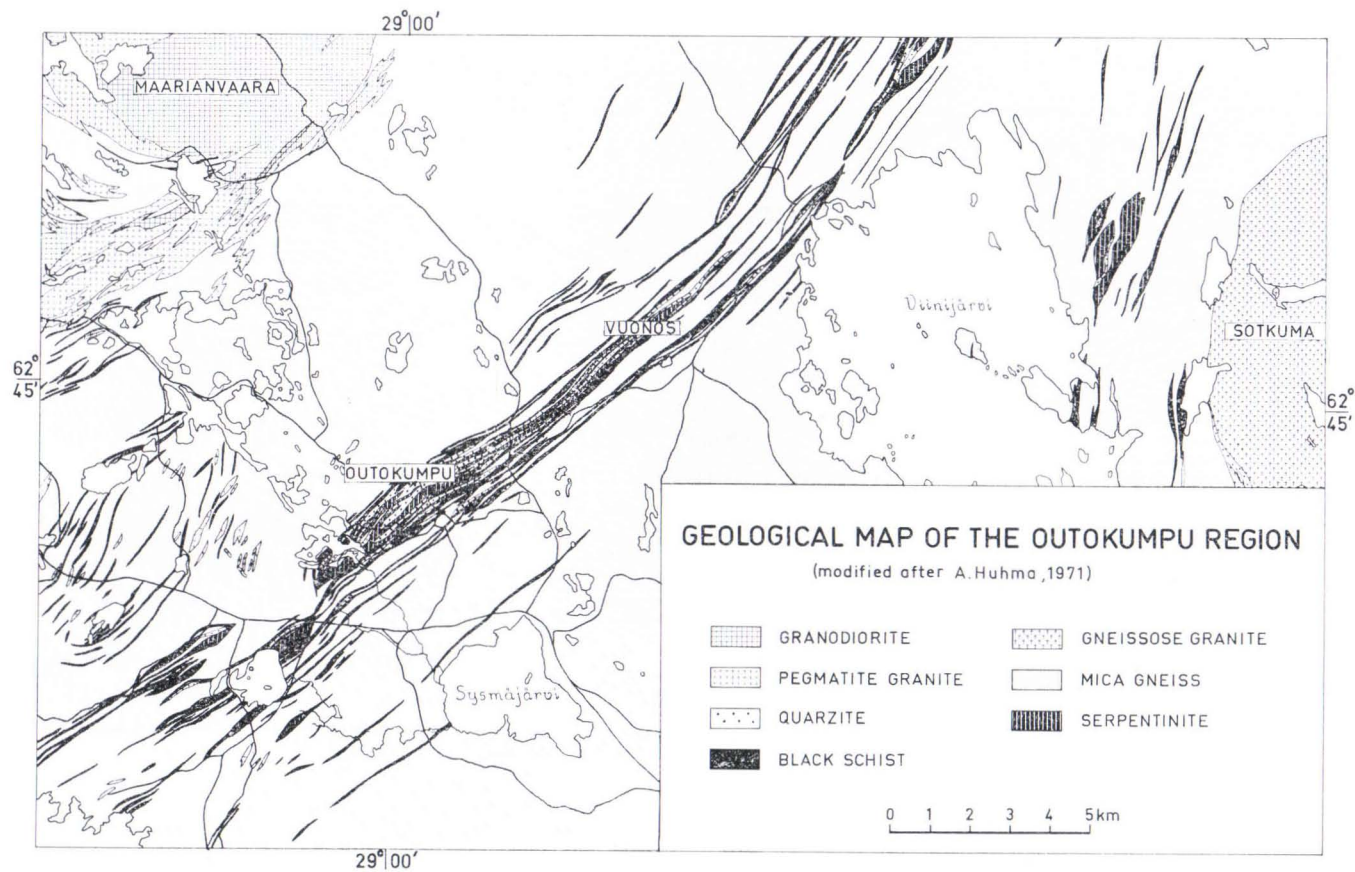


FIG. 1. Geological and geographical location of the Outokumpu copper ore deposit,

regularly contain small amounts of almandine porphyroblasts (Peltola, 1960). The high feldspar content is a characteristic feature. Inside the complex the schists are more homogenic as the bedding becomes less distinct or is entirely absent. This is due to the decrease in the amount of biotite. Instead of biotite, muscovite occurs frequently in schists encountered in the central parts of the complex.

The black schists form the outermost unit of the complex against the surrounding mica schists. They also intercalate the quartzite. The structure is banded due to the alteration of fine-grained carbon-bearing layers with the coarser quartz- and sulfide-bearing layers. There are two peculiarities, the occurrence of thucholite as an accessory and the small but regular vanadium content (mean 0.1 % V_2O_5) in the black schists (Peltola, 1960).

The thickness of the black schists varies from a few meters to 100 m., the length of individual layers being some hundreds of meters or even a few kilometers.

Quartzite is the immediate host rock of the ore. It occurs in layers varying in thickness from a few meters to 100 meters, their length being several hundreds of meters or even a few kilometers. The Outokumpu quartzites always occur together with the large serpentinite bodies, the larger the bodies are the thicker are the quartzites. In general, quartzites of the Outokumpu type are encountered only in connection with large serpentinite bodies (Huhma and Huhma, 1970). In their purest form the quartzites are almost monomineral quartz rocks. There exist also skarn-bearing varieties with diopside and/or tremolite in narrow bands or wider zones parallel to the schistosity. Megascopically quartzites are banded, the structure being most conspicuous in the skarn-bearing varieties or varieties containing mica, graphite and sulfide pigment. They do not contain detrital heavy minerals, which are invariably present in the sedimentary quartzites of common Karelian type (Huhma and Huhma, *op.cit.*). The clastic texture is absent, and graded bedding or current bedding has not been encountered. Actually, Huhma and Huhma (*op.cit.*) have interpreted the Outokumpu quartzites as being chemical colloidal silica precipitates.

Dolomite usually occurs in the immediate contacts of the serpentinite. There are plate-like or irregular serpentine inclusions in the dolomite, the amount of which increases towards the serpentinite. A lime-bearing transitional series between quartzite and dolomite or ophidolomite can invariably be encountered as follows: quartzite — diopside skarn — diopside tremolite skarn — tremolite skarn — tremolite dolomite rock — dolomite — ophidolomite. The thickness of the series varies from a few centimeters to several meters. Dolomite is of metasomatic origin (Haapala, 1936) and the skarns were formed through the reaction between the quartz and dolomite.

On a large scale, the serpentinite lenses, conformly following the structural features of the surrounding schist zone, form the central parts of the Outokumpu complex. The dimensions of the lenses vary a great deal, the largest being a few hundreds of meters in width and several kilometers in length. The information obtained from the diamond drillings suggests that the serpentinites are also surrounded by mica schists at the bottom. According to the mode of occurrence, the

Outokumpu serpentinites may be interpreted as ophiolites in the sense of Rittmann (1960, p. 180). Serpentinites are almost monomineral serpentine rocks containing variable amounts of magnetite as a fine dust and clinochlore-sheridanite. Pseudomorphs after olivine and amphibole are frequently met whereas those after pyroxenes are less common.

The Outokumpu stratiform ore body lies in one of the quartzite layers pinching out into the serpentinite. On a large scale, the ore follows the folding of the quartzite layer everywhere. The thickness of the ore body is usually from 7 to 9 meters, but can in places reach a thickness of up to 40 meters. The width varies within the limits of 200 to 400 meters, the length being 4 000 meters. In its upper parts the ore body dips 60°—30° to the south-east, bending in its lower parts to an almost horizontal position. The average mineralogical composition of the ore is chalcopyrite 10.7 %, pyrite 21 %, pyrrhotite 24.6 %, and sphalerite 1.5 % the rest being mainly quartz. The chemical composition is: Cu 3.71 %, Fe 28.19 %, S 24.75 %, Zn 1.07 %, Co 0.20 %, Ni 0.11 %, Ag 8.9 ppm., and Au 0.6 ppm., respectively. The ore reserves were originally about 28 milj. metric tons.

Structurally the ore can be divided into two portions, a banded and a massive one. In general the banded portion is pyrite-predominant, whereas pyrrhotite prevails in the massive ore type.

The orientated banded portion containing variable amounts of pyrite and chalcopyrite as a fine- or medium-grained dissemination is encountered in particular in the central and upper foot-wall parts of the ore body (Fig. 3). In its most striking form, the banded structure parallel to the schistosity occurs in the satellite ore body some 20 meters below the main ore lens (cross section 73), where the sulfide bands vary in thickness from a few millimeters to several decimeters, alternating with quartzite, black schists and a leptitic rock type, petrologically interpreted by the author as an acid volcanic rock (Figs. 7, 8).

In the foot-wall parts of the main ore body there are also sulfide bands separated from each other by purer quartz- or occasionally skarn-bearing intercalates, which belong to the host rock of the ore. The amount of the clearly visible siliceous intercalates diminish towards the inner parts of the ore body.

In comparison with the clearly orientated and banded portion, the pyritic ore in the inner parts shows many epigenetic features. It is strongly folded and brecciated, with pyrrhotite and chalcopyrite filling up tectonically favourable spaces in the originally banded pyritic ore. In the extreme case, a banded and subsequently folded ore type occurs as separate fragments in the more sulfide containing and coarser-grained matrix.

The massive portion of the ore, with pyrrhotite and chalcopyrite as sulfidic matter, is in particular encountered in the lower edge and in the hanging-wall side of the ore body (Figs. 3, 4). To the south-west from the profile 75 (Fig. 2), the percentile share of the pyrrhotite-predominant ore type increases until the south-westernmost end of the ore body consists entirely of this ore type. The pyrrhotitic ore type tends

to occur in the vicinity of the skarn-bearing intercalates (Fig. 9). The transition between the two ore types is gradual taking place within a maximum distance of some decimeters. Pyrite porphyroblasts as large as 1 000 μm^3 are occasionally encountered in the massive pyrrhotitic ore.

It should be pointed out that ore types such as banded pyrrhotite-predominant ones and massive ore with pyrite prevailing do occur in the deposit. Thus, the division compatible with structure and mineral content is to a certain extent artificial. However, the division has as its basis the fact that two distinct but highly consistent ore types are characteristic of conformable pyritic ore bodies such as that at Outokumpu — a banded pyritic ore and a non-banded pyrrhotite-chalcopyrite ore (Stanton, 1960).

SAMPLE POPULATIONS AND LABORATORY PROCEDURES

The location of various sample populations containing 258 analysed sulfide specimens (126 pyrite, 98 pyrrhotite, 24 chalcopyrite, and 10 sphalerite) are marked in Figs. 2, 3, and 4. All the samples, except the population K 1724, represent the ore proper, the sulfur isotope composition of the host rocks being omitted from this study.

The samples were crushed and screened to such a grain size that no intergrowths and/or inclusions could be seen in sulfides intended for sulfur isotope analysis. Chalcopyrite and sphalerite were isolated by hand selection under a binocular microscope from a fraction with the grain size varying from 1.0 mm to 0.63 mm. Concentrates of pyrite and pyrrhotite were prepared by the standard technique of heavy liquid and magnetic separation from a fraction with the grain size varying from 0.105 mm to 0.074 mm. The effectiveness of these treatments was controlled by ore microscopy using the point-counting method and X-ray analysis. The amount of foreign sulfide contaminants was less than 4 percent in pyrite and pyrrhotite concentrates.

The samples from the sample population K 1724 containing only minor amounts of sulfides, mainly pyrite, were crushed and the pyrite was oxidized to BaSO_4 . The sulfate was then reduced with $\text{Fe} + \text{Zn}$ at 950°C and converted into CdS by precipitation in a Cd-formiate solution.

The SO_2 preparation for mass spectrometer measurement was carried out by reacting 0.14 mMol sulfide with 0.44 mMol V_2O_5 at $1\,000^\circ\text{C}$ in an evacuated and sealed silica tube (Ricke, 1964).

The analyses were performed on an Atlas CH 4 mass spectrometer, equipped with a double gas handling system for viscous gas flow (Brunnée and Voshage, 1964, p. 101). The samples were introduced into this system by breaking the silica tubes in vacuum. The double collector null bridge of the mass spectrometer has a direct digital read-out from which the data are transferred to punch cards together with other information concerning the samples. At the computer the $\delta^{34}\text{S}$ values are calculated from the input values, and the results are listed in a table and punched into cards (Nielsen, 1967). Measurements are done as a sample-to-sample comparison.

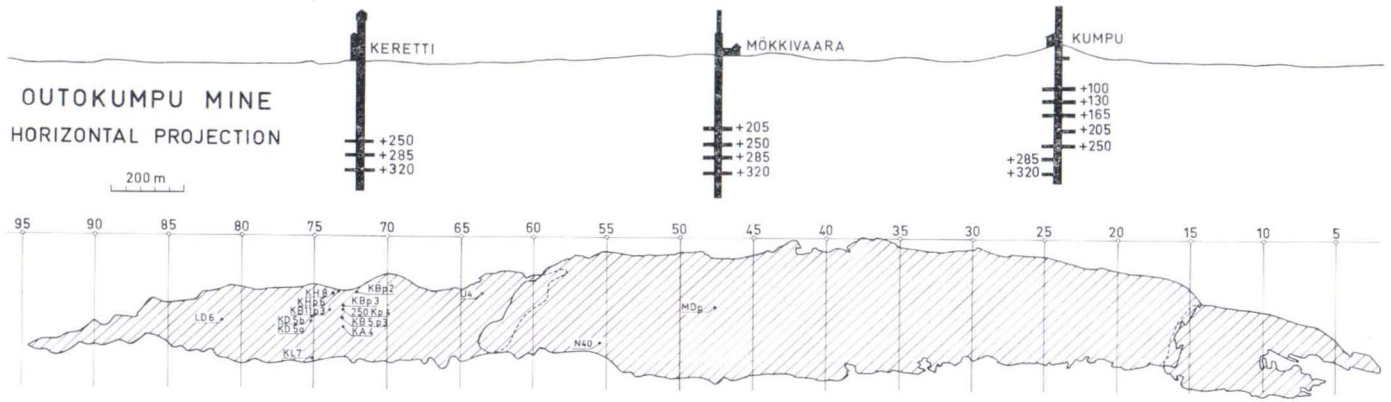


FIG. 2. Location of sample populations in horizontal projection.

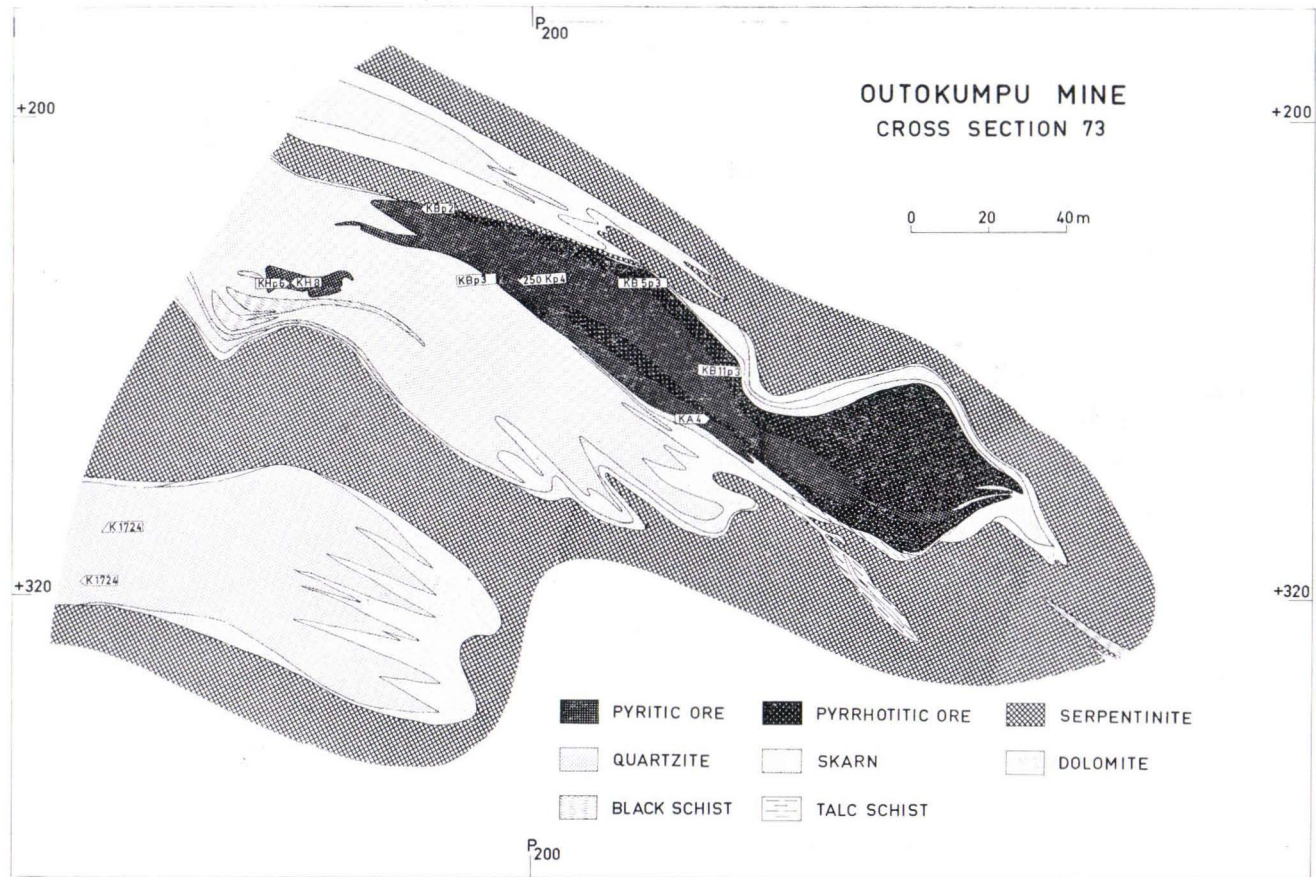


FIG. 3. Location of sample populations in cross section 73.

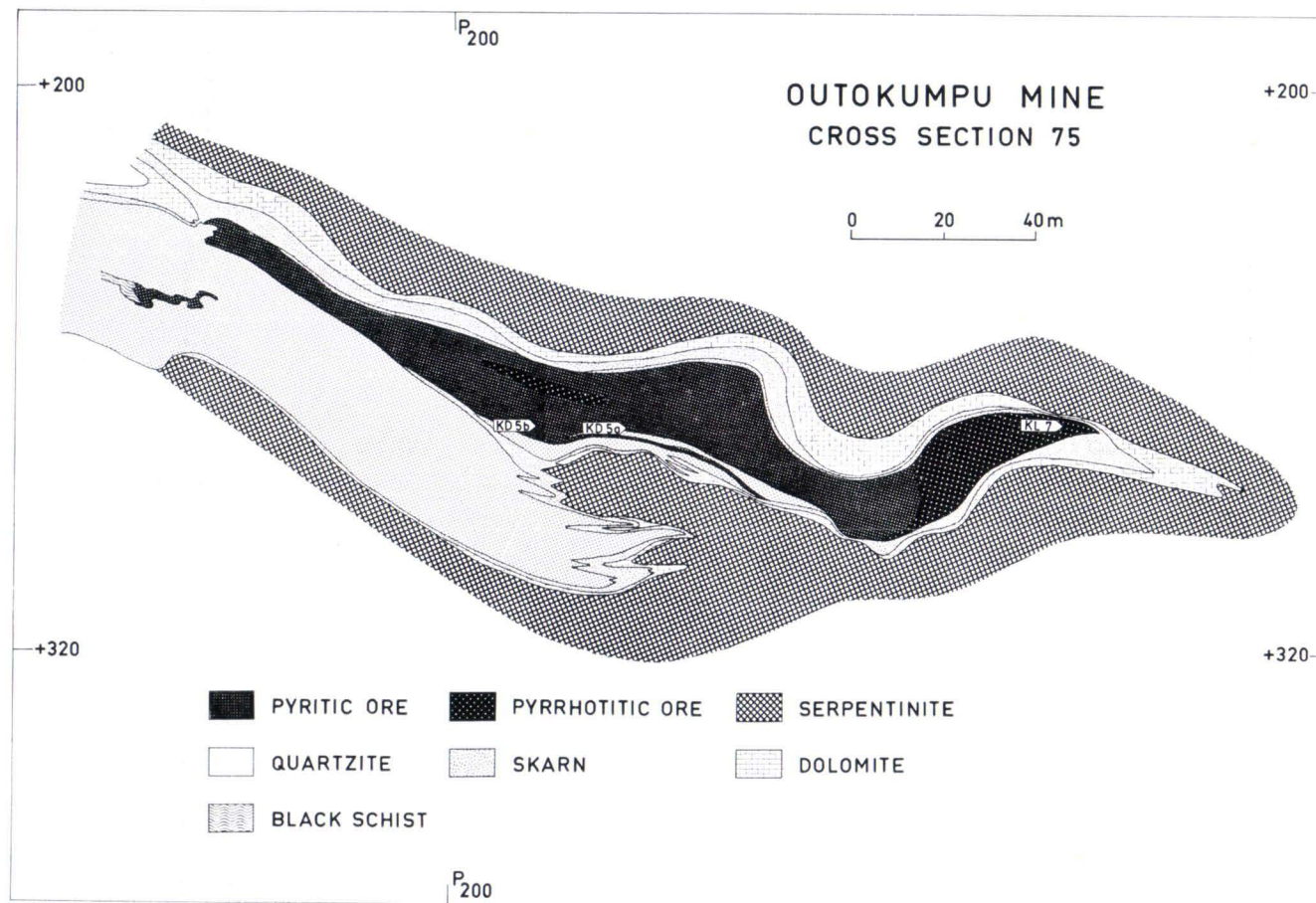


FIG. 4. Location of sample populations in cross section 75.

Groups of samples are linked together to form a cycle, terminated by working standards on both sides. All working standards are again linked to the standard sulfide, Canyon Diablo troilite. The analytical precision of the data is within ± 0.2 permil.

The pyrite oxidation, the preparation of SO_2 for mass spectrometer measurements, as well as mass spectrometric analyses were carried out by the author in the Isotope Laboratory of the Geochemical Institute of the University of Göttingen.

RESULTS AND DISCUSSION

The $\delta^{34}\text{S}$ values for sulfidic sulfur in the Outokumpu deposit range from $+5.8$ to -19.2 permil: the arithmetic mean is -3.5 permil. The overall range of 25 ‰ can be divided into three groups according to the frequency of various $\delta^{34}\text{S}$ values (Fig. 5). Beginning with the more negative values, the first group consists of sulfides from the banded pyritic ore in the satellite ore body together with the

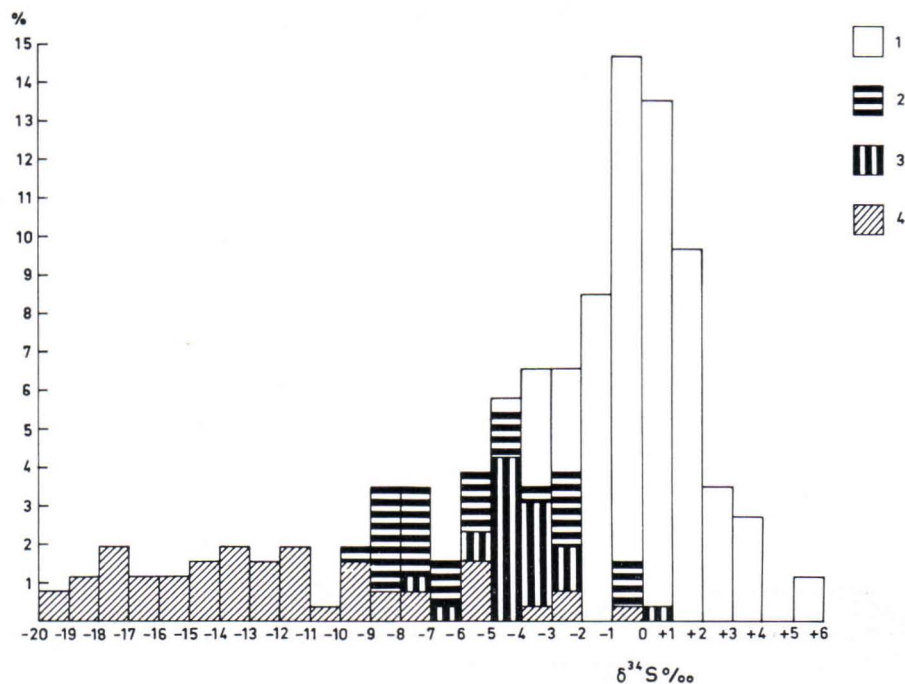


FIG. 5. Histogram of the $\delta^{34}\text{S}$ values of Outokumpu sulfides.

- 1 pyritic ore without banding and massive ore with pyrrhotite and chalcopyrite as sulfidic matter in the main ore body
- 2 remobilized sulfide material
- 3 banded pyritic ore of the main ore body
- 4 banded pyritic ore in the satellite ore body and pyritic sulfides from a quartzite layer outside the ore proper.

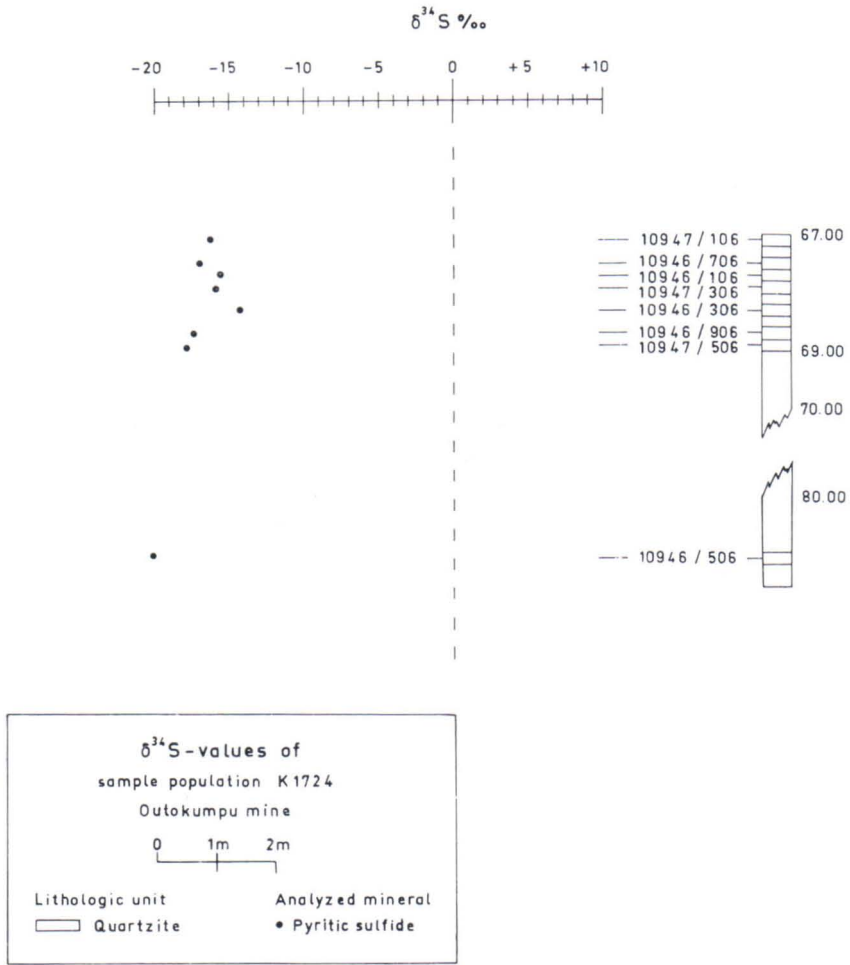


FIG. 6.

pyritic sulfides from a quartzite layer outside the ore proper containing only minor amounts of sulfides. The second and intermediate group contains the samples from the banded pyritic ore type on the foot-wall side of the main ore body together with the samples representing the remobilized sulfide material in the main ore body. The remaining 58 percent of the present data belong to the third group containing the samples from the pyritic ore type without clear banding, as well as the massive ore with pyrrhotite and chalcopyrite as sulfidic matter.

The analytical data of 13 separate sample populations and their relationships are presented in following paragraphs. All $\delta^{34}\text{S}$ values of the analyzed 258 sulfide specimens are given in the appended table.

Quartzite outside the ore proper

Fig. 6 gives the $\delta^{34}\text{S}$ values of the sample population K 1724 containing pyritic sulfides from quartzite in its present position some 60 meters below the main ore body (Fig. 3). Only minor amounts of sulfides can be seen even microscopically in this quartzite.

The $\delta^{34}\text{S}$ values are fairly uniform ranging from -14.3 ‰ to -17.9 ‰ in the core distance of 14 meters and thus reflect comparatively stable conditions during the precipitation of these insignificant quantities of sulfide material. As will be discussed in connection of the interpretation of the isotopic patterns across the satellite ore body, the deficiency of sulfides together with the uniform but negative $\delta^{34}\text{S}$ values of those present are explained by high f_{O_2} conditions in the parental fluid outside the stability field of pyrite.

Satellite ore body

The sample populations KHp 6 and KH 8 are taken from the satellite ore body at its present position some 20 meters below the main ore body and 40 meters above the sample population K 1724 described above (Fig. 3). The horizontal distance between these channel samples is 18 meters. Figs. 7 and 8, giving the $\delta^{34}\text{S}$ values and lithology of the channel samples, are placed on adjacent pages in such a manner that their mutual relationship corresponds to that in nature. The transition from the foot-wall side to the hanging-wall means that the observation of the diagrams is from bottom to top.

The regular fluctuation of the $\delta^{34}\text{S}$ values is the most striking feature in both channel samples. In KHp 6 the $\delta^{34}\text{S}$ values range from $+1.9$ ‰ to -19.2 ‰. The extreme values in KH 8 are -1.1 ‰ and -17.3 ‰ respectively. The correspondence of the isotopic patterns is good according to the curve fittings. The fittings have been calculated using the method based on least squares. The result is indicative of synchronous precipitation of sulfides in conditions temporarily the same in both places. The lack of well-defined interdependence between the isotopic composition and lithologic unit in both channel samples indicates in turn the existence of a single sulfur source. If the channel samples are divided into fractions of the same length (22 cm) used for the curve fitting calculations, there exists a positive correlation between the sulfide content of the fractions and the more positive $\delta^{34}\text{S}$ values.

The patterns showing a regular fluctuation could also originate from tight isoclinal folding of material originally lying flat and exhibiting progressively more negative $\delta^{34}\text{S}$ values from bottom to top. According to the detailed structural mapping carried out by Koistinen (Gaál, Koistinen, and Mattila, 1974) in KH 8, only the portions from 1/KH 8 to 5/KH 8 and 21/KH 8 to 26/KH 8 are critical with respect to isoclinal folding.

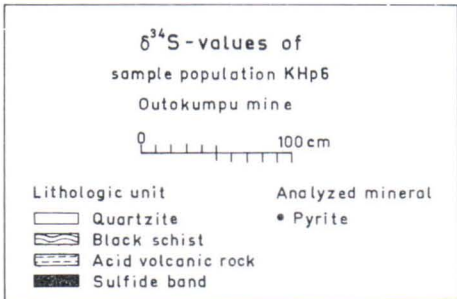
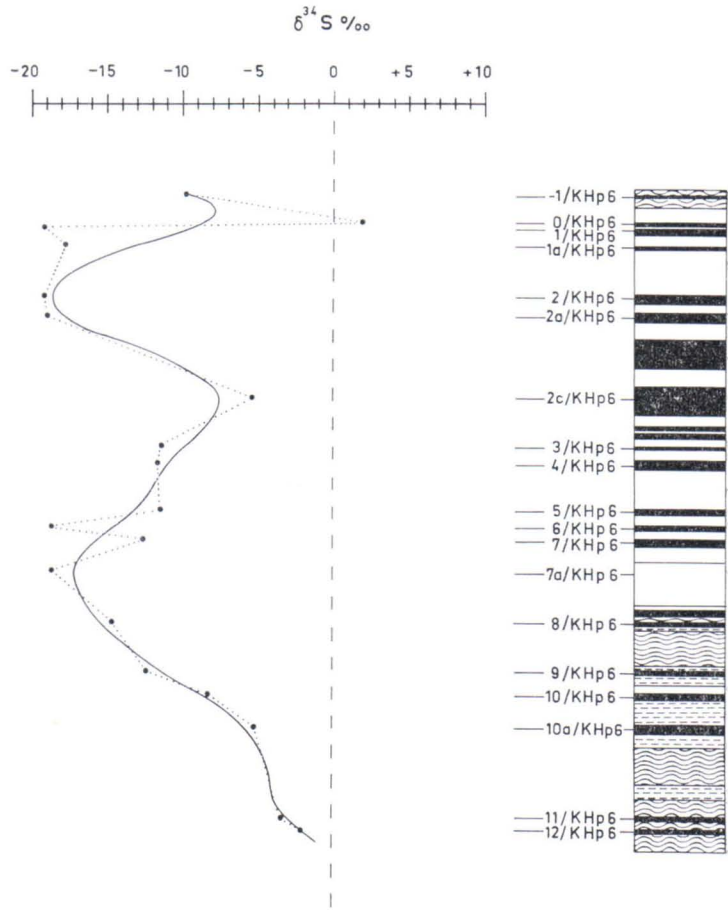


FIG. 7.

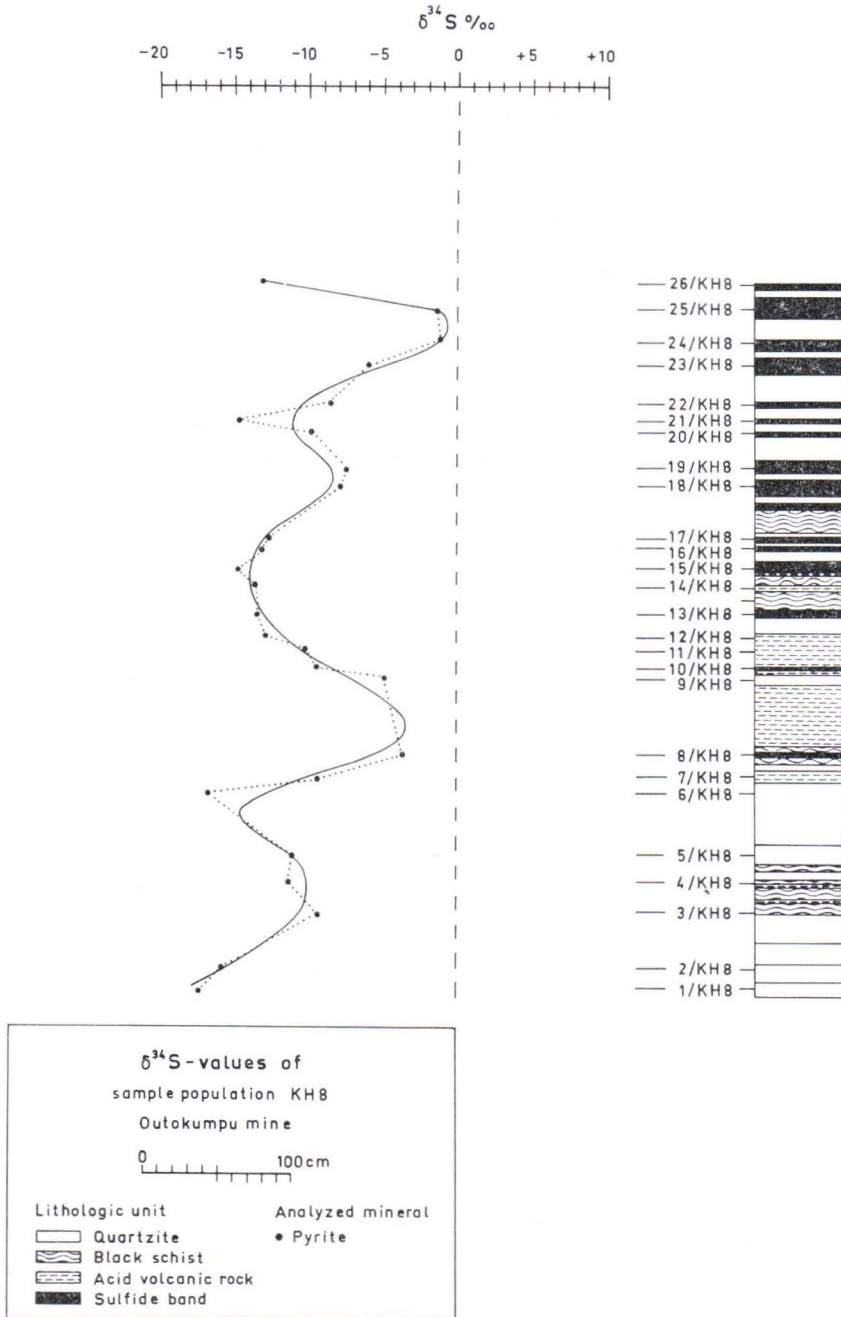


FIG. 8.

On the basis of the mineralogical as well as isotopic data the sedimentary deposition of the material is beyond doubt. Settling of successive sulfide precipitates alternating with silica accumulation has produced the mineralogical layering, and the thermochemical conditions associated with the precipitation of each layer are reflected in the isotopic data. Two alternative mechanisms of sulfide precipitation, one biologic and the other volcanic-exhalative, fulfil the requirement of sedimentary derivation.

A wide variation in sulfur isotope composition or the existence of $\delta^{34}\text{S}$ values far removed from zero (i.e., more than ca. 7 permil deviation from zero) have been taken to be highly indicative of a biologic origin for native sulfides (Jensen, 1967). A general lack of consistency characterizes the patterns of sulfur isotope variation for pyrite sulfur within the sedimentary column (Thode *et al.*, 1960). This is because the sulfur isotope composition of bacterially produced sulfur species are dependent on a variety of factors of which age and local environmental conditions including temperature, nature and abundance of the nutrient source, sulfate concentration, magnitude of reservoir, pH and redox potential, are all important. In order to produce such regularly fluctuating isotopic patterns observed across the satellite ore body, it is required that this multivariable system would have remained interdependent. This for its part leads to the requirement of extremely high sedimentation rates.

In the euxinic basin of the Black Sea, radiocarbon dating shows an average sedimentation rate of about 1 cm per 100 years (Ross *et al.*, 1970). In the Red Sea, radiocarbon dating indicates average accumulation rates for brine-derived materials of about 1 cm per 25 years (Ku *et al.*, 1969). During burial and lithification the sediments typifying the stratiform ore deposit would probably be compared to something like one third, or even less, of their original thickness (Trudinger *et al.*, 1972). Taking the sedimentation rates in the Black Sea and Atlantis II Deep in the Red Sea as representative of relatively low and high sedimentation rates respectively, and taking the influence of burial and lithification into account, the sedimentary column studied in KH 8 would have required something between 36 450 and 145 800 years for accumulation. It is improbable that the multivariable system controlling the isotopic composition of bacterially produced sulfidic sulfur would have stayed interdependent for such a long period.

In the biologic or normal-sedimentary mechanism an organic mass is necessary as the source of the external energy needed for reduction of SO_4^{2-} to S^{2-} . There are black schists at the foot-wall side and as intercalates in the satellite ore body (Figs. 7, 8) to form this mass, provided that carbon, now present as graphite, is organic in origin. Assuming this is the case, the bacterial population density would thus have been exceptional during the sedimentation of the black schists. This should in turn be reflected as an anomaly in the sulfur isotope patterns. The $\delta^{34}\text{S}$ values of the samples taken from the black schist intercalates do not, however, deviate from the overall fluctuation trends of the isotopic patterns. The result is thus in contradiction to the idea of biologic precipitation.

A submarine volcanic-exhalative mechanism implies that stratiform sulfide ores are formed from hot metal- and sulfur-bearing fluids discharged from a volcanic vent system on the sea floor. The exhaled fluids would cool rapidly on contact with sea water. Lusk (1972) regards a temperature in the range 100°C to 600°C as reasonable for submarine volcanic vent fluids that have been contaminated by marine or connate waters. The cooling, together with other physiochemical changes in the reservoir conditions (i.e. conditions of the system sea water — exhaled fluids), lead to the precipitation of metal sulfides with extremely high accumulation rates. The physiochemical changes are time-dependent due to the pulsative character of the mechanism.

The effects of the chemistry of ore-forming fluids on the sulfur isotope composition of hydrothermal minerals have been quantitatively evaluated by Ohmoto (1972) from available thermochemical data and isotopic fractionation factors. According to him the isotopic composition of sulfur in minerals formed at temperatures in the hydrothermal range is strongly controlled by the f_{O_2} and pH values of the fluids, as well as the temperature and isotopic composition of the total sulfur in the fluids, $\delta^{34}S_{\Sigma S}$. The situation becomes evident from Fig. 9, where the stability fields of the Fe—S—O minerals and barite, calculated by Ohmoto, are also given.

In conditions where low f_{O_2} and low pH prevail, sulfide minerals precipitating from solutions would exhibit $\delta^{34}S$ values similar or close to that of the parental fluid. This is based in the relative order of ^{34}S enrichment: sulfate species \gg $H_2S \simeq$ sulfide minerals $>$ S^{2-} (Sakai, 1968) and the fact that H_2S is overwhelmingly predominant among aqueous species in the given conditions. When high f_{O_2} prevails sulfates predominate, and sulfides, if precipitating, would show $\delta^{34}S$ values much more negative than the $\delta^{34}S_{\Sigma S}$ value. In conditions, where low f_{O_2} and high pH prevail S^{2-} is the predominant species, and sulfide minerals, if present, would show $\delta^{34}S$ values slightly higher than that of the parental fluid. However, in the intermediate f_{O_2} and pH conditions, where both H_2S and sulfate species are present in significant quantities, a slight change in pH and/or f_{O_2} can change the $\delta^{34}S$ value of the precipitating sulfides considerably. A change in f_{O_2} by 1 log unit or in pH by 1 unit at 250°C within this region can change the $\delta^{34}S$ value of the precipitating sulfide species by 19 ‰, an amount comparable to the overall range observed in KHp 6 and KH 8. The situation is illustrated by the arrows in Fig. 9. A corresponding change of f_{O_2} and/or pH value can cause a larger variation in the $\delta^{34}S$ of the precipitating sulfide species at a lower temperature, as the isotopic enrichment factors are larger at lower temperatures.

The above cited computations carried out by Ohmoto (1972) have been made on the assumption that both chemical and isotopic equilibria are established among aqueous species and between aqueous species and precipitating mineral phases during the deposition. With regard to the submarine volcanic-exhalative mechanism the requirement demands that marine sulfate has participated to a certain extent in forming the parental fluid from which sulfides precipitate. There is insufficient evi-

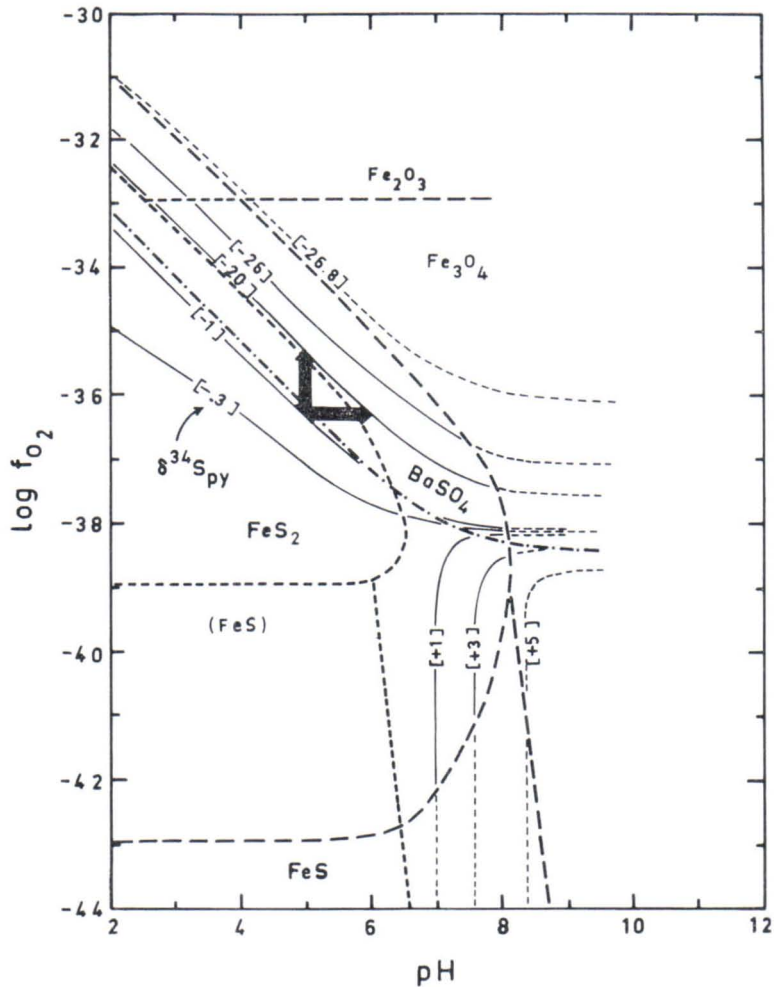


FIG. 9. Comparison of the positions of $\delta^{34}\text{S}$ contours with the stability fields of Fe—S—O minerals and barite at 250°C, after Ohmoto (1972).

- : Fe—S—O mineral boundaries at $S = 0.1$ moles/kg H_2O .
- - -: Fe—S—O mineral boundaries at $S = 10^{-3}$ moles/kg H_2O .
- · - ·: barite soluble/insoluble boundary at $m_{\text{Ba}}^{2+} \cdot m_{\text{S}} = 10^{-4}$.

dence concerning the isotopic composition of the Precambrian marine sulfate. As a reference a $\delta^{34}\text{S}$ value of +14.6 ‰ reported by Thode and Monster (1965) can be given. For sulfur compounds of exhalative origin a $\delta^{34}\text{S}$ of around zero permil (Sakai, 1957) would be valid. Since the rates of both chemical and isotopic exchange reactions between the reduced and the oxidized sulfur forms are extremely slow at temperatures below about 200°C (Ohmoto, 1971; Kajiwarra and Krouse, 1971), a mixing or exchange zone must be assumed in the vicinity of the vent outlet, where

the temperature is sufficiently high (p. 21). Being in isotopic equilibrium with each other, the exhaled sulfur compounds and marine sulfate would thus produce the $\delta^{34}\text{S}_{\Sigma\text{S}}$ enriched in ^{34}S . Although the marine sulfur is considered to be more effective in determining the $\delta^{34}\text{S}_{\Sigma\text{S}}$, the calculations used are still valid. The isotopic composition of total sulfur in the parental fluid depends on the mixing proportions of the two participants, and can change periodically. It is suggested here that the changes in these proportions alone could cause a part of the observed fluctuation in the isotopic patterns concerned.

A volcanic-exhalative mechanism is favored for generating the regularly fluctuating isotopic, as well as the mineralogic patterns in the satellite ore body. This is because a pulsative mechanism appropriately explains the oscillating character of the isotopic patterns and because the interdependence of the variables controlling the isotopic composition of precipitating sulfides is more easily achieved than in the alternative biologic mechanism.

The foot-wall side of the main ore body

In Fig. 10 the $\delta^{34}\text{S}$ values and the lithologic data of the sample population KBp 3 are given. The lowermost portion of the channel sample represents the clearly banded pyritic ore type comparable to that in the satellite ore body. In the middle and upper portions of the channel sample the amount of siliceous intercalates deficient in sulfides is diminutive, the structure of the ore being, however, stratified. Pyrite is predominant among the sulfide species, but pyrrhotite occurs regularly as an accessory. In the vicinity of a 35 cm thick skarn layer only pyrrhotite could be separated. This might support the suggestion that magnesian iron carbonate has played a part in the formation of pyrrhotite after pyrite during the metamorphism (Han, 1968)

As an overall trend the more negative $\delta^{34}\text{S}$ values, with the extreme of -7.5‰ from the banded portion, grow to zero permil towards the upper portions. The $\delta^{34}\text{S}$ values from the banded portion may be interpreted as showing an oscillation equal to the regular fluctuation observed across the satellite ore body in KHp 6 and KH 8 (Figs. 7, 8). Thus during the accumulation of the banded portion the f_{O_2} and/or pH conditions of the parental fluid have changed from those within the intermediate region (p. 21, Fig. 9) to those near the pyrite-pyrrhotite boundary, where low f_{O_2} and low pH prevail during the deposition of upper portions without siliceous intercalates. The isotopic data further indicate that the exhaled sulfur compounds are essentially responsible for the $\delta^{34}\text{S}_{\Sigma\text{S}}$.

Theoretical studies (Sakai, 1968; Bachinski, 1969), as well as experimental data of sulfur isotope fractionation between coexisting metallic sulfides (Kajiwara and Krouse, 1971), place the sulfide minerals under the equilibrium exchange conditions in the following order of ^{34}S enrichment: pyrite > pyrrhotite \approx sphalerite > chalcopyrite > galena. The majority of pyrite-pyrrhotite pairs in KBp 3 are in accordance

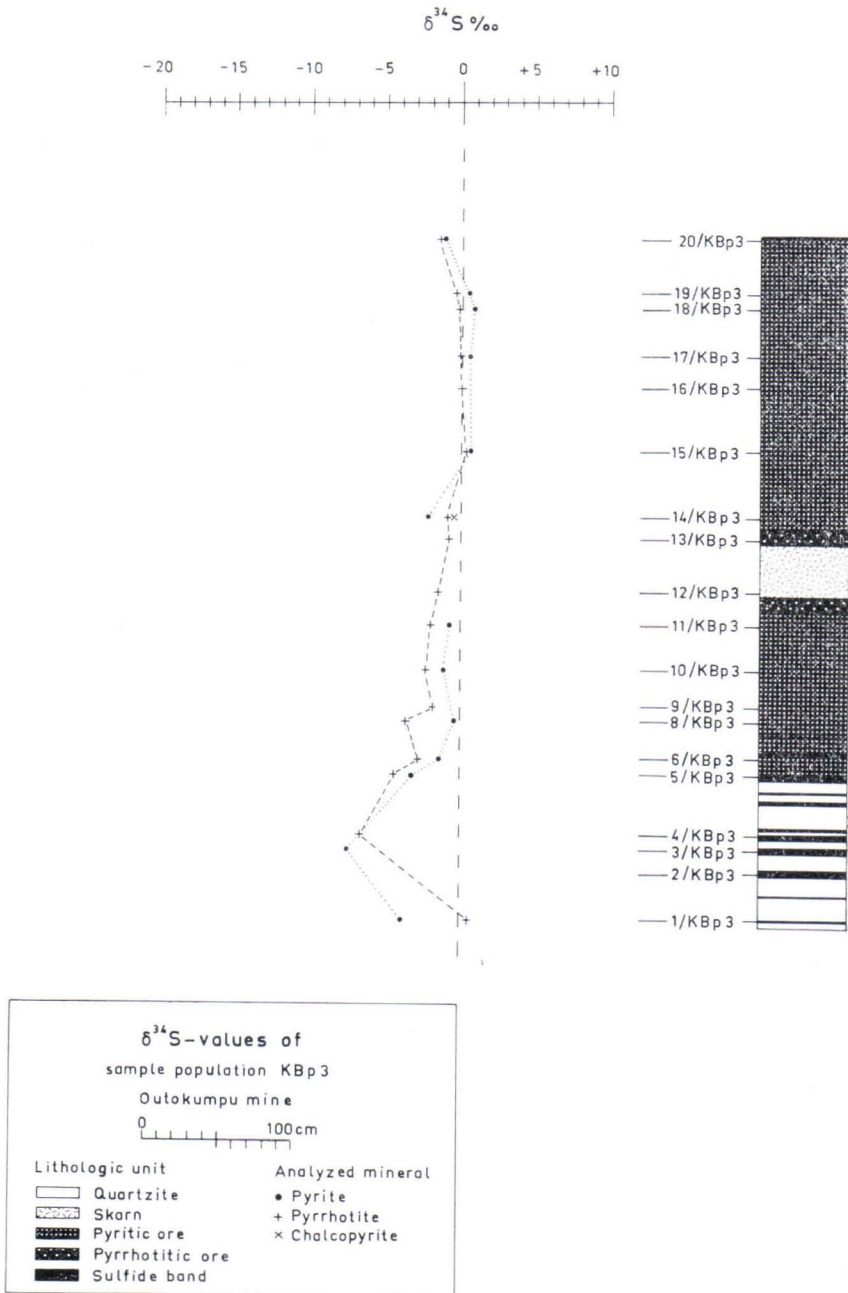


FIG. 10.

with this order. The two reversals, 1/KBp 3 and 14/KBp 3, of the commonly observed fractionation for the pair involved may be evidence for local isotopic disequilibrium. At 14/KBp 3, where the intercalating skarn layer may have influenced the isotopic composition of sulfides, the disequilibrium is emphasized by chalcopyrite.

Lateral $\delta^{34}\text{S}$ variation in the main ore body

Solute diffusion would theoretically favor the depletion of ^{34}S in fluids with increasing distance from the source i.e. from the vent outlet. It could also be expected that temperatures lower than those in the mixing or exchange zone would tend to cause a decrease in the $\delta^{34}\text{S}$ values of the precipitating sulfides. The sample populations K 1476, K 1603, and K 1232 (Fig. 11) as well as that composed of scattered samples MDp, N 40, U 4, KA 4, KD 5 a, and LD 6 (Appended table) have been taken in order to study the lateral variation of the $\delta^{34}\text{S}$ values in the main ore body. The data obtained covers 1 400 meters i.e. 35 percent of the total length of the ore.

The isotopic patterns of the channel samples each intersecting the ore body indicate that $\delta^{34}\text{S}$ values close to zero permil are generally representative of the main ore body. In the lateral direction there is a slight tendency for the average $\delta^{34}\text{S}$ values to decrease from the channel sample K 1476 through K 1603 to the channel sample K 1232. The overall decrease expressed as an arithmetic mean is 2.5 ‰. If the extreme values of +5.8 ‰ and +5.6 ‰ in K 1476 for pyrrhotite and pyrite respectively are neglected due to lack of determinations around them, the overall decrease falls to 2.0 ‰. With regard to the scattered samples the tendency for ^{34}S depletion towards the south-westernmost end of the ore body remains uncertain. This may be due to the lack of precise information of the sample positions in the vertical isotopic patterns. Assuming the decrease to be a real and original feature, it could be explained by solute diffusion and/or decreasing temperatures. If, however, the magnitude of the decrease is taken into consideration, it can be concluded that there has been no significant differences in the reservoir conditions along the length axis of the accumulation area during the precipitation of the main ore body. This may indicate that exhalations responsible for the ore formation have been discharged on the sea floor from a fissure rather than a conduit.

Relation between pyritic and pyrrhotitic ore types

Uncertainty exists as to whether the massive portion of the ore containing pyrrhotite and chalcopyrite as sulfidic matter is a result of primary deposition of monosulfides or an alteration product of pyritic ore.

On the basis of the volcanic-exhalative mechanism, the differences between the two ore types may be depositional and due to the facies change. According to the calculations (Ohmoto, 1972) previously cited (Fig. 9) this facies change, pyrrhotite precipitating instead of pyrite, is mainly attributed to a decrease in the oxidation

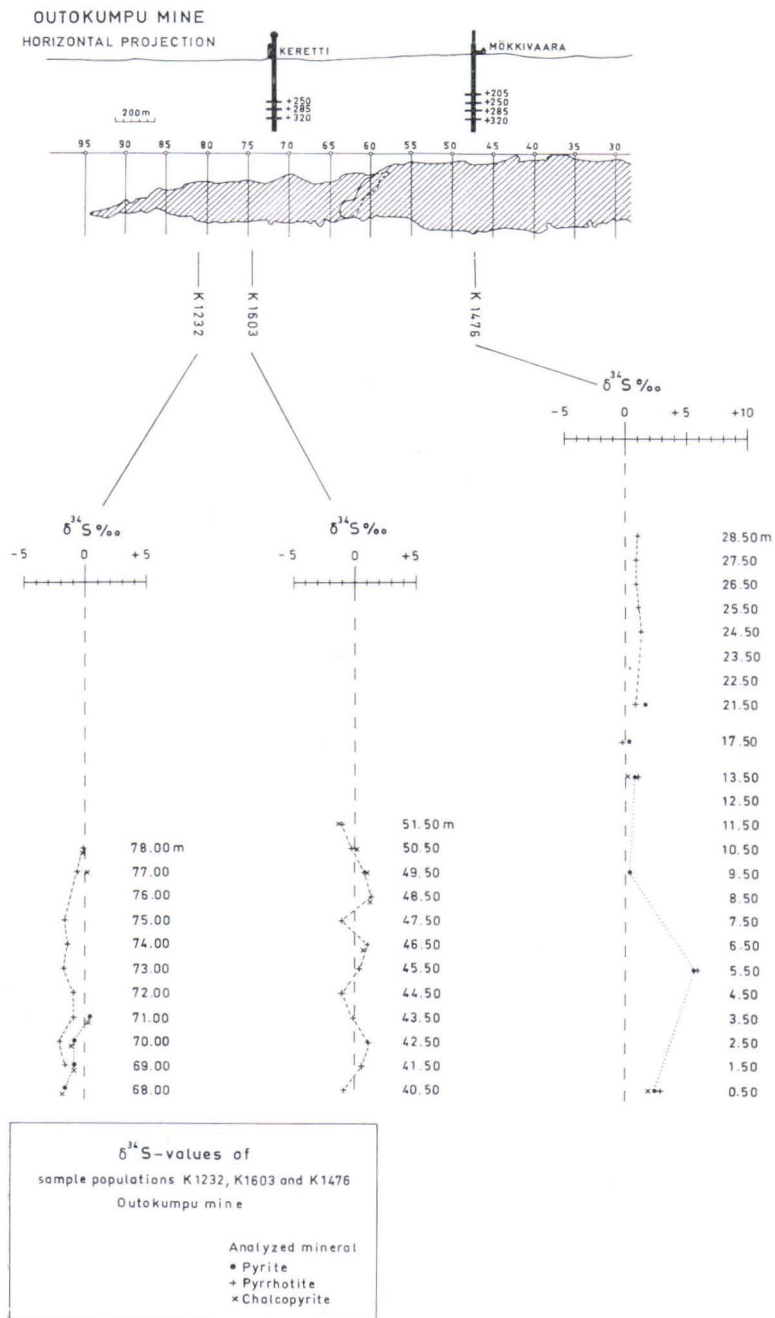


FIG. 11.

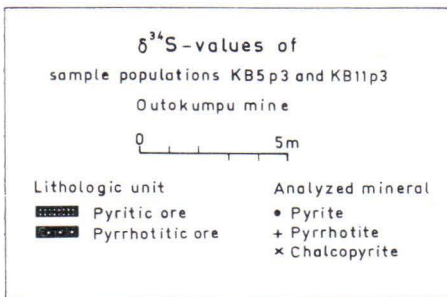
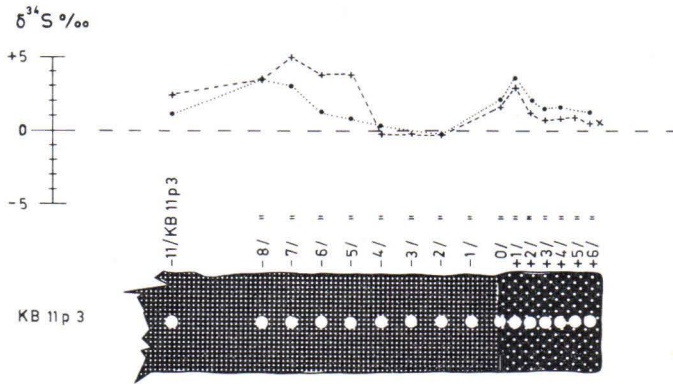
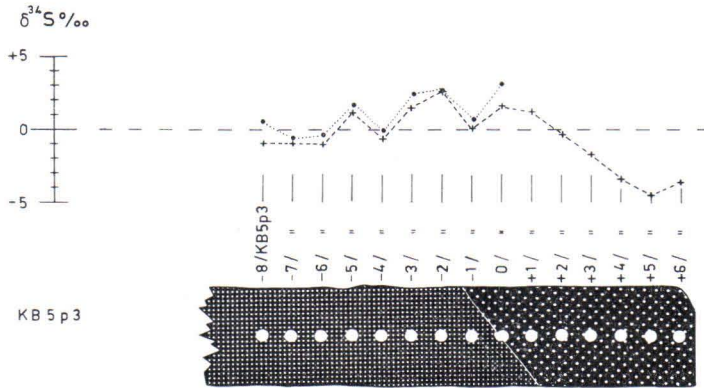


FIG. 12.

state of the parental fluid. The fugacity of sulfur and the sulfur concentration in the fluid defining the stability fields of sulfur-bearing minerals may also have decreased, thus enlarging the stability field of pyrrhotite. The wide differences in structure and texture between the ore types may in turn be due to the different behaviour during subsequent folding and metamorphism.

Two facts support the idea that the pyrrhotitic ore is an alteration product, with serpentinite having had an obvious influence on the alteration. Firstly, the transitional zone between the two ore types seldom follows the internal structure of the ore but the pyrrhotitic ore instead forms a layer parallel to the contact against the serpentinite (Fig. 3). Secondly, there is a tendency for the chrome and nickel tenors of the ore to increase towards the serpentinite (Peltola, 1968).

In order to examine the probability of each alternative in terms of sulfur isotope fractionation, the sample populations KB 5 p 3 and KB 11 p 3 (Fig. 12) have been taken.

No significant changes in the sulfur isotope composition should occur when the reservoir conditions are shifted from those prevailing in the pyrite field near the pyrite-pyrrhotite boundary to those in the pyrrhotite field (Fig. 9), provided that the $\delta^{34}\text{S}_{\Sigma\text{S}}$ remains constant. The data observed in KB 5 p 3 are not, however, in accordance with this statement. The pyritic ore exhibits a saw-tooth type pattern oscillating around $+1\text{‰}$ with pyrite-pyrrhotite pairs at isotopic equilibrium, whereas the $\delta^{34}\text{S}$ values of pyrrhotite from the pyrrhotitic portion progressively grow more negative by 6.1 permil. In KB 11 p 3, where the depositional conditions should have been analogous, pyrite-pyrrhotite pairs from the pyritic ore, with the exception of $-4/\text{KB 11 p 3}$, indicate an isotopic disequilibrium pyrrhotite, being in an extreme case at $-5/\text{KB 11 p 3}$ as much as 3.0 permil heavier than pyrite. Since the corresponding sulfide pairs from the pyrrhotitic ore in KB 11 p 3 are consistently indicative of the isotopic equilibrium reached, no comparison between the isotopic patterns of each ore type can be made.

If pyrite is converted into a stoichiometric FeS , one mole of S_2 per two FeS_2 must be released. Since the bonds formed by the light isotope are more readily broken than bonds involving the heavy isotope during a chemical reaction, molecules bearing the ^{32}S will react slightly more readily than those with the ^{34}S . A ^{34}S enriched pyrrhotite and ^{32}S depleted sulfur atmosphere should thus be produced. At a later stage, if the reactive sulfur forming the atmosphere and diffusing towards the serpentinite is then caught by iron released in the serpentinization of olivine, an isotopic pattern with progressively decreasing $\delta^{34}\text{S}$ values towards the serpentinite should result. The trend observed in the pyrrhotitic ore in KB 5 p 3, i.e. the progressive depletion of ^{34}S towards the serpentinite, thus supports the idea that pyrrhotitic ore is an alteration product of the pyritic ore. In KB 11 p 3, where the situation should be the same, no analogous trend in the pyrrhotitic portion can be seen. There is a positive peak at $+1/\text{KB 11 p 3}$ with the $\delta^{34}\text{S}$ values of $+3.6$ and $+2.9$ permil for pyrite and pyrrhotite respectively, the remaining pyrites and pyrrhotites showing fairly uniform $\delta^{34}\text{S}$ values, the former around $+1.7\text{‰}$ and the latter around $+1.0\text{‰}$.

The contradiction in the sulfur isotope data available i.e. that of the channel samples KB 5 p 3 and KB 11 p 3, does not allow any firm decision to be made between the two possibilities presented, the pyrrhotitic ore type being a result of primary deposition of monosulfides or an alteration product of the pyritic ore.

Influence of remobilization on sulfur isotope composition

Post-depositional changes exist in the ore. Chalcopyrite, pyrrhotite, and sphalerite have locally concentrated filling up tectonically favourable spaces in the originally banded pyritic ore, as the crests and troughs of folds and the pressure shadows of boudinage and breccia structures. These textural and structural changes were caused by the remobilization of sulfides during metamorphism (Mikkola and Väisänen, 1972). The remobilization grade is proportional to the intensity of folding with the result that the banded and subsequently folded ore in the extreme case occurs as separate fragments in the more sulfide-rich and coarser-grained sulfide matrix. Often the edges of the fragments are poorer in sulfides than the cores (Peltola, 1968).

With the intention of investigating the influence of the remobilization of sulfides on the sulfur isotope composition, 26 analyses from fragment sulfides as the basis for comparison, and 28 analyses from sulfides of the sulfide matrix between the fragments were performed. The data is presented with reference to the sample population KBp 2 in Fig. 13, whereas that of separate sample pairs 250 Kp 4, KBp 2 a, and KD 5 b are given only in the appended table.

As a net effect, there is a depletion of ^{34}S in the remobilized sulfides by an average of 2.6 permil compared with the fragment sulfides. With regard to different sulfide species the depletion amounts to 3.0 ‰ for pyrite, 1.9 ‰ for pyrrhotite and 2.7 ‰ for both chalcopyrite and sphalerite.

According to Mikkola and Väisänen (1972) three different mechanisms are of importance in having caused the remobilization of sulfides in the Outokumpu copper ore during the regional metamorphism. The plastic flow of sulfides was the most obvious mechanism for remobilization in the initial stage. Solid-state diffusion is considered as the main transport mechanism of the material now filling up the tension joints. The third mechanism was the formation of the so-called metahydrothermal solutions that formed sulfide veins, usually containing idiomorphic quartz.

In interpreting the sulfur isotope data two mechanisms, namely the plastic flow of sulfides and solid-state diffusion, may be combined. Theoretically they both act in the same direction and explain the observed depletion of ^{34}S in remobilized sulfides. Diffusion is the common factor of both mechanisms and leads to kinetic separation, molecules containing the light isotope moving more rapidly than those with the heavy one. In the case of the plastic flow of sulfides, solid-state diffusion is associated with recrystallization. In addition to this there is a free energy increase of the material under the plastic deformation preceding the actual flow of sulfides, which may lead to the depletion of ^{34}S in the remobilized phase. This is because

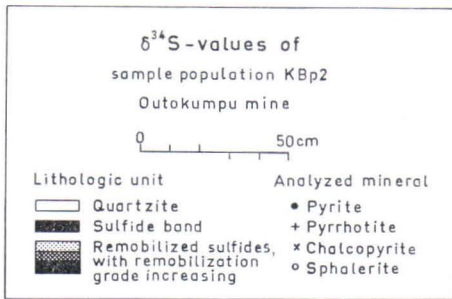
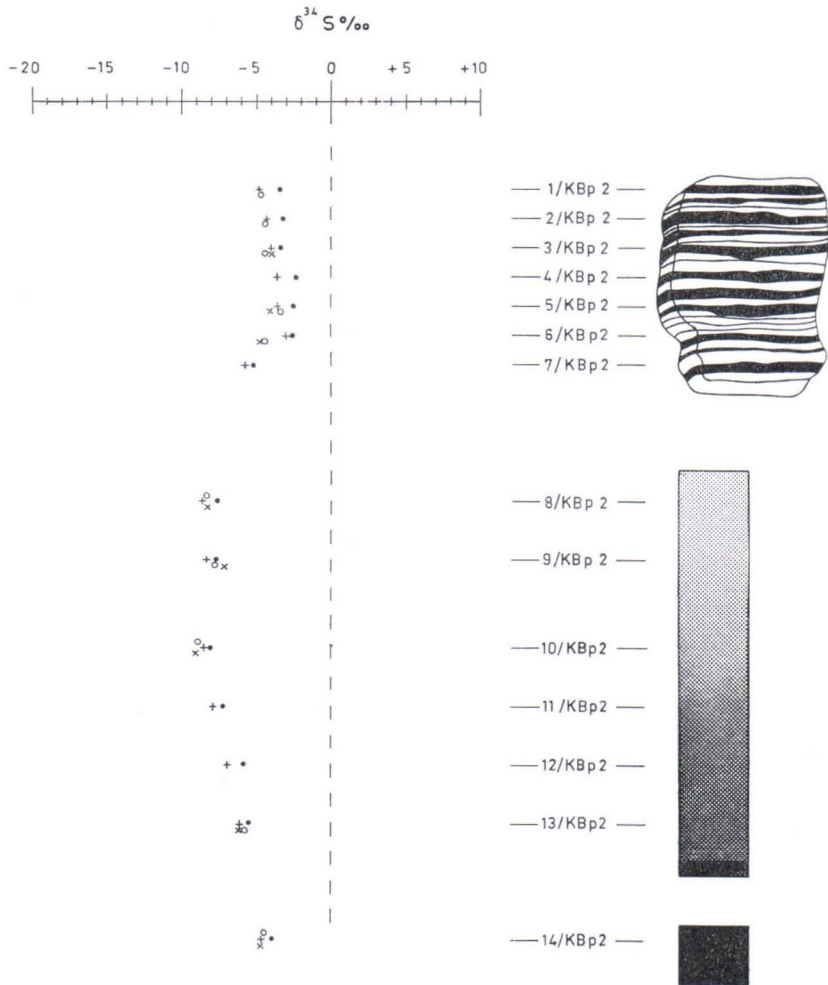


FIG. 13.

the free energies of the isotopic molecules are approximately inversely proportional to the square roots of their masses (Rankama, 1963, p. 12). The lighter ^{32}S isotope should thus slightly favor the remobilizing phase.

Only two remobilizates, 14/KBp 2 and 1/250 Kp 4, contain milky idiomorphic quartz and are thus considered to have been formed through the so-called meta-hydrothermal solutions. In either case the $\delta^{34}\text{S}$ values are close to those taken to be representative of the protolithic material; sulfides analyzed from 14/KBp 2 are 0.4 permil lighter than the average value for fragment sulfides of the same sample population, whereas the sample pair 250 Kp 4 exhibits the opposite relation, the remobilized pyrrhotite being 0.4 permil heavier than that used as the basis for comparison. The isotopic composition of meta-hydrothermal solutions are essentially determined by the $\delta^{34}\text{S}$ values of sulfur-bearing minerals which have penetrated into this fluid phase. Thus, the end result is due to the tendency of the meta-hydrothermal solutions to the average $\delta^{34}\text{S}$ values existing within the sphere of their influence.

In Fig. 14 the mutual relationships of the coexisting sulfides in KBp 2 are illustrated. It appears that the $\delta^{34}\text{S}$ values of the remobilized sulfides are more compactly packed than those of fragment sulfides. This is due to the isotopic homogenization associated with the remobilization. The sequence from the greatest to least enrichment in ^{34}S isotope for sulfides coexisting in the breccia fragment exhibiting a banded structure may be written: pyrite > pyrrhotite \geq sphalerite \geq chalcopyrite. In the samples taken from the remobilized sulfide matrix, pyrrhotite tends to occupy the position of the lightest sulfide species in four cases out of five. In two cases, however, pyrrhotite shows the least enrichment of ^{34}S together with chalcopyrite. The sequence for remobilized sulfides may thus be written: pyrite > sphalerite \geq chalcopyrite \approx pyrrhotite.

As stated in the preceding paragraphs, the remobilization is controlled to a considerable degree by solid-state diffusion, which in part is a function of bond strength (Bachinski, 1969). Barton *et al.* (1963) have pointed out that sphalerite and pyrite are much more sluggish in their solid-state reactions than are chalcopyrite and pyrrhotite. Koren and Sirota (1967) have studied reactive diffusion in a variety of semiconducting compounds; they generalize that the stronger are the interatomic forces of atoms or ions in the crystal lattice, the higher will be the activation energy of diffusion. They found that the activation energy of sphalerite is higher than that of pyrrhotite. The sequential interchange between pyrrhotite and sphalerite from coexisting sulfides in the original banded structure to the remobilized material is thus a result of the diffusion phenomena.

One more sample population, KL 7, should be discussed in connection with the remobilization of sulfides. In the pyrrhotitic ore type there exist pyrite porphyroblasts up to 10 cm in diameter. The greatest abundance of porphyroblasts is found in shear zones, which indicates that deformation has activated their formation. Väisänen (1972) holds the opinion that the growth of the porphyroblasts is controlled by short distance remobilization mainly through diffusion.

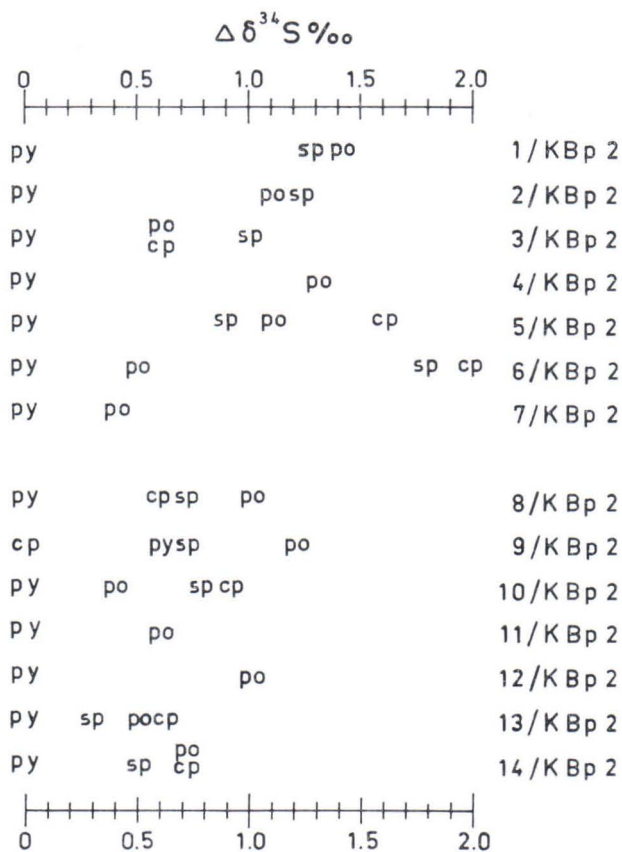


FIG. 14. Mutual relationships of the coexisting sulfides of the sample population KBp 2.

The possible variation of the $\delta^{34}\text{S}$ values from the centre of a porphyroblast to its outer shells, observed by Gehrish (1970) for the Sulitjelma pyrite porphyroblasts, was studied by means of four sulfur isotope analyses. A porphyroblast 23 mm in diameter was drilled through and the core 7.7 mm in diameter was divided into 10 parts of equal length. Two samples, 5/KL 7 and 6/KL 7, were taken symmetrically from the centre of the porphyroblast, whereas the samples 1/KL 7 and 10/KL 7 represent the outermost shell. The pyrite and pyrrhotite of the growth environment were also compared with the pyrite porphyroblast. The data is presented in the appended table.

No distinct variation of the heavy sulfur in the centre with the $\delta^{34}\text{S}$ values growing more negative towards the outer shells in the manner of porphyroblasts in Sulitjelma could be seen. Pyrite of the growth environment shows a $\delta^{34}\text{S}$ value 1.0 permil lighter than that of the porphyroblast, whereas pyrrhotite in the environment has exactly the same $\delta^{34}\text{S}$ of -2.7‰ as does pyrite of the porphyroblast.

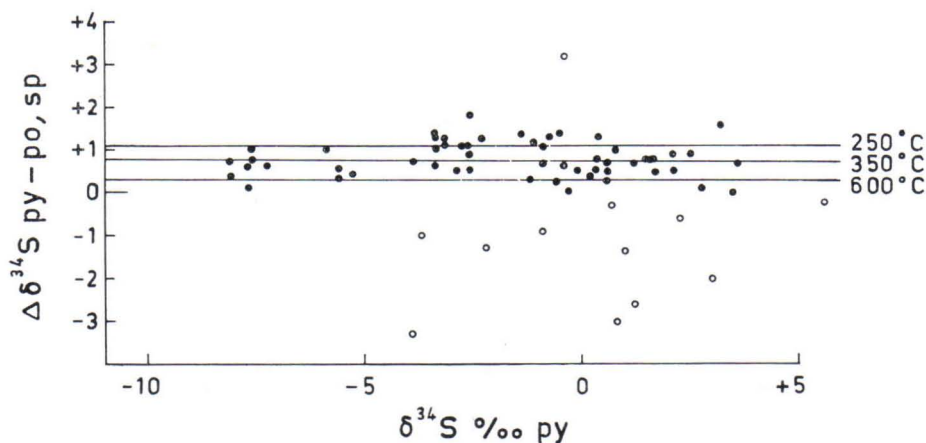


FIG. 15. Plot of delta values for pyrite-pyrrhotite and pyrite-sphalerite pairs versus $\delta^{34}\text{S}$ values of pyrite: temperature lines according to the calibration curves of Kajiwara and Krouse (1971).

Temperature estimate based on sulfur isotope fractionation

Since the fractionation factor, i.e. the partitioning of isotopes between two compounds in an equilibrium isotope exchange reaction, is inversely proportional to temperature, it may serve as a potentially useful geothermometer. The data reported by Tatsumi (1965) seem to be the first suggesting this idea. The employment of the isotope fractionation between sulfides as a geothermometer implies that the minerals of the pair have formed contemporaneously, that isotopic equilibrium has prevailed, and that a calibration curve for the mineral equilibria has been determined experimentally.

Kajiwara and Krouse (1971) have determined sulfur isotope fractionation factors involving the pairs pyrite, pyrrhotite, sphalerite, chalcopyrite, and galena experimentally over the temperature range 250°C to 600°C. According to them the equilibrium exchange constant K for a given mineral pair depends on temperature as follows: $1000 \ln K \div \Delta \delta^{34}\text{S} = AT^{-2}$, where A is a constant. The A values with $\pm 10\%$ uncertainties for mineral pairs pyrite-pyrrhotite and pyrite-sphalerite is the same, namely 3.0×10^5 .

The delta values involving 59 pyrite-pyrrhotite pairs, as well as 10 pyrite-sphalerite pairs, are plotted against the $\delta^{34}\text{S}$ values of pyrite in question (Fig. 15). The temperature lines presented are based on the experimental calibration curve already reported.

The negative delta values, which in all probability represent isotopic disequilibrium conditions, as well as a positive one for the pyrite-pyrrhotite pair at 8/KBp 3 amounting to +3.2 permil, where the constituents are probably of diverse generation, are marked with open circles (Fig. 15) and are disregarded in the temperature calculations. The regression line calculated for the remaining values equals the delta value

of $+0.77$ permil. The corresponding temperature is then 350°C . Since the differences in the isotopic composition of coexisting sulfides may result either from simple equilibrium isotope effects or from depositional isotope effects followed by partial or complete equilibrium during metamorphism, the value of 350°C can only be accepted as a statistical value indicating the temperature at which the isotopic equilibrium was reached.

CONCLUDING REMARKS

The available geologic and sulfur isotopic evidence suggests that the Outokumpu stratiform pyritic copper ore was deposited by volcanic exhalations discharged from a fissure type vent system on the sea floor. The uniform but negative $\delta^{34}\text{S}$ values of the quartzite outside the ore proper, the regularly fluctuating isotopic patterns on the negative side characteristic of the satellite ore body, and finally the $\delta^{34}\text{S}$ values growing towards zero permil in the main ore body can all be explained by changes in the chemical state of the ore-forming fluids controlled by a submarine volcanic-exhalative mechanism. Although marine sulfate has participated in forming the parental fluid from which sulfides have precipitated, a volcanic-exhalative origin is favored in generating the bulk of the sulfur in the deposit. The temporal compatibility between the radiometric ages of Outokumpu galenas and the diabases resulting from the Early Karelian volcanic activity also support the idea that the ore is of volcanic origin.

With regard to post-depositional or epigenetic features in the ore produced by remobilization of sulfides, the sulfur isotope data emphasizes the significance of solid-state diffusion in the redistribution of elements. The isotopic data also supports the concept of metahydrothermal fluids as one of the principal remobilization mechanisms. The data concerning the isotope fractionation between coexisting sulfides indicates temperatures of around 350°C for reaching the isotopic equilibrium. Indirectly it may be considered to be representative of temperatures associated with the regional metamorphism undergone by the ore deposit.

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APPENDED TABLE

Analyses of individual samples

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
K 1724/67.00—67.20	10947/106	-16.3	0.18
K 1724/67.40—67.60	10946/706	-16.9	0.14
K 1724/67.60—67.80	10946/106	-15.6	0.21
K 1724/67.80—68.00	10947/306	-15.9	0.15
K 1724/68.20—68.40	10946/306	-14.3	0.17
K 1724/68.60—68.80	10946/906	-17.4	0.17
K 1724/68.80—69.00	10947/506	-17.9	0.13
K 1724/81.00—81.20	10946/506	-17.8	0.13
— 1/KHp 6	10901/206	- 9.8	0.21
0/KHp 6	10901/106	1.9	0.65
1/KHp 6	10901/406	-19.2	0.36
1a/KHp 6	10901/306	-17.7	0.23
2/KHp 6	10901/706	-19.1	0.56
2a/KHp 6	10901/506	-18.9	0.18
2c/KHp 6	10901/806	- 5.4	0.25
3/KHp 6	10902/106	-11.4	0.29
4/KHp 6	10902/406	-11.6	0.27
5/KHp 6	10902/706	-11.4	0.26
6/KHp 6	10903/106	-18.6	
7/KHp 6	10903/406	-12.6	0.55
7a/KHp 6	10903/506	-18.6	0.23
8/KHp 6	10903/706	-14.6	0.87
9/KHp 6	10904/106	-12.3	0.27
10/KHp 6	10904/406	- 8.2	0.33
10a/KHp 6	10904/506	- 5.1	0.15
11/KHp 6	10904/706	- 3.4	0.26
12/KHp 6	10905/106	- 2.1	0.25
26/KH 8	10967/906	-13.1	0.18
25/KH 8	10967/806	- 1.4	0.13
24/KH 8	10967/706	- 1.1	0.11
23/KH 8	10967/506	- 5.8	0.15
22/KH 8	10967/306	- 8.5	0.17
21/KH 8	10967/106	-14.7	0.21
20/KH 8	10966/906	- 9.8	0.19
19/KH 8	10966/706	- 7.4	0.15
18/KH 8	10966/506	- 7.9	
17/KH 8	10966/306	-12.6	
16/KH 8	10966/106	-13.1	
15/KH 8	10965/906	-14.8	
14/KH 8	10965/706	-13.6	
13/KH 8	10965/506	-13.4	

APPENDED TABLE (continued)

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
12/KH 8	10965/306	-12.9	0.15
11/KH 8	10965/106	-13.1	0.17
10/KH 8	10964/906	-10.2	0.19
9/KH 8	10964/706	- 5.3	0.21
8/KH 8	10964/506	- 3.9	0.21
7/KH 8	10964/306	- 9.4	0.19
6/KH 8	10964/106	-16.7	0.12
5/KH 8	10963/906	-11.0	0.16
4/KH 8	10963/706	-11.3	0.17
3/KH 8	10963/506	- 9.3	0.21
2/KH 8	10963/306	-15.7	0.24
1/KH 8	10963/106	-17.3	0.19
1/KBp 3	10906/105	0.6	0.15
1/KBp 3	10906/106	- 3.9	0.12
3/KBp 3	10906/506	- 7.5	0.19
4/KBp 3	10906/705	- 6.6	0.12
5/KBp 3	10906/905	- 4.4	0.17
5/KBp 3	10906/906	- 3.2	0.14
6/KBp 3	10907/105	- 2.8	0.14
6/KBp 3	10907/106	- 1.4	0.16
8/KBp 3	10907/505	- 3.6	0.10
8/KBp 3	10907/506	- 0.4	0.11
9/KBp 3	10907/705	- 1.8	0.16
10/KBp 3	10907/905	- 2.3	0.15
10/KBp 3	10907/906	- 1.1	0.18
11/KBp 3	10908/105	- 2.0	0.13
11/KBp 3	10908/106	- 0.7	0.13
12/KBp 3	10908/305	- 1.5	0.11
13/KBp 3	10908/505	- 0.8	0.12
14/KBp 3	10908/703	- 0.5	0.11
14/KBp 3	10908/705	- 0.9	0.17
14/KBp 3	10908/706	- 2.2	0.15
15/KBp 3	10908/905	0.3	0.11
15/KBp 3	10908/906	0.6	0.10
16/KBp 3	10909/105	0.0	0.13
17/KBp 3	10909/305	- 0.1	0.14
17/KBp 3	10909/306	0.6	0.16
18/KBp 3	10909/505	- 0.2	0.10
18/KBp 3	10909/506	0.8	0.12
19/KBp 3	10909/705	- 0.4	0.13
19/KBp 3	10909/706	0.4	0.12
20/KBp 3	10909/905	- 1.5	0.18
20/KBp 3	10909/906	- 1.2	0.17

APPENDED TABLE (continued)

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
K 1476/00.50	10933/103	1.9	0.12
K 1476/00.50	10933/105	2.9	0.09
K 1476/00.50	10933/106	2.3	0.12
K 1476/05.50	10934/105	5.8	0.20
K 1476/05.50	10934/106	5.6	0.17
K 1476/09.50	10934/906	0.3	0.17
K 1476/13.50	10935/503	0.2	0.14
K 1476/13.50	10935/505	1.0	0.13
K 1476/13.50	10935/506	0.7	0.15
K 1476/17.50	10936/305	— 0.2	0.18
K 1476/17.50	10936/306	0.2	0.17
K 1476/21.50	10937/105	0.9	0.15
K 1476/21.50	10937/106	1.7	0.19
K 1476/24.50	10937/705	1.3	0.12
K 1476/25.50	10937/905	1.1	0.16
K 1476/26.50	10938/105	0.9	0.20
K 1476/27.50	10938/305	0.9	0.24
K 1476/28.50	10938/505	1.0	0.21
K 1603/40.50	10956/105	— 0.9	0.13
K 1603/41.50	10956/305	0.5	0.15
K 1603/42.50	10956/505	1.1	0.17
K 1603/43.50	10956/705	— 0.1	0.18
K 1603/44.50	10956/905	— 1.0	0.19
K 1603/45.50	10957/105	0.3	0.14
K 1603/46.50	10957/303	0.7	0.12
K 1603/46.50	10957/305	1.0	0.15
K 1603/47.50	10957/505	— 1.1	0.17
K 1603/48.50	10957/703	1.2	0.18
K 1603/48.50	10957/705	1.3	0.18
K 1603/49.50	10957/903	1.0	0.14
K 1603/49.50	10957/905	0.7	0.11
K 1603/50.50	10958/103	0.1	0.13
K 1603/50.50	10958/105	— 0.2	0.12
K 1603/51.50	10958/303	— 1.4	0.17
K 1603/51.50	10958/305	— 1.1	0.15
K 1232/68.00	10953/103	— 1.8	0.18
K 1232/68.00	10953/106	— 1.6	0.19
K 1232/69.00	10953/303	— 0.8	0.14
K 1232/69.00	10953/305	— 1.6	0.12
K 1232/69.00	10953/306	— 0.9	0.12
K 1232/70.00	10953/503	— 1.1	0.19
K 1232/70.00	10953/505	— 2.0	0.21

APPENDED TABLE (continued)

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
K 1232/70.00	10953/506	— 0.9	0.19
K 1232/71.00	10953/703	0.3	0.17
K 1232/71.00	10953/705	— 0.9	0.15
K 1232/71.00	10953/706	0.4	0.16
K 1232/72.00	10953/905	— 0.9	0.19
K 1232/73.00	10954/105	— 1.7	0.19
K 1232/74.00	10954/305	— 1.4	0.14
K 1232/75.00	10954/505	— 1.6	0.11
K 1232/77.00	10954/803	0.3	0.16
K 1232/77.00	10954/805	— 0.6	0.13
K 1232/78.00	10954/903	— 0.1	0.18
K 1232/78.00	10954/905	— 0.1	0.17
MDp	10931/106	1.7	0.28
N 40	10931/406	— 0.8	0.29
U 4	10931/706	— 2.0	0.24
KA 4	10932/106	— 0.7	0.15
KD 5a	10961/106	— 0.3	0.09
LD 6	10932/406	— 0.4	0.10
— 8/KB 5p 3	10915/705	— 0.9	0.10
— 8/KB 5p 3	10915/706	0.5	0.14
— 7/KB 5p 3	10915/505	— 0.9	0.16
— 7/KB 5p 3	10915/506	— 0.6	0.17
— 6/KB 5p 3	10915/305	— 1.0	0.11
— 6/KB 5p 3	10915/306	— 0.4	0.12
— 5/KB 5p 3	10915/105	1.2	0.13
— 5/KB 5p 3	10915/106	1.7	0.10
— 4/KB 5p 3	10912/405	— 0.6	0.35
— 4/KB 5p 3	10912/406	— 0.1	0.54
— 3/KB 5p 3	10912/105	1.6	0.30
— 3/KB 5p 3	10912/106	2.5	0.41
— 2/KB 5p 3	10911/705	2.7	0.37
— 2/KB 5p 3	10911/706	2.8	0.43
— 1/KB 5p 3	10911/405	0.1	0.09
— 1/KB 5p 3	10911/406	0.6	0.11
0/KB 5p 3	10911/105	1.6	0.26
0/KB 5p 3	10911/106	3.2	0.17
1/KB 5p 3	10912/705	1.2	0.21
2/KB 5p 3	10913/105	— 0.3	0.14
3/KB 5p 3	10913/405	— 1.7	0.26
4/KB 5p 3	10913/705	— 3.3	0.36
5/KB 5p 3	10914/105	— 4.5	0.40
6/KB 5p 3	10914/405	— 3.7	0.42

APPENDED TABLE (continued)

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
— 11/KB 11p 3	10918/905	2.4	0.17
— 11/KB 11p 3	10918/906	1.0	0.15
— 8/KB 11p 3	10918/805	3.5	0.11
— 8/KB 11p 3	10918/806	3.5	0.10
— 7/KB 11p 3	10918/705	5.0	0.14
— 7/KB 11p 3	10918/706	3.0	0.18
— 6/KB 11p 3	10918/505	3.8	0.19
— 6/KB 11p 3	10918/506	1.2	0.15
— 5/KB 11p 3	10918/305	3.8	0.11
— 5/KB 11p 3	10918/306	0.8	0.12
— 4/KB 11p 3	10918/105	— 0.2	0.16
— 4/KB 11p 3	10918/106	0.3	0.20
— 3/KB 11p 3	10917/905	— 0.2	0.20
— 2/KB 11p 3	10917/705	— 0.3	0.15
— 2/KB 11p 3	10917/706	— 0.3	0.09
0/KB 11p 3	10917/305	1.6	0.09
0/KB 11p 3	10917/306	2.1	0.12
1/KB 11p 3	10916/105	2.9	0.12
1/KB 11p 3	10916/106	3.6	0.18
2/KB 11p 3	10916/305	1.2	0.16
2/KB 11p 3	10916/306	2.1	0.14
3/KB 11p 3	10916/505	0.7	0.20
3/KB 11p 3	10916/506	1.5	0.18
4/KB 11p 3	10916/705	0.8	0.12
4/KB 11p 3	10916/706	1.6	0.17
5/KB 11p 3	10916/905	0.9	0.13
6/KB 11p 3	10917/103	0.5	0.16
6/KB 11p 3	10917/105	0.5	0.18
6/KB 11p 3	10917/106	1.2	0.16
1/KBp 2	10924/102	— 4.7	0.19
1/KBp 2	10924/105	— 4.8	0.17
1/KBp 2	10924/106	— 3.4	0.15
2/KBp 2	10924/302	— 4.4	0.10
2/KBp 2	10924/305	— 4.3	0.16
2/KBp 2	10924/306	— 3.2	0.13
3/KBp 2	10924/502	— 4.4	0.19
3/KBp 2	10924/503	— 4.0	0.22
3/KBp 2	10924/505	— 4.0	0.21
3/KBp 2	10924/506	— 3.4	0.19
4/KBp 2	10924/705	— 3.6	0.15
4/KBp 2	10924/706	— 2.3	0.14
5/KBp 2	10924/902	— 3.5	0.12
5/KBp 2	10924/903	— 4.2	0.17

APPENDED TABLE (continued)

Sample No.	Laboratory code	$\delta^{34}\text{S}$ ‰	s
5/KBp 2	10924/905	- 3.7	0.20
5/KBp 2	10924/906	- 2.6	0.16
6/KBp 2	10925/102	- 4.4	0.17
6/KBp 2	10925/103	- 4.6	0.20
6/KBp 2	10925/105	- 3.1	0.21
6/KBp 2	10925/106	- 2.6	0.19
7/KBp 2	10925/305	- 5.7	0.22
7/KBp 2	10925/306	- 5.3	0.17
8/KBp 2	10925/502	- 8.3	0.16
8/KBp 2	10925/503	- 8.2	0.20
8/KBp 2	10925/505	- 8.6	0.22
8/KBp 2	10925/506	- 7.6	0.24
9/KBp 2	10925/702	- 7.8	0.20
9/KBp 2	10925/703	- 7.1	0.20
9/KBp 2	10925/705	- 8.3	0.18
9/KBp 2	10925/706	- 7.7	0.13
10/KBp 2	10925/902	- 8.9	0.17
10/KBp 2	10925/903	- 9.0	0.14
10/KBp 2	10925/905	- 8.5	0.16
10/KBp 2	10925/906	- 8.1	0.18
11/KBp 2	10926/105	- 7.9	0.16
11/KBp 2	10926/106	- 7.3	0.13
12/KBp 2	10926/305	- 6.9	0.19
12/KBp 2	10926/306	- 5.9	0.19
13/KBp 2	10926/502	- 5.9	0.14
13/KBp 2	10926/503	- 6.2	0.12
13/KBp 2	10926/505	- 6.1	0.14
13/KBp 2	10926/506	- 5.6	0.18
14/KBp 2	10926/702	- 4.4	0.10
14/KBp 2	10926/703	- 4.6	0.18
14/KBp 2	10926/705	- 4.6	0.18
14/KBp 2	10926/706	- 3.9	0.18
2/250 Kp 4 F ⁽¹⁾	10922/405	- 1.2	
1/250 Kp 4 R ⁽²⁾	10921/105	- 0.8	0.12
1/KBp 2a F	10923/105	- 3.8	0.43
1/KBp 2a F	10961/406	- 2.7	0.34
2/KBp 2a R	10922/705	- 5.0	0.48
1/KD 5b F	10951/106	- 0.1	0.17
2/KD 5b R	10951/406	- 0.9	0.11
2/KD 5b R	10923/405	0.0	0.08
1/KL 7	10942/106	- 2.3	0.17
5/KL 7	10942/906	- 2.8	0.13

APPENDED TABLE (continued)

Sample No	Laboratory code	$\delta^{34}\text{S}$ ‰	s
6/KL 7	10943/106	— 2.7	0.14
10/KL 7	10943/906	— 2.6	0.20
KL 7 T ⁽³⁾	10941/106	— 2.7	0.40
KL 7 GE ⁽⁴⁾	10941/406	— 3.7	
KL 7 GE ⁽⁴⁾	10923/705	— 2.7	0.40

06 — Pyrite 05 — Pyrrhotite 03 — Chalcopyrite 02 — Sphalerite

⁽¹⁾ — Fragment sulfide

⁽²⁾ — Remobilized sulfide

⁽³⁾ — Total pyrite of the porphyroblast

⁽⁴⁾ — Sulfide from the growth environment

