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THE FIRST REPORT OF COBALT PENTLANDITE FROM A MID-ATLANTIC RIDGE HYDROTHERMAL DEPOSIT

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Abstract

We report the first occurrence of cobalt pentlandite in oceanic deposits at 14°45′N, Mid-Atlantic Ridge (MAR). The mineral occurs as small (less than 20 μm), round to irregular grains and aggregates associated with chalcopyrite, bornite, isocubanite, chalcocite, digenite, with minor pyrite and marcasite, and with rare covellite and Au-bearing zincian copper. On the basis of twenty-two analyses, the compositional range (in wt.%) is: Co 42.9–53.9, Ni 7.2–12.4, Fe 3.4–5.5, Cu 0.7–9.4 and S 31.6–32.9. Seventeen of the twenty-two compositions plot between Me_9S_8 and $Me_{15}S_{13}$. The narrow range of sulfur contents corresponds closely with those of synthetic pentlandite (44.2–47.9 at.%). The cobalt content of a pentlandite-group mineral depends on the mineral assemblage with which it is associated.

Keywords: cobalt pentlandite, Mid-Atlantic Ridge, electron-microprobe data.

Sommaire

Nous décrivons le premier exemple de cobalt pentlandite d'un gisement océanique, situé à 14°45′N sur la crête médio-atlantique. Le sulfure se présente sous forme de petits (<20 μm) grains ronds ou irréguliers et en agrégats, associés à chalcopyrite, bornite, isocubanite, chalcocite, digenite, avec pyrite et marcasite accessoires, et covellite et cuivre zincifère et aurifère rares. Nous avons effectué vingt-deux analyses, qui documentent les intervalles suivants, en pourcentages pondéraux: Co 42.9–53.9, Ni 7.2–12.4, Fe 3.4–5.5, Cu 0.7–9.4, et S 31.6– 32.9. Dix-sept des vingt-deux compositions se situent entre les stoechiométries Me_9S_8 et $Me_{15}S_{13}$. L'intervalle restreint de teneurs en soufre correspond étroitement à celles de la pentlandite synthétique (44.2–47.9%, en termes atomiques). La teneur en cobalt du minéral du groupe de la pentlandite dépend de la nature des minéraux associés.

(Traduit par la Rédaction)

Mots-clés: cobalte pentlandite, crête médio-atlantique, données de microsonde électronique.

Introduction

Cobalt pentlandite $(Co,Ni,Fe)_9S_8$ was first described by Kuovo *et al.* (1959) from several localities in Finland. Subsequently, it was reported from various localities world-wide (Stumpfl & Clark 1964, Petruk *et al.* 1969, Harris & Nickel 1972, Lindahl 1973). The cobalt contents of cobalt-bearing pentlandite range from less than 10 at.% to more than 80 at.% within the (Co,Ni,Fe) sites. As noted by Harris & Nickel (1972), all compositions of cobalt pentlandite fall within the solid-solution field of synthetic pentlandite. Guidelines for naming members of a solid-solution series were recently published by Nickel (1992). In a partial solid-solution series where the known compositions extend beyond the 50% mark, for example pentlandite $(Ni,Fe)_9S_8$, the composition of which centers on Ni:Fe = 1:1, and where the end members are not known, only one name should be given to the compositional range. For the cobalt-bearing pentlandite, the name cobalt pentlandite is used for compositions where Co is the major component in the (Co,Fe,Ni) sites, and cobaltian pentlandite is used for the other compositions of cobalt-bearing pentlandite.

Variations in Ni/Fe ratio of synthetic and natural pentlandites in relation to assemblages of associated minerals have been discussed by several authors. Lindahl (1973) indicated that the cobalt content of cobalt-bearing pentlandite reflects the sulfide assemblage in which it occurs. Where the mineral occurs with linnaeite or cobalt arsenides, the Co content is more than 80 at.% in the (Co,Ni,Fe) sites; where it is associated with pyrrhotite – chalcopyrite – cubanite – sphalerite assemblages, the Co content ranges from 50 to 80 at.%; in Co–Ni ores dominated by pyrrhotite – pyrite – chalcopyrite, the Co content ranges from 10 to 55 at.%. The Co content of normal pentlandite is generally below 10 at.%.

Cobalt-bearing minerals have not been reported from massive sulfide deposits on the ocean floor, even though up to 0.5 wt.% Co has been reported in sulfide aggregates from a near-axis seamount at 12°50′N, East Pacific Rise (Hekinian & Fouquet 1985). In a comparison of massive sulfide deposits from sedimented oceanic ridges with ancient sediment-hosted Besshi-type deposits, Zierenberg *et al.* (1993) noted that cobalt minerals are common in Besshi-type deposits, but not in occurrences on the present-day seafloor. Pentlandite has been reported in strongly altered gabbro from the Carlsberg Ridge in the Indian Ocean (Rozanova & Baturin 1971, Rozanova 1972) and from the Gorda Ridge in the Pacific Ocean (Hart *et al.* 1990), but no data on cobalt content were given.

In this paper, we describe the first find of cobalt pentlandite in an ocean-floor deposit, at 14°45′N, Mid-Atlantic Ridge (MAR). The samples were obtained by a TV-controlled hydraulic grab sampler at a depth of about 3000 m.

General Description of the Hydrothermal Field

The hydrothermal field within the MAR rift valley was discovered in late 1993 during cruise 7 of R/V "Professor Logatchev" organized by the Sevmorgeologiya Association, St. Petersburg (Batuev *et al.* 1994, Krasnov *et al.* 1995a). The field lies within an uplifted block of the rift valley, adjacent to its eastern wall (Fig. 1a). Ultramafic rocks (peridotite, pyroxenite and serpentinite) along with gabbro are prominent within the block. Basalt is less common and totally absent within the area of hydrothermal activity

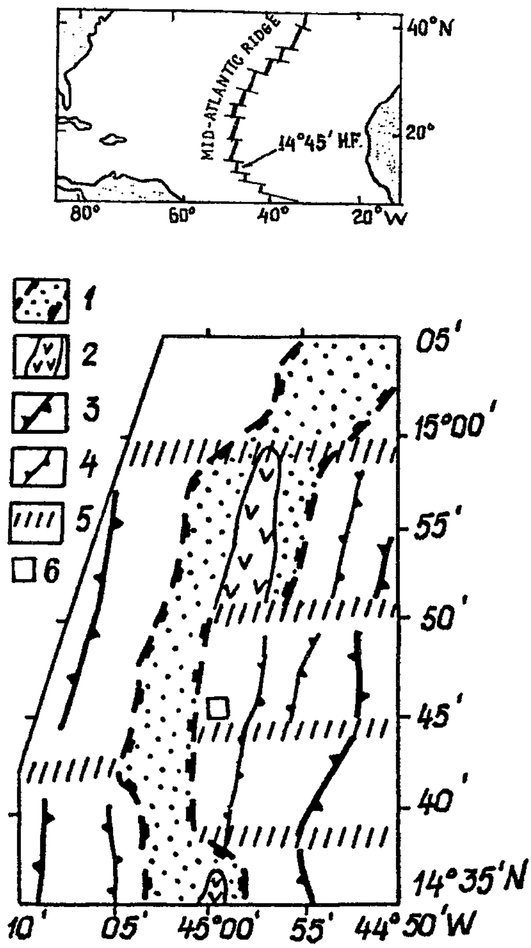

FIG. 1a. Location and morphology of the 14°45′N Mid-Atlantic Ridge (MAR) hydrothermal field. 1: rift-valley floor, 2: volcanic zones, 3: crests of linear highs flanking the rift valley, 4: crests of linear highs on the rift-valley slopes, 5: transverse dislocations, 6: position of area in Fig. 1b.

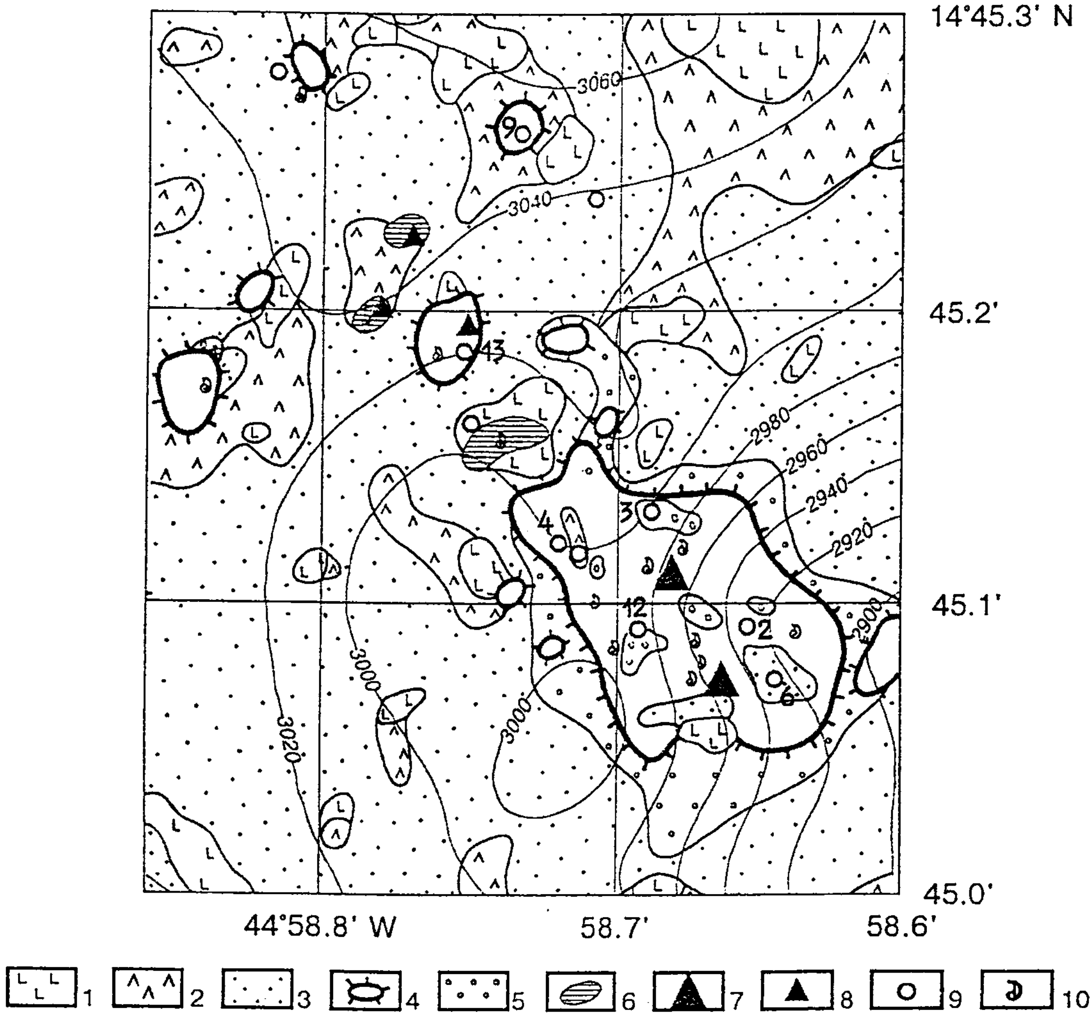

FIG. 1b. Geological map. 1: mafic and ultramafic rocks, 2: rocks talus, 3: carbonate sediments, 4: sulfide mounds, 5: sulfide sediments, 6: low-temperature hydrothermal deposits, 7: black smokers, 8: shimmering waters, 9: sample sites; 10: hydrothermal benthos communities.

(Fig. 1b). Twelve sulfide mounds up to 20 m high were mapped. The largest mound is about 200 × 100 m in plan. Two black smokers were observed on its top, but no chimneys appear on the photographs, and chimney fragments are rare among the sulfide samples (Krasnov *et. al.* 1995b). The position of the sampling sites is shown in Figure 1b.

OCCURRENCE AND ASSOCIATION OF COBALT PENTLANDITE

Cobalt pentlandite occurs in sample 9 (Fig. 1b) as small (less than 20 μm) round to irregular grains and aggregates associated with chalcopyrite, bornite, isocubanite, chalcocite, digenite; minor pyrite and marcasite are present, as are rare covellite and Au-bearing zincian copper. Cobalt pentlandite commonly occurs in bornite veinlets or is partly rimmed by bornite and digenite in a chalcopyrite matrix. Thin veinlets of chalcocite cut cobalt pentlandite and bornite (Fig. 2). Under reflected light, cobalt pentlandite is white, without pleochroism or anisotropism. Compared to chalcopyrite, its reflectance and hardness are higher. The grains are too small for quantitative measurements.

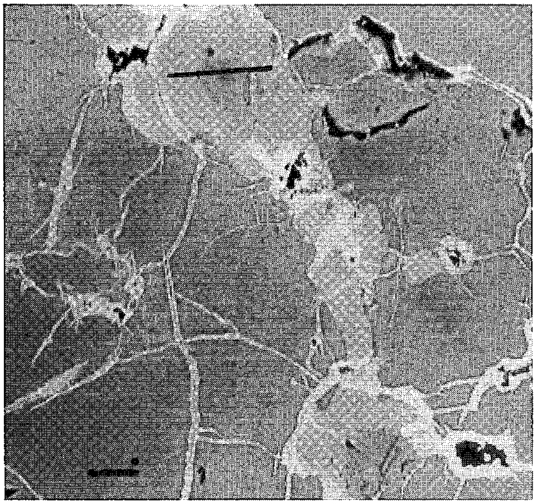

FIG. 2. Back-scattered electron image of two inclusions of cobalt pentlandite (grey) in a veinlet of bornite (light grey) within a matrix of chalcopyrite. Thin veinlets of chalcocite (white) cut the chalcopyrite and the veinlet of bornite. The scale bar at the bottom of the image is 10 μm. The compositional profile was measured along the traverse shown.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF COBALT PENTLANDITE, 14°45'N, MID-ATLANTIC RIDGE

No.	Co	Ni	Fe	Cu	S	Total	Formulae (based on 17 atoms)
1	42.9	9.6	5.5	9.4	32.5	99.9	$(Co_{5.75}Ni_{1.29}Fe_{0.78}Cu_{1.17})_{\Sigma 8.99}S_{8.01}$
2	44.2	9.1	5.1	8.1	32.2	98.7	$(Co_{5.99}Ni_{1.24}Fe_{0.73}Cu_{1.02})_{\Sigma 8.98}S_{8.02}$
3	46.1	9.1	5.5	6.3	32.6	99.6	$(Co_{6.18}Ni_{1.22}Fe_{0.77}Cu_{0.79})_{\Sigma 8.96}S_{8.04}$
4	46.2	9.1	4.6	5.4	32.1	97.4	$(Co_{6.33}Ni_{1.24}Fe_{0.66}Cu_{0.68})_{\Sigma 8.92}S_{8.08}$
5	48.6	10.5	4.6	3.9	32.4	100.0	$(Co_{6.50}Ni_{1.41}Fe_{0.65}Cu_{0.48})_{\Sigma 9.04}S_{7.96}$
6	49.1	9.6	4.0	4.6	32.4	99.7	$(Co_{6.58}Ni_{1.29}Fe_{0.57}Cu_{0.57})_{\Sigma 9.01}S_{7.99}$
7	49.9	10.0	4.6	3.0	32.5	100.0	$(Co_{6.67}Ni_{1.34}Fe_{0.64}Cu_{0.37})_{\Sigma 9.02}S_{7.98}$
8	50.2	12.4	4.7	0.7	32.5	100.5	$(Co_{6.68}Ni_{1.65}Fe_{0.65}Cu_{0.09})_{\Sigma 9.07}S_{7.93}$
9	50.5	9.1	4.0	3.4	32.3	99.3	$(Co_{6.79}Ni_{1.22}Fe_{0.57}Cu_{0.43})_{\Sigma 9.01}S_{7.99}$
10	51.3	8.5	4.0	2.4	32.0	98.2	$(Co_{6.98}Ni_{1.16}Fe_{0.57}Cu_{0.30})_{\Sigma 9.01}S_{7.99}$
11	51.4	9.2	4.3	2.7	32.2	99.8	$(Co_{6.88}Ni_{1.24}Fe_{0.61}Cu_{0.34})_{\Sigma 9.07}S_{7.93}$
12	51.4	10.6	4.6	1.6	32.4	100.6	$(Co_{6.83}Ni_{1.42}Fe_{0.64}Cu_{0.20})_{\Sigma 9.09}S_{7.91}$
13	51.6	10.2	4.4	1.8	32.4	100.4	$(Co_{6.87}Ni_{1.37}Fe_{0.61}Cu_{0.22})_{\Sigma 9.07}S_{7.93}$
14	52.0	9.4	4.2	2.5	32.5	100.6	$(Co_{6.91}Ni_{1.26}Fe_{0.59}Cu_{0.31})_{\Sigma 9.07}S_{7.93}$
15	52.4	10.1	4.4	1.7	32.9	101.5	$(Co_{6.89}Ni_{1.34}Fe_{0.61}Cu_{0.20})_{\Sigma 9.04}S_{7.96}$
16	52.5	9.6	3.7	2.4	32.8	101.0	$(Co_{6.94}Ni_{1.28}Fe_{0.52}Cu_{0.29})_{\Sigma 9.04}S_{7.97}$
17	52.6	10.9	4.5	0.9	32.6	101.5	$(Co_{6.93}Ni_{1.44}Fe_{0.63}Cu_{0.11})_{\Sigma 9.11}S_{7.89}$
18	52.6	9.1	3.7	2.1	31.6	99.1	$(Co_{7.12}Ni_{1.23}Fe_{0.53}Cu_{0.26})_{\Sigma 9.14}S_{7.86}$
19	52.6	9.9	3.9	1.4	32.3	100.1	$(Co_{7.02}Ni_{1.33}Fe_{0.55}Cu_{0.18})_{\Sigma 9.08}S_{7.92}$
20	53.1	8.4	4.0	2.5	32.4	100.4	$(Co_{7.07}Ni_{1.12}Fe_{0.57}Cu_{0.30})_{\Sigma 9.06}S_{7.94}$
21	53.4	8.4	4.0	2.4	32.1	100.3	$(Co_{7.13}Ni_{1.13}Fe_{0.56}Cu_{0.30})_{\Sigma 9.12}S_{7.88}$
22	53.9	9.1	3.4	2.0	32.8	101.2	$(Co_{7.12}Ni_{1.20}Fe_{0.47}Cu_{0.24})_{\Sigma 9.03}S_{7.97}$

The analytical results are quoted in weight %.

CHEMICAL DATA

The average concentration of eight elements in sample 9 and several large (tens to hundreds of kg) bulk samples is listed in Table 1. The cobalt pentlandite identified in sample 9 was analyzed on a CAMEBAX electron microprobe operated at 20 kV, 20 nA, using the following standards and X-ray lines: pure metals (Co*K*α, Ni*K*α, Fe*K*α, Cu*K*α) and FeS_2 (S*K*α). Results of the electron-microprobe analyses are listed in Table 2. Given the amount of copper present, the mineral can be considered a cuprian cobalt pentlandite. The microprobe analyses show that some grains are homogeneous, whereas others are zoned, with the central portion richer in Cu and Fe, and poorer in Co, than the outer zone. Statistical treatment of the twenty-two data sets shows a positive correlation between concentrations of Fe and Cu, and a negative correlation between the concentration of each of these elements and Co (Table 3). The sulfur contents (in at.%) are plotted on a frequency-distribution diagram (Fig. 3). The results show a slight shift to the metal-rich side of the ideal formula Me_9S_8 (47.05 at.% S). The compositions are within the range of sulfur contents

TABLE 1. BULK CHEMICAL COMPOSITION OF SULFIDE SAMPLES STUDIED COMPARED TO AVERAGE COMPOSITION OF MASSIVE SULFIDES FROM OTHER SITES ON THE OCEAN FLOOR

Sample locality	Fe	Cu	Zn	Pb	Cd	Co	Ag	Au
14°45'N Field:								
Sample 9	27.0	8.4	2.10	0.05	40	600	65	8.2
Average of 7 samples	22.3	19.0	1.51	0.04	34	329	70	9.2
TAG Field, active mound	30.2	9.2	5.24	0.05	144	363	70	2.1
MARK Field, surficial samples	33.6	9.0	4.59	0.03	175	273	62	1.8
MARK Field, core samples	37.2	10.1	4.65	0.03	192	644	16	0.6
East Pacific Rise	31.0	9.5	6.33	0.04	259	741	51	0.5

Concentrations of Fe, Cu, Zn and Pb are quoted in wt.%; concentrations of the other elements are quoted in ppm. Average data on other hydrothermal fields are taken from Krasnov et al. (1995b). Analyses were carried out in the Institute of Geological Prospecting for Rare and Noble Metals. The concentration of Cu, Zn and Pb was established by atomic absorption spectroscopy, and that of the other elements, by wet-chemical methods.

TABLE 3. CORRELATION COEFFICIENTS BETWEEN CONCENTRATIONS OF ELEMENTS IN COBALT PENTLANDITE, MID-ATLANTIC RIDGE

	Co	Ni	Fe	Cu	S
Co	1		0.88	–0.91	–0.68
Ni		1		–0.29	
Fe			1	0.71	0.46
Cu				1	0.69
S					1

Based on results of 22 electron-microprobe analyses. $R_{crit.}$ = 0.32 for P = 95%.

(46.2–47.9 at.%) for synthetic pentlandite with Fe/Ni = 1.0 quenched from 600°C (Shewman & Clark 1970). Comparison of our data on cobalt pentlandite with data from several land-based deposits (Fig. 4) reveals that the ocean-floor compositions are closest to those found in the deposits in Finland and Norway, where cubanite is one of the principal sulfide minerals.

Discussion

The nonstoichiometry of pentlandite has been discussed by Harris & Nickel (1972). Many authors have noted that both natural and synthetic pentlandites as well as cobalt pentlandite are slightly sulfur-deficient (Curlook & Pidgeon 1953, Stumpfl & Clark 1964, Knop *et al.* 1965, Shewman & Clark 1970). However, Harris & Nickel stated that the evidence for appreciable deviation from a 9:8 metal:sulfur ratio is not strong because the sulfur values were not considered sufficiently accurate.

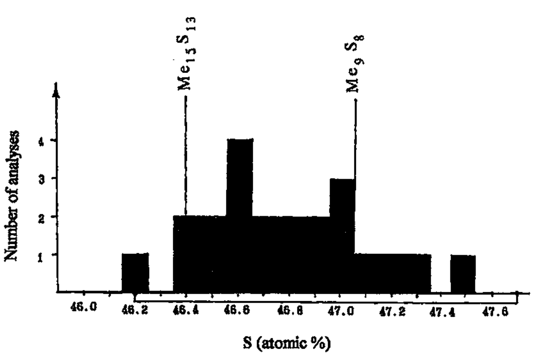

FIG. 3. Frequency distribution of sulfur contents (at.%) in ocean-floor cobalt pentlandite. $Me_{15}S_{13}$ and Me_9S_8 represent range of sulfur proportions in synthetic pentlandite (after Shewman & Clark 1970).

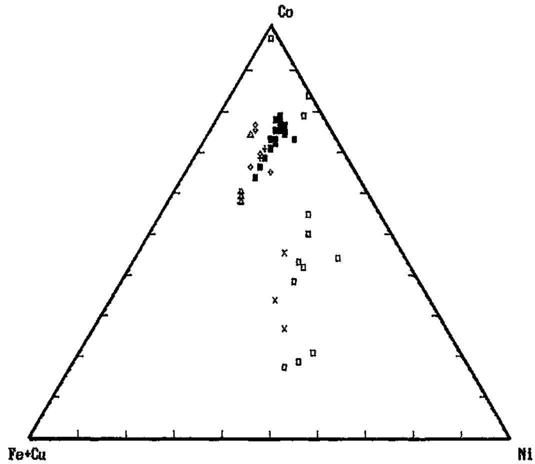

FIG. 4. Plot of proportions of Co, (Fe + Cu) and Ni in ocean-floor cobalt pentlandite and some land-based occurrences. Symbols: full squares: this study; open triangles: Kongsfjell, Norway, pyrrhotite – chalcopyrite – cubanite – sphalerite assemblage (Lindahl 1973); plus signs: Varislahti, Finland, pyrrhotite – cubanite – chalcopyrite assemblage (Kuovo *et al.* 1959); crosses: Outokumpu mine, Finland, pyrrhotite – chalcopyrite – pyrite assemblage (Kuovo *et al.* 1959); open squares: Canadian deposits, association of Co-sulfides, Co-arsenides with pyrite, marcasite and other minerals (Stumpfl & Clark 1964, Harris & Nickel 1972); open diamonds: Birtavarre, Norway, pyrrhotite – chalcopyrite – cubanite – sphalerite assemblage (Lindahl 1973).

The data obtained for the ocean-floor cobalt pentlandite (22 electron-microprobe analyses obtained under the same analytical conditions and partly from the same zoned grain) show a narrow range of sulfur content, compared to that recorded in synthetic pentlandite. This finding corresponds to early observations and is consistent with the suggestion of a narrow field of nonstoichiometry in this mineral. The change of the oxidation state of iron from Fe^{2+} to Fe^{3+}, along with a slightly increasing quantity of Fe^{3+}, may account for the small range in sulfur content. Our data also support the conclusion of Lindahl (1973) that the cobalt content of the pentlandite-group mineral in continental deposits depends upon the associated sulfides.

Compared to other occurrences of massive sulfide in the Pacific and Atlantic oceans (Krasnov *et al.* 1995a), the samples examined in this study are richer in Cu and Au, with lower Zn and Cd, but they show comparable Co contents. However, Bogdanov *et al.* (1995) reported a relative enrichment of sulfides from this site in cobalt. The main feature of the 14°45′N site is the wide distribution of ultramafic rocks. The presence of Ni minerals should be expected on the basis of elevated

Ni contents of ultramafic rocks, which are subject to leaching by hydrothermal solutions. However, Ni has limited mobility in chloride solutions, and is captured from solutions by chlorite, serpentine and other secondary magnesian minerals present in ocean-floor rocks (Grichuk & Krasnov 1989). Therefore, Ni is expected to have low mobility in oceanic hydrothermal processes, and never becomes enriched in massive sulfides. This is evidently the reason for the formation of cobalt pentlandite instead of pentlandite in the samples studied.

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References

Batuev, B.N., Krotov, A.G., Markov, V.F., Cherkashev, G.A., Krasnov, S.G. & Lisitsyn, Ye.D. (1994): Massive sulphide deposits discovered and sampled at 14°45′N, Mid-Atlantic ridge. *BRIDGE Newsletter* **6**, 6-10.

Bogdanov, Yu.A., Sagalevich, A.M., Chernyaev, E.S., Ashidze, A.M., Gurvitsch, E.G., Lukashin, N.V., Ivanov, G.V. & Peresipkin, V.J. (1995): The hydrothermal field at 14°45′N, Mid-Atlantic Ridge. *Dokl. Akad. Nauk* **343**(3), 353-357 (in Russ.).

Curlook, W. & Pidgeon, L.M. (1953): The Co–Fe–S system. *Can. Inst. Mining Metall. Bull.* **46**, 297-301.

Grichuk, D.V. & Krasnov, S.G. (1989): Sources of ore-forming elements in modern hot springs of the ocean floor. *Lithology and Mineral Deposits* **1**, 80-88 (in Russ.).

Harris, D.C. & Nickel, E.H. (1972): Pentlandite compositions and associations in some mineral deposits. *Can. Mineral.* **11**, 861-878.

Hart, R., Hoefs, J. & Pyle, D. (1990): Multistage hydrothermal systems in the Blanco fracture zone. *In* Gorda Ridge, a Seafloor Spreading Center in the United States Exclusive Economic Zone (G.R. McMurray, ed.). Springer-Verlag, New York, N.Y. (51-57).

Hekinian, R. & Fouquet, Y. (1985): Volcanism and metallogenesis of axial and off-axial structures of the East Pacific Rise near 13°N. *Econ. Geol.* **80**, 221-249.

Knop, O., Ibrahim, M.A. & Sutarno (1965): Chalcogenides of the transition elements. IV. Pentlandite, a natural π phase. *Can. Mineral.* **8**, 291-316.

Krasnov, S.G., Gherkashev, G.A., Stepanova, T.V. and ten others (1995b): Detailed studies of hydrothermal fields in the North Atlantic. *In* Hydrothermal Vents and Processes (L.M. Parson, C.L. Walker & D.R. Dixon, eds.). *Geol. Soc., Spec. Publ.* **87**, 43-64.

________, Poroshina, I.M. & Cherkashev, G.A. (1995a): Geological setting of high-temperature hydrothermal activity and massive sulfide formations on fast and slow-spreading ridges. *In* Hydrothermal Vents and Processes (L.M. Parson, C.L. Walker & D.R. Dixon, eds.). *Geol. Soc., Spec. Publ.* **87**, 17-32.

Kuovo, O., Huhma, M. & Vuorelainen, Y. (1959): A natural cobalt analogue of pentlandite. *Am. Mineral.* **44**, 897-900.

Lindahl, I. (1973): Cobalt pentlandite from Kongsfjell, Norway and Birtavarre, northern Troms. *Norges Geol. Unders. Nr* **294**, 9-19.

Nickel, E.H. (1992): Solid solutions in mineral nomenclature. *Can. Mineral.* **30**, 231-234.

Petruk, W., Harris, D.C. & Stewart, J.M. (1969): Langisite, a new mineral, and the rare minerals cobalt pentlandite, siegenite, parkerite and bravoite from the Langis mine, Cobalt–Gowganda area, Ontario. *Can. Mineral.* **9**, 597-616.

Rozanova, T.V. (1972): New data on petrology of metamorphic rocks of Rift zone of Arabian–Indian ridge. *Oceanology* **12**(6), 1028-1036 (in Russ.).

________ & Baturin, G.N. (1971): On the hydrothermal ore occurrences on the Indian ocean floor. *Oceanology* **11**(6), 157-164 (in Russ.).

Shewman, R.W. & Clark, L.A. (1970): Pentlandite phase relations in the Fe–Ni–S system and notes on the monosulfide solid solution. *Can. J. Earth Sci.* **7**, 67-85.

Stumpfl, E.F. & Clark, A.M. (1964): A natural occurrence of Co_9S_8, identified by X-ray microanalyses. *Neues Jahrb. Mineral., Monatsh.*, 240-245.

Zierenberg, R.A., Koski, R.A., Morton, J.L., Bouse, R.M. & Shanks, W.C., III (1993): Genesis of massive sulfide deposits on a sediment-covered spreading center, Escanaba Trough, southern Gorda Ridge. *Econ. Geol.* **88**, 2069-2098.

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