

Preliminary Sulfur Isotope Investigations and Origin of Massive Sulfides in Asmara Area, Ethiopia

Milan Hamrla

Ljubljana, Prešernov trg 3

Precambrian conformable massive sulfide deposits have been discovered in Eritrea province of Northern Ethiopia in recent years. The ore bodies are associated with the greenschist-metavolcanic sequence, and have in all appearance originated as "exhalative-sedimentary" precipitations in the upper Precambrian eugeosynclinal environment. Later hydrothermal events evidently affected and enriched the deposits.

Preliminary sulfur isotope investigations of forty eight random samples of sulfides suggested that part of the sulfur was of magmatic origin, and part of it derived from marine sulfate. Hence the isotopic data would support the concept of basically submarine volcanogenic formation of deposits. Consequently, a wide potential target in search for possible ore is indicated in the corresponding beds.

Introduction

Geological investigations of the Eritrean deposits have been conducted by the Ministry of Mines of the Ethiopian Government in the period 1963 to 1972. Field surveys and drilling were applied. The preliminary isotope study was completed in 1972. It was attempted to see whether isotopic pattern could contribute to the interpretation of the history of mineralizations. Forty eight samples of sulfides were tested, all but one originating from drill cores. Half of them belong to Embaderho deposit. For Adi Rassi three core samples from 1965 drilling campaign were available only.

The initial examinations of Embaderho, Adi Nefas, Debarwa and Adi Rassi deposits revealed that favourable grading and location of some of them, though small in size, offer a reasonable chance for economic exploitation. In addition there is a number of localities where mineralizations of the same type are indicated. Since 1971 Nippon Mining Co. has been developing Debarwa deposit and diligently exploring other localities. The long awaited development of modern mining has thus started in Ethiopia.

The study of Eritrean sulfide deposits and geological controls of ore accumulation is a challenging task from both theoretical and practical points of

view. The understanding of the relationship between ore, its origin and geological environment would hopefully provide guidance to other potentially promising areas. So far a close genetical relationship with the Precambrian geosynclinal sedimentary and volcanic activity has been suggested for these deposits, but more detailed investigations are required.

The author is greatly indebted to the Ministry of Mines of the Ethiopian Government, in which service he was when involved in investigations of Eritrean deposits. The permission to use the data was obtained from H. E. Ato Teshome Gebremariam, the Minister of State. The support and interest for this study shown by Ato Shiferaw Demissie, the former Acting Head of Geological survey, is acknowledged. The responsibility for the interpretations rests solely with the author.

General geology and mineralogy of ore deposits

From gathered geological evidence the writer has been led to regard the mineralizations as basically of syngenetic submarine "exhalative-sedimentary" type, having originated in Precambrian eugeosynclinal environment. Considering alternative interpretations, such as replacement or magmatic injection, this concept has been favoured. Although the deposits show differences in structure, lithology and mineralogy, with massive siliceous or disseminated ores of variable grades prevailing at places, the mechanism of formation seems to have been essentially the same. There is evidence that the deposits combine an early "sedimentary" stage in close association with submarine volcanism, and subsequent "vein type" stage or more of them. The sulfides which precipitated in the first stage were probably remobilized and enriched by hydrothermal activity in newly opened channels, shears and faults. Gold and sulfides in quartz veins, known to occur at many localities in Eritrea (Jelenc, 1966), seem to be associated with hydrothermal action in dilatant features.

Figure 1 shows the geological set-up of the Asmara area. The host rocks in which the mineralizations occur are Upper Precambrian greenstones derived from shallow-water assemblages of sedimentary argillaceous and volcanoclastic rocks, not surpassing the greenschist facies due to low-grade regional metamorphism. Silicic to intermediate leucocratic sheet extrusives are in close time and space relationship with the greenschist rocks. These ancient flows are porphyritic calc-sodium types, pervasively affected by deuteritic alteration. The ore appears in numerous layers more or less conformable with the greenschist sequence (Fig. 2). The age of the complex is possibly of the order between 700 and 1,000 m. y. (Kazmin, 1972). The whole Asmara area is underlain by apparently late- or post-tectonic felsic magmatics, which might have been involved in later mineralizing episodes.

The ores of Eritrean massive sulfide deposits are composed prevalingly of pyrite with minor amounts of copper, zinc and lead sulfides which are enriched at places. Pyrite is the dominant and the oldest mineral. The early pyrite is idiomorphic and extensively replaced by other sulfides. In Embarderho and Adi Rassi ores varying amounts of magnetite and pyrrhotite are present, both intimately mixed with pyrites as fine-banded ore, or forming a sort of irregular narrow channels. Pyrite, pyrrhotite and magnetite are coexistent; the close

intergrowth excludes that some pyrite would have broken down to pyrrhotite due to metamorphism. Chalcopyrite occurs intimately associated with pyrrhotite occasionally, but for the most part it is an apparent later constituent in mineral assemblage. It also forms veinlets and nests in vein quartz, indicating a later epigenetic introduction. Sphalerite is generally closely associated with chalcopyrite and occurs, too, in at least two generations. Galena is present as minor disseminations in schists and irregular inclusions in quartz veins. It is the latest constituent of the polymineral ores. Bornite, tennantite and enargite occur at places, mostly as secondary minerals (Hamrila, 1971).

The prevailing gangue is quartz. In Adi Nefas ore pyrite and sphalerite are intimately intergrown with barite and quartz. Barite is abundant at Debarwa where it forms the central part of the ore bodies. It is confined to near-surface portions and seems to disappear at depth. Chlorite, calcite, mica (phlogopite)

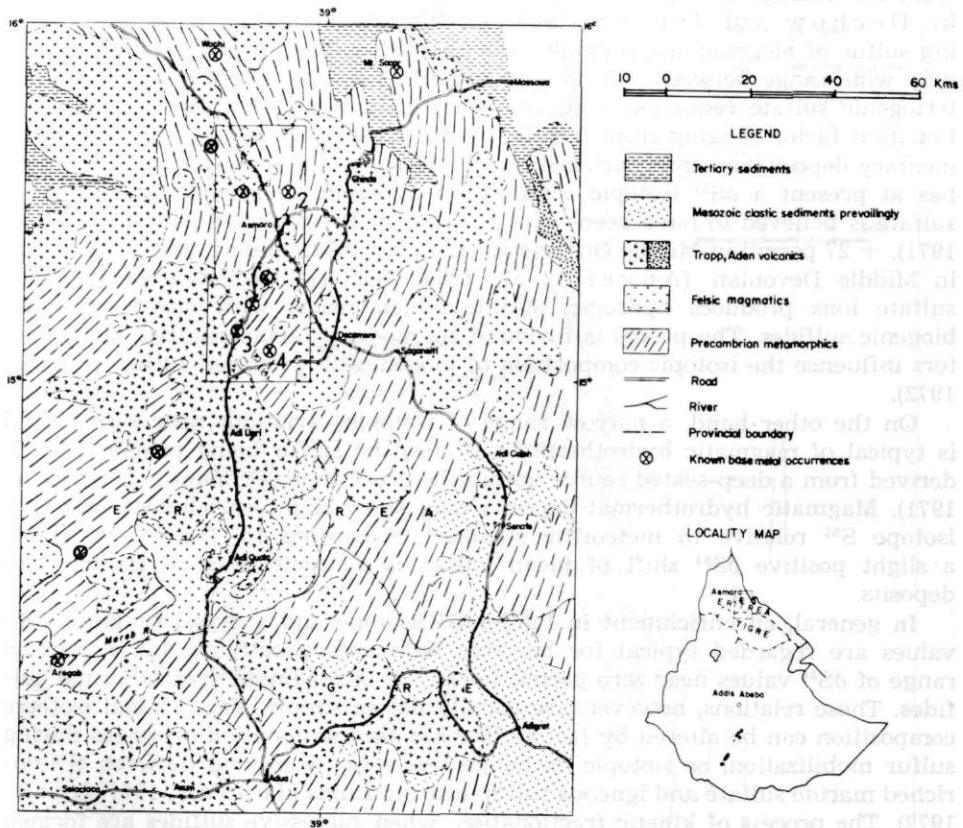


Fig. 1. Geological sketch-map of Asmara-Adua area, showing location of sulfide occurrences. General location of the area in inset. (After various sources)

Sl. 1. Geološka skica območja Asmara-Adua z doslej znanimi nahajališči sulfidov. Položaj območja desno spodaj. (Po različnih virih).

1 Embaderho, 2 Adi Nefas, 3 Debarwa, 4 Adi Rassi

and lime silicates of epidote and tremolite groups are intimately associated with massive sulfides at places, especially in Embaderho deposit.

Detailed account of the lithological environment, morphology and composition of ores and rocks of the four deposits will be presented in another paper.

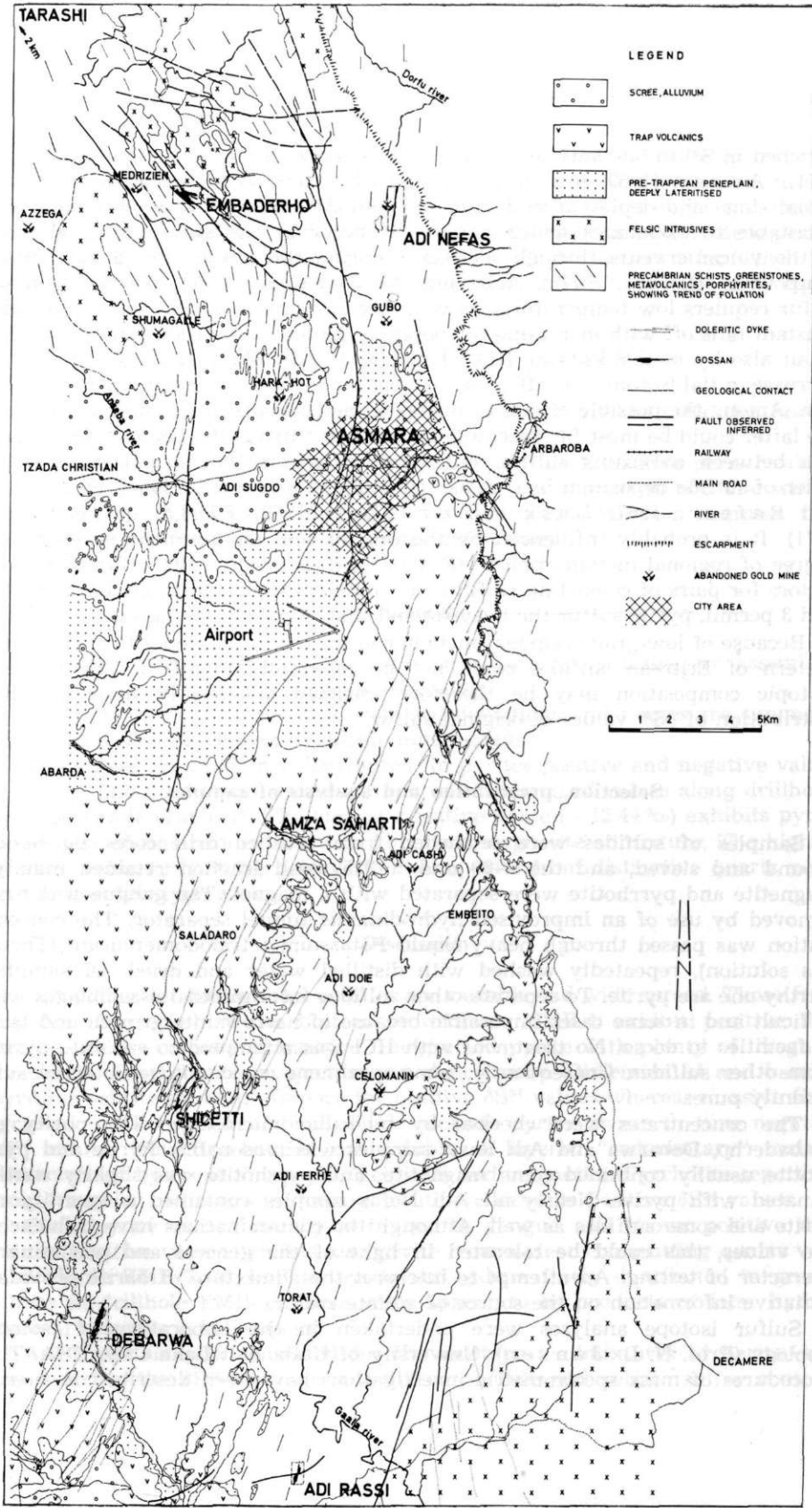
Sulfur isotope studies

A large number of data on sulfur isotope composition from various sulfide ore deposits have been published. Smirnov (1968) summarized the variations of sulfur isotope composition in sulfides, and Thode (1963), Dechow and Jensen (1965), Anger et al. (1966), Field (1966), Anderson (1969), Jensen (1971), Lusk (1972) and others discussed the sulfur isotope data of various deposits. The interpretations are variable and refer to deviations from the average zero permil isotopic composition of crustal sulfur. As shown by Dechow and Jensen (1965), stratiform sedimentary deposits containing sulfur of biogenic origin exhibit random δS^{34} values spread over comparatively wide range between +5 to -50 permil. Thode (1963) stated that bacteriogenic sulfate reduction produces isotopically lighter sulfides with a fractionation factor ranging from 0 to 25 permil, averaging about 15 permil. Sedimentary deposits are thus enriched in S^{32} relative to the seawater sulfate, which has at present a δS^{34} isotopic composition of about 20 permil. The seawater sulfate is believed to have been +14.5 permil in Precambrian period (Guhá, 1971), +27 permil in Middle Ordovician (Lusk, 1972), and around +32 permil in Middle Devonian (Anger et al., 1966). Bacterial reduction of seawater sulfate ions produces hydrogen sulfide which reacts with metals, forming biogenic sulfides. The process is favoured by moderate temperatures. Many factors influence the isotopic composition of biogenically produced sulfur (Lusk, 1972).

On the other hand, a narrow range of isotopic variations near zero permil is typical of magmatic hydrothermal sulfides, the sulfur being primordial and derived from a deep-seated source within the crust or upper mantle (Jensen, 1971). Magmatic hydrothermal deposits may show slight enrichment in heavy isotope S^{34} relative to meteoritic standard. According to Dechow (1960) a slight positive δS^{34} shift of mean values is characteristic of fissure vein deposits.

In general, an enrichment in lighter S^{32} isotope and a broad range of δS^{34} values are regarded typical for biogenic sedimentary sulfides, and a narrow range of δS^{34} values near zero permil for sulfur of magmatic hydrothermal sulfides. These relations, however, are usually not so simple. The original isotopic composition can be altered by factors like kinetic fractionation processes during sulfur mobilization, or isotopic exchange reactions by mixing between S^{34} enriched marine sulfate and igneous sulfur-bearing fluids (Jensen, 1971; Lusk, 1972). The process of kinetic fractionation, when successive sulfides are formed in various stages of ore genesis, shows a general trend from early sulfides

Fig. 2. Geological map of Asmara area. — Enlarged inset from Fig. 1
Sl. 2. Geološka karta asmarskega območja. — Povečani del sl. 1



enriched in S^{34} to late sulfides relatively depleted in S^{34} (Field and Moore, 1971). Anger (1969) has stated the opposite view of S^{32} enrichment in the initial stage and depletion in a later one. An S^{34} enrichment by mixing is attributable to exchanges which apparently occur at the sea floor or already in the volcanic vents through sediments during the passage of igneous fluid compounds (Lusk, 1972). According to Jensen (1958), fractionation of sulfur requires low temperatures as well, because isotope exchange equilibrium constant falls off with increasing temperature. Isotopic alteration can be brought about also by metamorphism (Dechow and Jensen, 1965), which would decrease initial isotopic variations in ore and tends towards isotopic homogenization. Among the possible effects of diffusion, metasomatism and metamorphism, the latter could be most far-reaching. In addition there is the primary fractionation between coexisting sulfide suites, which affects the normal paragenetic order of sulfide deposition by a depletion in S^{34} (Tatsumi, 1965; Stanton and Rafter, 1967; Lusk and Crocket, 1969; Field and Moore, 1971). It is probably influenced by the depositional environment or even the degree of regional metamorphism (Field and Moore, 1971). Fractionation factors for pairs of coexisting sulfides are quite constant and range between 0.5 and 3 permil, pyrite sulfur the heaviest and that of galena the lightest.

Because of low-grade regional metamorphism the initial depositional isotopic pattern of Eritrean sulfides could not be essentially modified. The present isotopic composition may be therefore assumed sufficiently indicative for distribution of δS^{34} values of original sulfur.

Selection, preparation and analysis of samples

Samples of sulfides were separated from crushed drill cores by hand, ground and sieved, and the -60 and +325 mesh fraction retained mainly. Magnetite and pyrrhotite were separated with a magnet. The gangue was first removed by use of an improvised hydrodynamic funnel separator. The concentration was passed through heavy liquid Potassium tetraiodomercurate (Thoulets solution), repeatedly washed with distilled water and dried. Of samples thirty one are pyrite. To separate other sulfides from mineral assemblages was difficult and in some cases impossible because of narrow intergrowth and lack of facilities to do so. No treatment with HCl was attempted to separate pyrite from other sulfides. Consequently, some specimens could not be obtained sufficiently pure.

The concentrates were checked by binocular microscope. The purity of Embaderho, Debarwa and Adi Rassi samples was reasonable. Pyrite and pyrrhotite usually contained some magnetite, and pyrrhotite was slightly contaminated with pyrite. Nearly all Adi Nefas samples contained a quantity of barite and some sulfides as well. Although the contaminations have influenced the values, this could be tolerated in light of the general and preliminary character of testing. An attempt to interpret the admixture of barite provided tentative information on the source of sulfate sulfur.

Sulfur isotope analyses were undertaken in the Laboratory of Isotope Geology (Prof. N. L. Jensen), University of Utah, Salt Lake City, USA. The procedures of mass spectrometric investigations have been described in litera-

ture. Duplicate analyses of twelve of the samples tested indicate an average precision of the measurements in the order of ± 0.2 permil. The analytical data are expressed as δS^{34} permil values, it being deviations (δ) in permil (‰) of S^{34} isotope in the sample relative to the standard meteoritic sulfur. Zero permil is the composition of the troilite phase of Cañon Diablo meteorit for which the ratio S^{32}/S^{34} is 22.220 (Jensen, 1971). The ratio and δS^{34} are related by equation

$$\delta S^{34} (\text{‰}) = \left(\frac{R_x - R_s}{R_s} \right) 10^3 = \left(\frac{R_x}{R_s} - 1 \right) 10^3$$

where R_x is the measured ratio S^{34}/S^{32} of the sample, and R_s the known S^{34}/S^{32} ratio of the standard.

Samples enriched in S^{34} relative to the standard have positive permil values, and negative values indicate depletion in S^{34} or enrichment in S^{32} . The widely used term "fractionation" refers to isotopic variations between samples, that is differences in isotopic ratios and hence δS^{34} values.

Results

The δS^{34} values and pertinent data for sulfide concentrates are assembled in Table 1 for each of four deposits separately.

Mean δS^{34} permil values with standard deviations and ranges are summarized in Table 2 with respect to sulfide mineralogy.

The values are randomly distributed. In pyrites positive and negative values alternate, and no vertical zonation trend or clustering of values along drillholes are discernible (Table 1). The highest negative value (-12.44 ‰) exhibits pyrite in samples of fine-banded ore with abundant magnetite admixture. The highest positive value ($+12.80$ ‰) belongs to chalcopyrite from distinctive quartz veinlets in hornfels-type rock.

Discussion

δS^{34} values for **Embaderho** samples are variable and wide spread. Those from sulfides intersected at the bottom of drillhole EMB-1 exhibit positive δS^{34} values; the ore consists of massive fine-grained pyrite with plenty of irregular inclusions of pyrrhotite, magnetite and chalcopyrite. Disseminated and banded pyrite in schists shows preference for positive δS^{34} values whereas massive fine-grained ore, composed of banded and cockade pyrite, shows in turn negative δS^{34} values. This fine-banded ore exhibits a layered "sedimentary" texture characterized by coexisting pyrite, gelpyrite and magnetite. Pyrrhotite separated from irregular inclusions in massive pyrite ore exhibits positive δS^{34} values.

Chalcopyrite occurs usually with quartz gangue and shows positive δS^{34} values. Positive values exhibits also pyrite from a clear crosscutting quartz vein in drillhole EMB-7, as well as pyrite and galena finely distributed in green-schists in drillhole EMB-4. These veins appear to be products of later hydrothermal episodes in the deposit.

Adi Nefas samples contained for the most part admixtures of barite, and consequently the δS^{34} values resulted from sulfide and sulfate sulfur content

The most intimate intergrowth of barite with sulfides points out that the mineral suite originated contemporaneously. Hence δS^{34} total distribution could be regarded as indicative for the environment.

The evaluation attempted is as follows. *Adi Nefas* samples contained from 10 to 40 percent barite, in average about 22 percent, which yielded about 8.5 percent of sulfate sulfur referring to total sulfur. Calculating 91.5 percent of sulfide (pyrite) sulfur with a mean δS^{34} value 1.26 permil, contaminated with an average 8.5 percent of sulfate (barite) sulfur of unknown initial δS^{34} value — the mean δS^{34} value of the mixed 8 samples being 2.47 permil, the resulting δS^{34} value of barite sulfur could be computed to about + 15 permil.

Such a high δS^{34} value for barite sulfur indicates that sulfate sulfur did not originate from magmatic sources. If the composition of Precambrian seawater sulfate was about + 14.5 permil or so, then the barite sulfur should have been derived from marine sulfate. There is evidence that bacteriogenic reduction of seawater sulfate was operative. Biogenic fractionation in an organic environment may produce under certain conditions also sulfate sulfur enriched in S^{34} relative to marine sulfate (Lusk, 1972). As to the barium ions, they were most probably brought in the depositional environment by magmatic fluid compounds.

Barite is a common admixture in deposits of massive sulfides. It forms extensive beds closely associated with sulfides as e.g. in Paleozoic Meggen deposit in Germany (Buschendorf et al., 1963). Masses of barite are associated with Japan's Kuroko ores (Matsukuma and Horikoshi, 1970). Anderson (1969) reported, however, that barite has not been found in Precambrian stratabound deposits of massive sulfides.

The single negative value of galena from an apparently epigenetic quartz vein is difficult to explain until more isotopic data will be available for *Adi Nefas* mineral assemblage.

Samples of *Debarwa* pyrites show a mean δS^{34} value near zero permil. The narrow spread would indicate a magmatic source of sulfur although some negative values might be associated with bacteriogenic influence in sulfide formation. Unfortunately no barite from *Debarwa* mineral assemblage has been analysed as yet.

The slightly negative values of only three *Adi Rassi* samples are insufficient for conclusions.

The results of the preliminary isotopic investigations are not indicative of a simple interpretation. They do not support a plain magmatic origin. The spread of δS^{34} values, especially those of pyrite, is greater than that of magmatic hydrothermal deposits, and must be regarded rather diagnostic of biogenic sulfur generated in a marine environment. The broad range of δS^{34} permil values for pyrite and the presence of sulfur enriched in S^{32} and S^{34} may be due to derivation from multiple sources; part of pyrite-forming sulfur could be of magmatic origin via submarine springs, and part derived from seawater sulfate. It is conceivable that a sort of exchanges between exhaled fluid sulfur compounds and marine sulfate took place.

Considerable difference exists between pyrites and other sulfides, which δS^{34} permil values show narrower ranges with mainly positive values. This would support the evidence that they originated as later hydrothermal pro-

ducts. The mineralizing fluids were different in isotopic sulfur composition from those of the sedimentary environment of early bedded ore formation. The formation of later mineral inclusions and crosscutting veins, following the precipitation of early layered and banded ores of the "sedimentary" stage, could be interpreted by solution-deposition phenomena through revived hydrothermal activity. The solutions could have extracted the metals either from the original source, or from already precipitated ore minerals, hence remobilization. Hydrothermal activity has evidently occurred already during most early stages of ore formation and had continued further on with recurrences of igneous events, possibly also postdating regional metamorphism. Especially Debarwa and Adi Nefas deposits show best evidence, structurally and mineralogically, of the cooperation of later hydrothermal events which enriched them. Adi Rassi deposit exhibits a stockwork character and was affected by post-sedimentary mineralization as well.

S^{34} enrichment could be possibly explained by mixing of marine or connate sulfate with metal- and sulfur-bearing fluids egressing from magmatic sources in the way assumed by Lusk (1972) for Canadian New Brunswick massive sulfide deposits. Analogous conditions were found by Anger et al. (1966) for Rammelsberg deposit in Germany, where about 50 percent of all pyrites and sulfides of Cu, Zn and Pb were interpreted to have been derived from submarine magmatic springs on the sea floor. The rest of pyrites, showing enrichment in S^{32} , formed due to uptake of bacteriogenic sulfur.

Whatever the interpretation of isotopic fractionation, the broad range of isotopic composition of sulfur from Eritrean ores is an indication that isotopically light bacteriogenic sulfur participated, at least, in the formation of the dominant early precipitated pyrite. If negative permil values reflect the proportion of biogenic sulfur than the massive, fine-grained, banded pyrite would be most enriched in S^{32} . This ore type is characterized at Embaderho by coexisting sulfidic and oxidic minerals.

On the mechanism of sulfide precipitation on the sea floor one can speculate. There is some microscopic evidence that colloidal processes were involved. The pH — Eh and other controls of the depositional environment must have been such that the contemporaneous deposition of sulfides and oxides was made possible: pyrite and magnetite are coexistent in fine-banded ore. It can be supposed that amorphous colloidal iron hydroxides were precursors to magnetite. Barite precipitated contemporaneously at places, its sulfur having been derived from marine sulfate.

Conclusions

The initial geological studies of some of the Eritrean massive sulfide deposits point out that the origin of ores could be related basically to ancient volcanism, which produced metal rich fluids entering the marine sedimentary environment. The preliminary isotopic study of sulfide sulfur would support the submarine volcanic-exhalative origin. Considering the isotopic variations, on assumption that the primary isotopic differences have not been affected essentially by modest regional metamorphism, it becomes evident that the source of sulfur was varying while the deposit was forming. The ore bodies formed initially as syngenetic depositions of massive sulfides precipitated primarily from metal- and sulfur-

Table 1

Embaderho

Drill-hole No.	Depth (m)	Sample No.	δS^{34} permil value				Estimated admixtures (%)
			py	po	cp	gl	
EMB-1	5.30	E 15	3.42				
	98.30	E 14	-1.16				
	113.35	E 13	0.88				
	114.30	E 11	6.60				
	118.90	E 12	-2.52				
	144.98	E 10	-4.03				
	155.20	E 9	-2.62				
		E 24			12.80		py 5
	163.00	E 8	-12.44				
	240.80	E 7	-6.98				
	264.25	E 6	4.17				
	280.50	E 5	-12.39				
	288.25	E 21		3.35			py 5
		E 4		3.35			
	292.60	E 20			1.42		
	301.30	E 19			5.18		
		E 3		3.51			
301.40	E 23				12.66		
	E 2		4.15				
302.50	E 18			4.03		py 5	
	E 22				2.24		
303.90	E 1		4.32				
EMB-4	161.65	E 17	5.64				
		E 25				1.18	
EMB-7	101.35	E 15	4.28				

Adi Nefas

			py	sl	cp	gl	
AN-5A	136.70	N 1	3.76				
	137.70	N 2	4.07				
	139.40	N 11		4.71			py 45, sl 25, ba 30
	140.90	N 3	-4.05				
		N 12		3.08			py 55, sl 25, ba 20
	143.40	N 9			1.58		py 5, ba 20
	145.50	N 4	2.91				ba 15
	146.35	N 7			0.44		ba 10
	148.10	N 8			-1.45		ba 40
	149.10	N 5	2.73				ba 15
	151.45	N 6	5.80				ba 25
Outcrop		N 10				-5.97	

Debarwa

			py	
D-6A	51.40	D 1	1.68	sl 5 sl 5
	59.00	D 2	-1.98	
	71.00	D 3	-1.68	
	73.00	D 4	0.05	
	74.70	D 5	-0.68	
	100.80	D 6	6.01	
	110.30	D 7	2.22	
D-1/70	92.00	D 8	-0.73	bo + cc 20

Adi Rassi

			py	po	cp	
AR-D1	99.00	R 1			-0.90	
AR-E1	134.0	R 2		-2.40		cp 20, m 15
	136.0	R 3	-0.52			

Abbreviations:

py	— pyrite	m	— magnetite
po	— pyrrhotite	bo	— bornite
cp	— chalcopyrite	cc	— chalcocite
sl	— sphalerite	ba	— barite
gl	— galena		

-bearing solutions around submarine outlets, with syngenetic or early-epigenetic participation of seawater sulfate through bacteriogenic activity. The relatively high irregular fractionation would indicate that the depositional environment was rather unstable and characterized by short-term variability.

The following vein type mineralizations were introduced already early and subsequently probably in more stages. They were either newly brought mineral components or remobilization of original ore minerals. The hydrothermal processes have been causally related to structural disturbances and magmatism. The precipitated sulfides originated probably through interaction of sulfur-bearing fluids of prevailing magmatic origin with marine or connate sulfate. It is conceivable that the trapped connate waters, released and activated by compaction and heating of the sedimentary sequence in the geosynclinal basin, took part as well and reacted with magmatic fluids to form metal sulfides. Such origin may account for a general S³⁴ enrichment.

A further conclusion is that the phenomenon of complex submarine mineralization in eugeosynclinal environment, having a considerable temporary extension, possibly could not be of restricted local dimensions. Consequently, from practical point of view to look for possible ore, the Precambrian geosynclinal metavolcanic sequence of greenschist facies in Northern Ethiopia must be considered as a wide potential target for search of sulfide mineralizations of

this type. The present data indicate that the zone of interest might extend from Eritrea south-westward through Tigre and Beghemder provinces into Wollega province of Western Ethiopia and even further south. It extends in all probability northwards through Northern Eritrea and could be linked across the Red Sea with Saudi Arabian Precambrian where similar deposits of massive sulfides reportedly exist (Dr. Garnet, pers. comm.).

Table 2

Locality	Mineral	No. of samples	Range ‰	Difference ‰	Mean δS^{34} ‰
Embaderho	py	17	-12.44 to +6.98	19.42	-0.11 \pm 5.97
	po	4	+1.42 to +5.18	3.76	+3.49 \pm 1.36
	cp	3	+2.24 to +12.80	10.56	+9.23 \pm 4.93
	gl	1			+1.18
	Overall	25	-12.44 to +12.80	25.24	+1.64 \pm 5.91
Adi Nefas	py	3	-4.05 to +4.07	8.12	+1.26 \pm 3.75
	sulfides + ba (av. 22% ba)	8	-1.45 to +5.80	7.25	+2.47 \pm 2.36
	gl	1			-5.97 (?)
	Overall	12	-5.97 to +5.80	11.77	+1.47 \pm 3.42
Debarwa	py	8	-1.98 to +6.01	7.99	+0.61 \pm 2.46
Adi Rassi	po	1			-2.40
	py + cp	1			-0.52
	cp	1			-0.90
	Overall	3	-2.40 to -0.52	1.88	-1.27 \pm 0.81

Predhodne preiskave žveplovih izotopov in nastanek »masivnih sulfidov« v okolici Asmare

Milan Hamrla
Ljubljana, Prešernov trg 3

Rudna nahajališča »masivnih sulfidov« so bila odkrita pred nekaj leti tudi v severni Etiopiji v okolici Asmare, glavnega mesta province Eritreje. Vezana so večidel na kloritske zelene kamenine zgornjega prekambrija, ki vsebujejo interkalacije porfiritskih magmatskih kamenin. Raziskave nekaterih lokalnosti so pokazale, da je rudarsko izkoriščanje ekonomsko mogoče. Japonsko podjetje Nippon Mining Co, je nedavno odprlo prvo rudišče Debarwa ter pričelo z odkopavanjem. Začetno geološko proučevanje štirih najbolj dostopnih nahajališč Embaderho, Adi Nefas, Debarwa in Adi Rassi je pokazalo, da je nastanek orudenj v ozki zvezi s sedimentacijskimi in vulkanskimi dogodki naorskem dnu v prekambrijski geosinklinalni fazi ter ga lahko razlagamo z vulkanskimi ekshalacijami.

Konkordantna plastovito-lečasta rudna telesa so na splošno zgrajena iz drobnozrnate, ozko pasaste, pretežno piritske rude ter presekana z nedvomno mlajšimi žilnimi orudjenji. Opazovanja so vodila do splošnega sklepa, da so rudišča v glavnem kombinacija osnovne prevladujoče »sedimentarne« faze in poznejših »žilnih« faz, ki so jih obogatile. Med naštetimi rudišči so sicer določene strukturne in mineraloške razlike, ki pa so videti zgolj kvantitativne.

Da bi videli, ali more izotopska sestava žvepla sulfidov pripomoči h genetskemu tolmačenju orudenja, smo kot začetni poskus naročili analize žveplovih izotopov za 48 vzorcev sulfidov, ki smo jih pripravili iz jeder vrtin. Zaradi nizke stopnje regionalnega metamorfizma, ki ne preseže kloritskega faciesa, smatramo, da izotopska sestava žvepla rudnih mineralov ni bila bistveno spremenjena. δS^{34} vrednosti žvepla so izpremenljive in kažejo, da je bilo poleg žvepla magmatskega izvora udeleženo tudi bakterijsko žveplo, ki izvira iz sulfatov morske vode. Izotopske variacije nakazujejo, da je bilo biogenetsko žveplo udeleženo ne samo med singenetskim usedanjem prvotne rude okrog izhodišč vulkanskih ekshalacij naorskem dnu, ampak tudi pozneje v času »žilnih« faz, ki pomenijo najbrž mobilizacijo in premeščanje prvotnih rudnih mineralov. Povišane vrednosti δS^{34} v vzorcih sulfidov iz žil moremo tolmačiti s tem, da so se raztopine magmatskega izvora mešale s konatnimi vodami, vsebujočimi morski sulfat.

Čeprav ne poznamo vzrokov izotopske frakcionacije, lahko trdimo, da je ruda nastala ob bistveni udeležbi morskega sulfata. To dejstvo potrjuje njen nastanek v morskem okolju in potemtakem njeno stratigrafsko zvezo z zeleznimi metavulkanskimi, prvotno sedimentnimi plastmi zgornjega prekambrija. Razlaga nastanka z metasomatozo ali magmatskimi injekcijami sulfidne taline potemtakem ne pride v poštev. Stratigrafski, oziroma litološki koncept nakazuje obširno območje, v katerem moremo pričakovati nahajališča tega tipa, kar potrjujejo že doslej najdene indikacije. Ustrezna cona se vleče iz Eritreje proti jugozahodu v smeri zahodne Etiopije ter zlasti proti severu in je verjetno v zvezi z analognimi kameninami Saudske Arabije, v katerih poročajo o rudah istega tipa.

References

- Anger, G. et al. 1966, Sulfur isotopes in the Rammelsberg ore deposit (Germany). *Econ. Geol.*, vol. 61, p. 511—536.
- Anger, G. 1969, Die genetischen Zusammenhänge zwischen deutschen und norwegischen Schwefelkieslagerstätten unter besonderer Berücksichtigung der Ergebnisse von Schwefelisotopen Untersuchungen. *Clausthaler Hefte zur Lagerstättenkunde und Geochemie der Mineralischen Rohstoffe*, Heft 3.
- Anderson, C. A. 1969, Massive sulfide deposits and volcanism. *Econ. Geol.*, vol. 64, p. 129—146.
- Buschendorf, F., Nielsen, H., Puchelt, H., and Riecke, W. 1963, Schwefelisotopen Untersuchungen am Pyrit — Sphalerit — Baryt-Lager Meggen (Lenne/Deutschland) und an verschiedenen Devon Evaporiten. *Geochim. et Cosmochim. Acta*, vol. 27, p. 501—523.
- Dechow, E. and Jensen, M. 1965, Sulfur isotopes of some Central African sulfide deposits. *Econ. Geol.*, vol. 60, p. 894—941.
- Dechow, E. W. 1960, Geology, sulfur isotopes and the origin of the Heath Steele ore deposits, Newcastle, N. B. Canada. *Econ. Geol.*, vol. 55, p. 539—616.
- Field, C. W. 1966, Sulfur isotope abundance data, Bingham district, Utah. *Econ. Geol.*, vol. 61, p. 850—871.
- Field, C. W. and Moore, W. J. 1971, Sulfur isotope study of the "B" Limestone and galena fissure ore deposits of the U. S. Mine, Bingham mining district, Utah. *Econ. Geol.*, vol. 66, p. 48—62.
- Guha, J. 1971, Sulfur isotope study of the pyrite deposit of Amjhore, Shahbad district, Bihar, India. *Econ. Geol.*, vol. 66, p. 326—330.
- Hamrla, M. 1966, 1970, 1971, 1973. Unpublished reports on Eritrean base metal deposits. Archives of the Ministry of mines. Addis Ababa.
- Jensen, L. M. 1958, Sulfur isotopes and the origin of sandstone-type uranium deposits. *Econ. Geol.*, vol. 53, p. 598—616.
- Jelenc, D. 1966, Mineral occurrences of Ethiopia. Published by the Ministry of Mines, Addis Ababa.
- Jensen, M. L. 1971, Provenance of Cordilleran intrusives and associated metals. *Econ. Geol.*, vol. 66, p. 34—41.
- Kazmin, V. 1971, Precambrian of Ethiopia. *Nature*, No. 16, p. 230.
- Lusk, J. and Crocket, J. H. 1969, Sulfur isotope fractionation in coexisting sulfides from the Heath Steele B-1 orebody, N. B. Canada. *Econ. Geol.*, vol. 64, p. 147—155.
- Lusk, J. 1972, Examination of volcanic-exhalative and biogenic origins for sulfur in the stratiform massive sulfide deposits of New Brunswick. *Econ. Geol.*, vol. 67, p. 169—183.
- Matsukuma, T. and Horikoshi E. 1970, Kuroko deposits in Japan, a review. In: *Volcanism and ore genesis*. Edited by Tatsumi, T. Tokyo.

Stanton, R. L. and Rafter, T. A. 1967, Sulfur isotope ratios in coexisting galena and sphalerite from Broken Hill, New South Wales. *Econ. Geol.*, vol. 62, p. 1088 to 1091.

Smirnov, V. J. 1968, The sources of ore-forming material. *Econ. Geol.*, vol. 63, k. 380—389.

Thode, H. G. 1963, Sulfur isotope geochemistry. In: *Studies in analytical geochemistry*. Roy. Soc. Can., Spec. Publ. No. 6. Edited by Shaw, D. M., p. 25—41.

Tatsumi, T. 1965, Sulfur isotopic fractionation between coexisting sulfide minerals from some Japanese ore deposits. *Econ. Geol.*, vol. 60, p. 1645—1659.