

Hydrothermal Alteration and Sulfide Mineralization in Gabbroids of the Markov Deep (Mid-Atlantic Ridge, 6° N)

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Abstract—A new type of sulfide occurrence related to metasomatically altered brecciated gabbroids has been studied at the Sierra Leone site situated in the axial rift valley of the Mid-Atlantic Ridge (Markov Deep, 6° N). Two associations of plutonic, subvolcanic, and volcanic rocks were dredged: (1) mid-ocean ridge basalts (MORB) and their intrusive analogues and (2) rocks of the silicic Fe–Ti-oxide series with dominating gabbro-norites and sporadic trondhjemites. Almost all igneous rocks at the Sierra Leone site are enriched in Pb, Cu, U, Ga, Ta, Nb, Cs, and Rb and depleted in Zr, Th, and Hf. The rocks of the Fe–Ti-oxide series are enriched in Zn, Sn, and Mo and depleted in Ni and Cr. The main ore-bearing zone is situated at the foot of the eastern wall of the deep, where it is hosted in cataclastic hornblende gabbro and gabbro-norite of the Fe–Ti-oxide series. Ore mineralization in metasomatically altered rocks is composed of quartz–sulfide and prehnite–sulfide veinlets, disseminated sulfide, and veined copper sulfide ore. The ore consists of pyrite, chalcopyrite, sphalerite, pyrrhotite, bornite, chalcocite, and digenite. The $\delta^{34}\text{S}$ value of sulfides varies from 3.0 to 15.3‰. At the foot of the eastern wall of the Markov Deep, directly downslope from the ore-bearing zone, loose sediments contain grains of native Cu, Pb, Zn, and Sn and intermetallic compounds (isoperplatinum, tetraferroplatinum, and brass) apparently derived from the ore. Mineral assemblages of ore-bearing metasomatic rocks and fluid inclusions therein were studied. Ore metasomatism developed under a low oxygen potential within a temperature interval from 400 to 160°C, though initial hydrothermal alteration of rocks proceeded at temperatures of 800–450°C. The temperature of stringer–disseminated ore mineralization is estimated at 170–280°C. The hydrothermal fluids are considered to be of magmatic origin; as the hydrothermal system evolved, they became diluted with sea-water that was contained in fractured oceanic crust. The ore matter could have been derived from magmatic fluids that were released from water-saturated melts of the Fe–Ti oxide series during their ascent and leached from host gabbroids in the process of metasomatic alteration.

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INTRODUCTION

The discovery of ore-forming systems in rift zones of oceans more than 20 years ago posed for geologists the new problem of estimating the scope and trends of recent ore formation over the greater part of our planet. This particularly refers to massive sulfide deposits, which are mostly related to ophiolitic associations and are often regarded as ancient analogues of the recent black smokers, which were discovered in the 1970s–1980s in the axial spreading zones of the World Ocean. The sulfide mounds were formed at the magmatic stage of rift evolution on neovolcanic rises directly above magma conduits. Recent ore-forming systems were discovered later in serpentinized ultramafic oceanic

rocks of the Logachev, Ashadze, and Rainbow hydrothermal fields (Batuyev et al., 1994; Krasnov et al., 1995; Fouquet et al., 1993; Bel'tenev et al., 2004a; Bortnikov and Vikent'ev, 2005). They were also discovered in the segments of the slow-spreading Mid-Atlantic Ridge (MAR) that are now at the tectonic stage of development and whose activity is controlled by faults in the walls of the axial rift valley. The mineralogical and geochemical features of these hydrothermal systems differ from those related to neovolcanic rises (Bogdanov et al., 2002).

In the axial MAR zone of the Markov Deep (the Sierra Leone site) during Cruise 10 of the R/V *Akademik Ioffe* in 2001–2002, we discovered one more type of ore mineralization that developed in a similar tectonic setting (Pushcharovsky et al., 2004), and this discovery was confirmed during Cruise 22 of the

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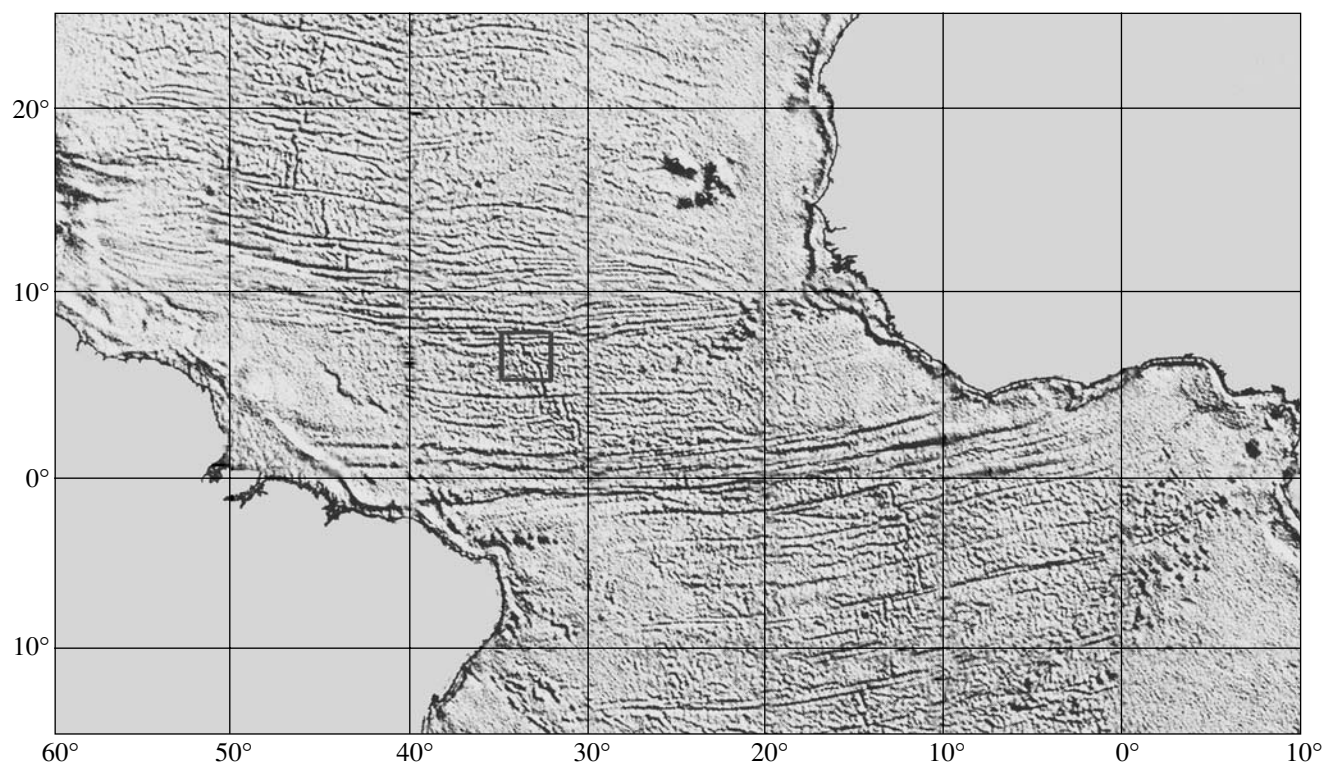


Fig. 1. Index map with location of the Sierra Leone site.

R/V *Professor Logachev* in 2003 (Bel'tenev et al., 2004b). This mineralization is related to zones of metasomatic reworking of gabbroids and comprises disseminated sulfides and sulfide veinlets and veins. About 100 dredgings yielded 2400 kg of bedrocks, including altered wall rocks with sulfide mineralization and fragments of copper sulfide veins (about 50 kg of ore material).

This paper presents the results of studying the geology of the ore-bearing zone, the petrography and geochemistry of host rocks, ore-bearing structural elements, and sulfide mineralization. The composition of fluid inclusions in metasomatic minerals and the isotopic sulfur composition of sulfides are characterized as well.

GEOLOGY

The studied MAR segment is situated close to the Sierra Leone Fracture Zone (FZ) between the Bogdanov FZ (7°10' N) and 5°00' N (Fig. 1). North of the Bogdanov FZ, the axial valley of the MAR was displaced by a number of large transform FZs (Vema, Arkhangel'sky, Doldrums, and Vernadsky). The topography of the ridge is intensely dissected; its minimum depth is ~2 km. Farther south of 5°00' N up to the Strakhov FZ, the MAR is a plateau crossed by a narrow NS-trending axial rift valley (Pushcharovsky et al., 2004). The morphostructure of this segment is distinguished by the absence of transform faults and a variable strike of the rift valley, formed by an en echelon system of grabenlike basins as deep as 4–5 km; the

Markov Deep is one of these basins. This MAR segment, unlike the adjacent areas, is characterized by low seismicity. As was pointed out by Mazarovich and Sokolov (1998), the large sulfide occurrences associated with black smokers are localized in precisely such a tectonic setting.

This site attracted particular attention because dolerites with sporadic sulfide disseminations along local zones of low-temperature alteration were carried up from the walls of the rift valley in the course of dredging during Cruise 22 of the R/V *Akademik Nikolai Strakhov*. The dredging was conducted in the adjacent rift structures as well, but the main efforts were focused on the Markov Deep, where the fairly coarse-grained stringer-disseminated, predominantly chalcopyrite mineralization is hosted in prehnite–chlorite–epidote metasomatic rocks that replaced mylonites and cataclasites in gabbro. The data on the composition of ferromanganese nodules (Bazilevskaya and Skolotnev, 2002), the thermohaline structure of seawater (Demidova et al., 2003), and its transparency (Pushcharovsky et al., 2004) indirectly indicate that hydrothermal systems, discharging on the seafloor, may have existed and might exist in the Markov Deep.

Geology of the Markov Deep

The Markov Deep extends for 20–22 km along the rift axis; its width varies from 8 to 11 km and its depth is about 4975 m. The basin is bounded by escarps 700–

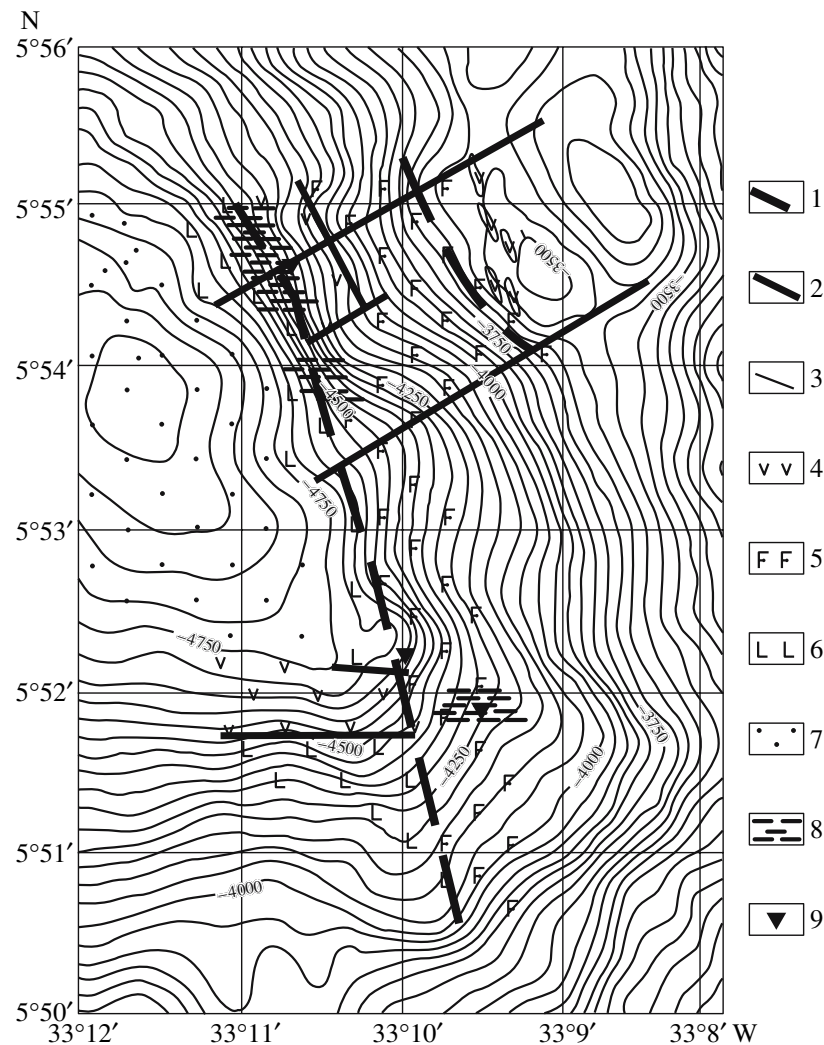


Fig. 2. Geological structure of the eastern wall of the Markov Deep after (Bel'tenev et al., 2004). (1) Zones of tectonic deformation and metasomatism; (2) fracture zones; (3) geological boundaries; (4–7) fields of (4) basalts, (5) gabbroic rocks, (6) ultramafic rocks, and (7) sedimentary cover; (8) zones of hydrothermally altered rocks; (9) sulfide mineralization in bedrocks.

800 m high. An ore occurrence has been revealed in the northern part of the basin near the foot of its eastern slope. Here the rift valley is asymmetric, bounded by a steep eastern wall where the depth varies from 5.0–4.6 to 2.2 km at a distance of 3–4 km and a gently dipping western wall with a depth varying from 5.0 to 4.6 km up to 2.8 km at a distance of 10.5 km from the rift axis. The thickness of loose sediments near the foot of the eastern slope amounts to 30 m.

The results of dredging have shown that the walls of the rift valley are composed of serpentinized peridotites and gabbroids locally transformed into mylonites and cataclasites and affected by metasomatic alteration. Intensely altered and tectonized basalts and dolerites are exposed at the valley bottom, on its flanks, and in the upper part of its slopes; fresh basalts with glassy crusts occur at the valley bottom and on slopes of neo-volcanic rises.

Based on detailed sampling at the eastern and south-eastern slopes of the Markov Deep, a geological scheme of the ore-bearing zone has been drawn (Fig. 2). At least two zones of intense tectonic deformation and metasomatism at depths of 4400–4600 and 3700 m extend in the northwestern direction along the basin wall; sulfide mineralization was found in the lower zone (Bel'tenev et al., 2004b).

Rock complexes characteristic of the entire oceanic crust section are developed in both walls of the rift valley. Remote sensing carried out at the eastern wall of the Markov Deep during Cruise 22 of the R/V *Professor Logachev* in 2003 using a GBO MAK-1M side scan sonar has shown that the crust is perfectly layered. This allows us to suggest that the majority of studied rocks are part of a layered complex similar to that observed in ophiolitic associations of the type of Monviso in the Western Alps (Lombardo et al., 2002).

Abundant sediments in the axial valley and widespread ultramafics and gabbro suggest that the present-day spreading of the oceanic crust in the studied segment of the MAR occurs under conditions where tectonic processes prevail over magmatic activity (Peive et al., 2003). At the same time, the dry spreading is accompanied by development of thick and extended neovolcanic ridges made up of fresh basalts with glassy crusts.

Lithology of the Oceanic Crust in the Markov Deep

The set of dredged rocks is common for slow-spreading ridges, including the MAR (Dick et al., 1992). The following rocks have been identified: (1) ultramafics, including lherzolite, harzburgite, and dunite; some of them are mantle restites, while others contain relics of cumulative structures and apparently belong to intrusive rocks; (2) gabbroids, which comprise troctolite, olivine gabbro, gabbro, norite, gabbronorite, hornblende gabbro, gabbro pegmatite, Fe–Ti-oxide gabbronorite, gabbrodiorite, and associated granodiorite and plagiogranite (trondhjemite); (3) dolerite of a dike (?) complex, ilmenite–hornblende varieties inclusive; and (4) fragments of pillow and massive basaltic lavas.

Virtually all rocks except fresh pillow lavas with chilled glassy crusts underwent cataclasis and regional metamorphism under conditions of greenschist and epidote-amphibolite facies. Metamorphosed ultramafics, gabbro, and dolerites are opposed to metasomatically altered rocks.

Petrography of Ocean Floor Bedrocks

Detailed petrographic and geochemical descriptions of igneous rocks and compositions of primary minerals were published by Pushcharovsky et al. (2004), Sharkov et al. (2005), Savel'eva et al. (2006), and Skolotnev et al. (2003), so that only a brief overview is given below.

The following abbreviations of minerals are accepted in the text: (Ol) olivine, (Opx) orthopyroxene, (Cpx) clinopyroxene, (Di) diopside, (Pl) plagioclase, (Ab) albite, (An) anorthite, (Qtz) quartz, (Hbl) brown hornblende of the kaersutite series, (Act) actinolite, (Trem) tremolite, (Chr) chromite, (Ilm) ilmenite, (Mag) magnetite, (Ap) apatite, (Zrn) zircon, (Srp) serpentine, (Chl) chlorite, (Ep) epidote, (Czo) clinozoisite, (Prh) prehnite, (Tlc) talc, (Prg) pargasite, (Ttn) titanite (sphene), (Py) pyrite, (Po) pyrrhotite, (Pn) pentlandite, (Ccp) chalcopyrite, and (Sp) sphalerite. The samples collected by the R/V *Akademik Strakhov* are marked by the index S; the *Akademik Ioffe*, by I; and the *Professor Logachev*, by L.

Ultramafic Rocks

Ultramafic rocks are exposed at the walls of the rift valley; at the summits of rift mountains; and, frequently, on the bottom of rift troughs. Ultramafic mantle restites and cumulates are recognized. Both experienced high-temperature cataclasis and subsequent low-temperature alteration expressed in intense serpentinization of rocks, turned locally into serpentine–chlorite and serpentine–amphibole–talc schists and, less frequently, talcites.

Among mantle restites, lherzolite and harzburgite with porphyroclastic structures are predominant; dunite samples are sporadic. In many cases, serpentinized peridotites contain veins of fine-grained and pegmatoid gabbro, both altered and fresh.

Intrusive peridotites with relics of cumulative structures presumably pertain to the layered series of the third layer of the oceanic crust. Sample I1060-43 shows a transition from cumulative dunite to cumulative melanocratic troctolite, thus indicating a zone of alternating dunite and troctolite. Unaltered lherzolite and harzburgite are retained as rounded and angular fragments in eruptive breccia cemented with hornblende gabbronorite and granodiorite. The peridotite fragments “sealed” in these rocks did not undergo low-temperature alteration. Pyroxenites (bronzitite and websterite) are noted occasionally.

Gabbroids and Associated Rocks

Gabbroids are abundant among the dredged rocks and diverse in modal composition, texture, and structure. Massive and banded varieties, fine-, medium-, and coarse-grained up to pegmatoid, are predominant. Most gabbroids have cumulative structures. Two groups of gabbroids are distinguished: (1) primitive magnesian gabbroids and (2) rocks of the silicic Fe–Ti-oxide association (Sharkov et al., 2005), which are characteristic of the lower part of the crustal section at the valley walls.

The primitive gabbroids, first of all, embrace troctolites (Ol–Pl cumulates), which are composed of subhedral crystals of olivine Fo_{83-85} and plagioclase An_{76-80} ; fine euhedral chromite crystals are present in small amounts. Several samples contain small irregular chalcopyrite grains. In addition, there are olivine gabbro (Ol + Cpx + Pl cumulates); gabbro (Cpx + Pl cumulates); and, occasionally, gabbroanorthosite (Pl cumulates). Subvolcanic analogues of these rocks are dolerites and olivine dolerites, and volcanic analogues are olivine and plagiophyric basalts.

The rocks of the silicic Fe–Ti-oxide series are commonly characterized by the occurrence of primary magmatic brown hornblende; Fe–Ti oxides (Ilm and Ti-Mag); clino- and orthopyroxene, including inverted pigeonite; apatite, zircon, and baddeleyite; and small copper sulfide segregations. This rock association comprises melanocratic troctolite, norite, gabbronorite, hornblende gabbro, Fe–Ti-oxide hornblende gabbronorite, gab-

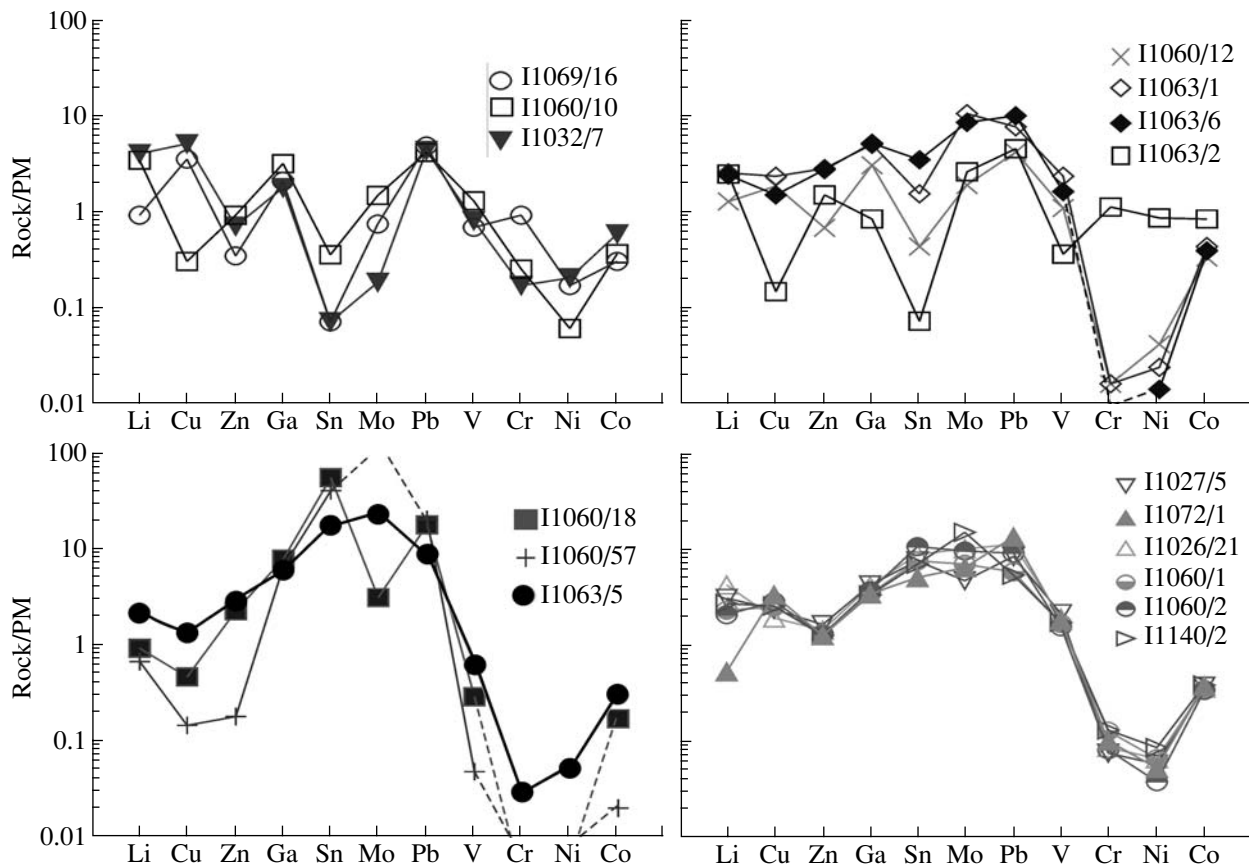


Fig. 3. Contents of ore components normalized to primitive mantle (PM) after (McDonough and Sun, 1995). Samples I1069/16, I1060/10, and I1032/7 are primitive troctolites and gabbroids; samples I1060/12, I1063/1, I1063/6, and I1063/2 are rocks of the silicic Fe–Ti-oxide series: I1063/1 and I1063/6 are hornblende ferrogabbroites, I1060/12 is cataclastic gabbro with brown hornblende, and I1063/2 is cataclastic cumulative harzburgite; samples I1060/18, I1060/57, and I1063/5 are granodiorites and trondhjemite (sample I1060/57); samples I1027/5, I1072/1, I1026/21, I1060/1, I1060/2, and I1140/2 are fresh basalts.

brodiorite, and diorite with small segregations of granodiorite composition; in some cases, irregular plagiogranite (trondhjemite) veins are noted. The aforementioned peridotite and pyroxenite with relics of cumulative structures probably belong to the same, Fe–Ti-oxide series. Fe–Ti-oxide dolerites and hornblende basalts with ilmenite are subvolcanic and volcanic analogues of this series. Unlike MORB, widespread all over the site, hornblende basalts are very rare.

Geochemistry of Igneous Rocks

The geochemistry of rocks was considered in detail by Pushcharovsky et al. (2004), Sharkov et al. (2005), and Savel'eva et al. (2006) and is not discussed here. We only focus on the results of normalization of ore element concentrations to primitive mantle. As follows from Fig. 3, nearly all igneous rocks in the Sierra Leone site are enriched in Pb, Cu, U, Ga, Ta, Nb, Cs, and Rb and depleted in Zr, Th, and Hf. The minimum contents of incompatible elements are established in primitive troctolites and gabbro; intermediate contents are characteristic of hornblende Fe–Ti-oxide gabbroite, and

the maximum are noted in diorite and plagiogranite. The rocks of the Fe–Ti-oxide series are enriched in Zn, Sn, and Mo along with moderate Cu and Pb contents and depletion in Ni and Cr. The contents of ore components in basalts are much closer to those in rocks of the Fe–Ti-oxide association than to primitive troctolite and gabbroids.

Origin of Plutonic Rocks in the Markov Deep

The primitive gabbroids most likely are derivatives of MORB-type melts, but the situation with the Fe–Ti-oxide series is not so clear. These rocks commonly occur in slow-spreading ridges (the MAR and West Indian) and are usually regarded as late differentiates of MORB tholeiites (Dick et al., 1992). However, their specific composition, characterized by abundant low-Ca pyroxenes, primary hornblende, and Fe–Ti-oxides, as well as depletion in incompatible elements, LREE inclusive, is not consistent with such an interpretation. The presence of primary hornblende and separate crystallization of ilmenite and magnetite indicate enrichment of initial melts in water, as supported by the

occurrence of 1.24 wt % H₂O in melt inclusions in chromite from melanocratic troctolite (Simonov et al., 2007). Geochemical data suggest that the rocks are rich in silica, Ti, Fe, Nb, Pb, Cu, Zn, and other components mobile in high-temperature fluid.

On the basis of these data, the origin of the Fe–Ti-oxide series should be explained by melting of hydrated oceanic lithosphere on its intrusion by asthenospheric plumes, or protuberances on the surface of the asthenospheric lens that maintains the existence and evolution of the MAR (Sharkov et al., 2005). The ore occurrence of the Markov Deep is hosted in gabbroids of this series.

Temporal relationships between the primitive and Fe–Ti-oxide associations remain unknown. At present, only the age of the second association has been dated, at 97.42 ± 0.15 Ma with the U–Pb method (TIMS) with zircon from hornblende gabbro-norite at Station I1028 (Sharkov et al., 2004). This estimation implies that the gabbroic complex of the third layer of the oceanic crust is heterogeneous and was not formed in one event. Most likely, the gabbroic complex is a combination of diverse intrusive bodies of different age (intermediate magma chambers) formed in the lower oceanic crust.

The studied area is not unique in the set of rocks. Similar serpentinized ultramafic and mafic rocks of the silicic Fe–Ti-oxide series make up the basement of the Logachev and Ashadze hydrothermal fields with high-grade sulfide mineralization in the axial MAR zone close to 13° N (Bel'tenev et al., 2004b). Hornblende Fe–Ti gabbroids are also known from the Vema transform FZ (Skolotnev, 2003) and the Kane FZ (our unpublished data on the dredging during Cruise 16 of the R/V *Akademik Ioffe*, 2004), north of the Sierra Leone site, and in the Atlantis Bank in the slow-spreading West Indian Ridge (Boreholes 735B, 1105, and others (Dick et al., 2001; Silant'ev, 1998)).

METAMORPHIC AND METASOMATIC PROCESSES

Three types of secondary alteration are observed in the studied rocks: (1) high-temperature alteration, including subsolidus rock transformation under conditions of ductile flow of ultramafic and gabbroic rocks; (2) medium- to low-temperature alteration related to brittle deformation of all rock varieties; and (3) zones of low-temperature metasomatic alteration of brecciated gabbroids and ultramafic rocks.

The high-temperature transformation of rocks is broadly similar to that observed in ophiolitic associations and is related to ductile flow of still hot material under dynamic conditions of the spreading axis. The further brittle deformation was accompanied by low-temperature alteration. Judging from assemblages of metamorphic minerals, this alteration proceeded under conditions of zeolite to epidote-amphibolite facies (serpentines of the lizardite series after olivine; fibrous amphiboles of the tremolite-actinolite series after

pyroxenes and kaersutite; saussuritization and epidotization of plagioclase; the appearance of Tlc, Czo, Chl, Prh, zeolites, etc.).

The most intense deformation is expressed in cataclasis and blastomylonitization of gabbroids and, less frequently, ultramafic rocks. These are fine-grained, locally thinly banded schistose amphibole-chlorite-epidote-clinozoisite rocks with fragments of minerals and rocks. Chaotic plication, marks of sliding on the surface of fragments, and fragments of small folds with clearly observed hinges emphasized by lineation show that tectonic movements developed under conditions of shearing.

Metamorphic Processes

Secondary alteration of ultramafic rocks (peridotites and dunites) in the course of their medium- and low-temperature hydration and dynamometamorphism is expressed in formation of the following rock series: amphibolized peridotites, actinolite-tremolite-serpentine schists, talcites, actinolite-talc-serpentine schists, serpentinites with abundant slickensides and serpentine asbestos veins.

The earliest and most high-temperature pargasite hornblende (Mg# = 86–90) with a high Cr₂O₃ content (1.2–1.8 wt %) was revealed in lherzolite along thin shear zones of olivine and enstatite recrystallization, where it probably is in equilibrium with olivine neoblasts: $Ol_1 + En_1 \pm Di_1 \rightarrow Parg + Ol_2$. Pyroxenes are more frequently replaced by amphibole of the actinolite-tremolite series (Mg# varies from 85 to 93) along the margins of large grains: $En \pm Di \rightarrow Trem-Act$; thereby, zonal magnetite and magnesian chlorite rims develop around Cr-spinel: $Chr \rightarrow Mag + Chl$. The talc-actinolite assemblage is more common in serpentinite schists and massive hydrated rocks, where talc replaces olivine and acicular actinolite ($Trem-Act$) forms rims around pyroxenes: $Ol + Di \rightarrow Tlc + Act$; chromite is replaced from margins by magnetite and chlorite.

A sample of massive talcite dredged from the eastern wall of the rift valley is a rare case of pseudomorphous substitution of enstatite dunite by fine-flaked talc with retention of all details of the primary texture and xenomorphic orange-yellow chromite. The cellular texture of serpentinized reticulate olivine appears through the talc aggregate. Thus, we deal here with pseudomorphous replacement of already serpentinized rock, i.e., its “steaming” with hot solutions, or, in other words, progressive metamorphism of the oceanic crust in this segment.

The reticulate serpentinization of ultramafic rocks over the entire region results in replacement of 60–99% of primary minerals and formation of the characteristic framework of the rocks. At the early stage, the formation of α -chrysotile is not accompanied by release of finely dispersed magnetite; however, such rocks are rare.

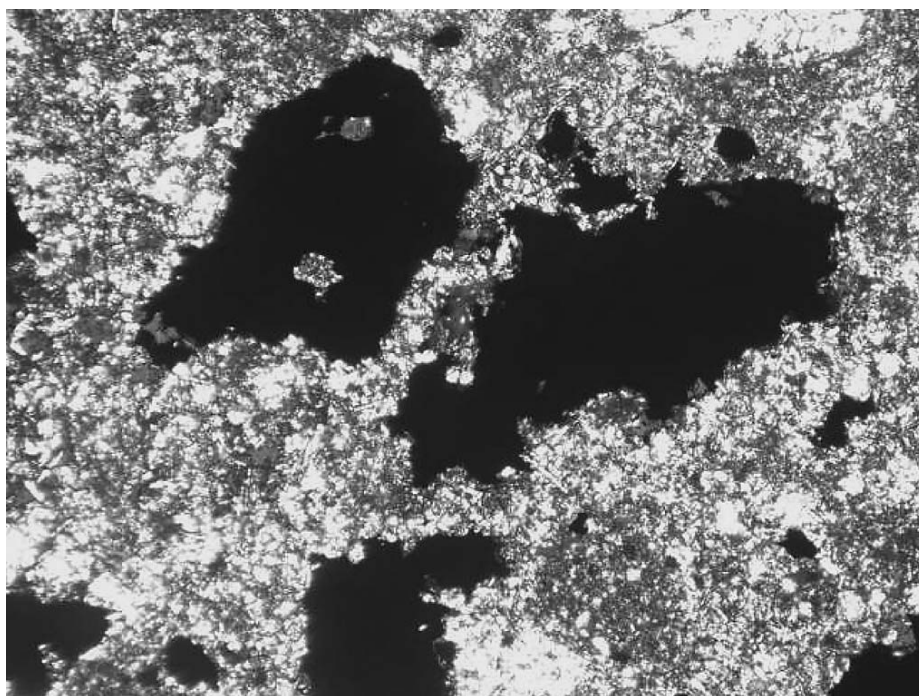


Fig. 4. Corrosion relationships between prehnite (light gray fine-grained aggregate) and sulfides (black). Sample L1141/203. Transparent polished thin section. Crossed polars. Mag. 10.

Commonly, serpentinites are composed of later lizardite and γ -chrysotile in close association with magnetite.

The foliated serpentinites consist of flaked and foliated lizardite and γ -chrysotile with an admixture of chlorite, talc, and magnetite; occasional actinolite; and relics of chromite. With an increase in the amount of talc, the primary structure of rocks is not retained, as a rule. Abundant sulfide mineralization (pyrite, pyrrhotite, pentlandite, and millerite (?)) is developed on slickensides in serpentinitized porphyroclastic peridotite (sample S2244/21). The size of ore grains is 0.3–2.5 mm; some of them have been ground along slickensides.

Ore-Bearing Metasomatic Processes

The earliest alteration of the gabbro complex is characterized by the development of brown-red amphibole, which replaces pyroxene. The first segregations of such amphibole certainly crystallized from melt as a late magmatic interstitial mineral. This amphibole is associated with plagioclase, in some cases, of a spherulitic structure; ilmenite; and magnetite. The already solidified gabbroids were altered with pseudomorphous replacement of primary minerals and concurrent development of veinlets and veinlike aggregates composed of actinolite-tremolite amphibole ($Mg\# = 0.74$), epidote, oligoclase An_{16} , chlorite 1, titanite, and pyrite. Tremolite replaces clinopyroxene and high-temperature hornblende, whereas fine-flaked Chl makes up irregular aggregates.

The ore stage proper is represented by epidosite, a cavernous rock mostly composed of epidote, chlorite, sulfides, and quartz. Epidote prevails over chlorite and quartz (10–20 vol %). Epidote shows a distinct zoning. The aggregate of epidote and chalcedony-like quartz is impregnated by sphalerite and chalcopryrite.

Minerals of the preore and ore stages were replaced by prehnite and transformed into rodingite. Almost all prehnitized rocks are cataclastic and brecciated. Gabbroids were altered most severely and transformed into almost monomineralic metasomatic rock composed of prehnite; the relict minerals, sulfides, in particular, vary from 50 to 10 vol % (Fig. 4). In addition to prehnite, tremolite and chlorite 2, which differs from the previously formed chlorite by a fibrous, felt texture and an anomalous violet-green interference color, are newly formed minerals.

Ultramafic rocks are resistant to prehnitization, and newly formed minerals of this stage appear only in the form of diffuse rims in serpentinites around prehnite ($Prh \pm Trem$) veins as products of replacement of gabbroic dikes that cut ultramafic rocks. The wall rocks exhibit a characteristic zoning (from host serpentinite to prehnite vein): $Srp + Tlc + Mag \rightarrow Srp + Trem + Mag \rightarrow Srp + Trem + Chl + Prh \rightarrow Prh + Trem + Chl$. The thickness of such rims varies from a fraction of a centimeter to 3–5 cm, while veins themselves are 3–10 cm thick.

During the overprinting of prehnitization on mineralized rocks, epidote and quartz of the ore stage are replaced by prehnite. In the course of prehnitization of

mineralized gabbroids, epidote and quartz are replaced first, testifying to a slightly alkaline character of the solution, whereas ore minerals are commonly retained, although in some cases they are slightly corroded with prehnite or make up cavernous intergrowths with this mineral. A narrow hematite rim occasionally coats pyrite grains. Due to intense postore prehnitization, the mineral assemblage $\text{Ep} + \text{Qtz} + \text{Chl}$ with ore minerals is commonly eliminated.

While prehnite is superimposed on serpentinite, magnetite is replaced by chlorite pseudomorphs enriched in Fe ($\text{Mg\#} = 0.60$, sample L1124-38a) relative to the earlier chlorite developed in the serpentinite groundmass ($\text{Mg\#} = 0.80\text{--}0.90$, sample L1124-38-2).

In addition to the aforementioned replacements, a type of late hydrothermal alteration is recognized. Such rocks appear as greenish gray cataclasites and mylonites mostly made up of prehnite and relict minerals of gabbroids. The cavernous porous appearance indicates that this mineral aggregate is a product of near-surface leaching. The sulfide mineralization in such rocks is completely replaced by iron hydroxides. Caverns and large pores contain druses of zeolites and iron hydroxides.

Thus, the following stages of hydrothermal mineral formation are established: (1) early high-temperature $\text{Hbl}\text{--}\text{Pl} \pm \text{Ilm}\text{--}\text{Mag}$ alteration; (2) $\text{Ab}\text{--}\text{Trem}\text{--}\text{Chl}$ alteration with pyrite; (3) $\text{Ep}\text{--}\text{Qtz}\text{--}\text{Chl}$ metasomatic alteration (epidosite) with pyrite, chalcopyrite, and sphalerite; (4) $\text{Pr}\text{--}\text{Chl}\text{--}\text{Trem}$ metasomatic alteration; and (5) low-temperature zeolite-hydroxide mineralization. The formation of $\text{Prh}\text{--}\text{Chl}\text{--}\text{Trem}$ metasomatic rocks requires a substantial supply of calcium, and these rocks may be classified as rodingites (Talbi et al., 1999).

The products of stages 1–3 have been almost completely eliminated by prehnitization. The early metasomatic alteration (stages 1 and 2) is characterized by pseudomorphous replacement and/or development of small veins in gabbro. In contrast, the formation of rodingite is accompanied by intense cataclasis and brecciation of rocks, which indicates rearrangement of the style of deformation at this stage.

Chemical Composition of Minerals

The chemical composition of minerals from metasomatic rocks was determined with a Camscan microprobe at Moscow State University (analysts E.V. Guseva and N.N. Korotaeva) and with a JSM5300 SEM/Link-ISIS EDS at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (analyst E.V. Koporulin).

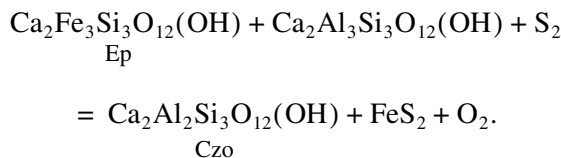
Amphiboles. Primary magmatic red-brown amphibole, close to pargasite (kaersutite) in composition, occurs in gabbroids of the Fe–Ti-oxide series and plagioclase–amphibole veinlets typical of gabbro associations in the MAR (Talbi et al., 1999). Euhedral amphibole crystals show distinct zoning characterized by decreasing (from the center of a grain towards its mar-

gin) Ti and Al contents and increasing Fe content. The late amphibole that replaces clinopyroxene and the early amphibole correspond to tremolite in composition.

Plagioclase coexisting with amphibole varies from An_{54} to nearly pure Ab. Plagioclase altered at this stage acquires a narrow rim (<1 mm) of a more sodic composition ($\text{An}_{52\text{--}54}$) against the core of the crystal ($\text{An}_{71\text{--}69}$, sample L1141). Sodic plagioclase comparable in size with amphibole occurs in pegmatoid gabbro, localizing in the interstices between magmatic minerals. Spherulite-like crystals of plagioclase An_{12} are noted occasionally.

The wide compositional range of the studied amphiboles and plagioclases likely reflects a wide interval of crystallization temperatures. According to the Holland–Blundy geothermometer (1990), the $\text{Pl}\text{--}\text{Hbl}$ couple crystallized at $800\text{--}450^\circ\text{C}$ (Fig. 5). This temperature implies that the hydrothermal alteration of gabbroic rocks began immediately after their crystallization and steadily continued during their cooling.

Epidote is characterized by a clearly expressed zoning (Fig. 6). In the central part of grains, the composition of the mineral corresponds to the proportion $X(\text{Fe}^{3+}) = 0.41\text{--}0.37$ and $X(\text{Al}^{3+}) = 0.59\text{--}0.63$, and at the margins, $X(\text{Fe}^{3+}) = 0.23\text{--}0.12$ and $X(\text{Al}^{3+}) = 0.77\text{--}0.88$, where $X(\text{Fe}^{3+})$ is the mole fraction of pistacite molecule $\text{Ca}_2\text{Fe}_3\text{Si}_2(\text{OH})$ and $X(\text{Al}^{3+})$ is the mole fraction of clinozoisite molecule $\text{Ca}_2\text{Al}_3\text{Si}_2(\text{OH})$. The transition from low-alumina zones to the zones enriched in clinozoisite molecule occurs at a distance of about ~ 10 μm . The sharp zoning of epidote grains indicates a rapid change in the crystallization conditions. The mole fraction of $\text{Ca}_2\text{Fe}_3\text{Si}_2(\text{OH})$ might have decreased with falling oxygen fugacity during the interaction of metabasic rocks with reduced S-bearing fluid according to the following schematic reaction:



A similar zoning was established in the hydrothermal epidotes that replaced basalt in the front part of the Tonga Basin (Banerjee et al., 2000).

The **chlorite** composition is determined by the composition of replaced dark-colored minerals. The Fe content of chlorite that replaced gabbro is higher than that of chlorite that replaced serpentinite. For example, in a prehnite–chlorite vein (sample L1124/38), $X_{\text{Mg}}^{\text{Chl}} = 0.6$, whereas, in prehnitized wall-rock serpentinite, $X_{\text{Mg}}^{\text{Chl}} = 0.9$. Chlorite that replaced magnetite in serpentinites is appreciably enriched in Fe as compared with chlorite that replaced tremolite. The least magnesian chlorite ($X_{\text{Mg}}^{\text{Chl}} = 0.45$) was detected in zones of hydrothermal alteration of ore-bearing Fe–Ti-oxide gabbroids (sam-

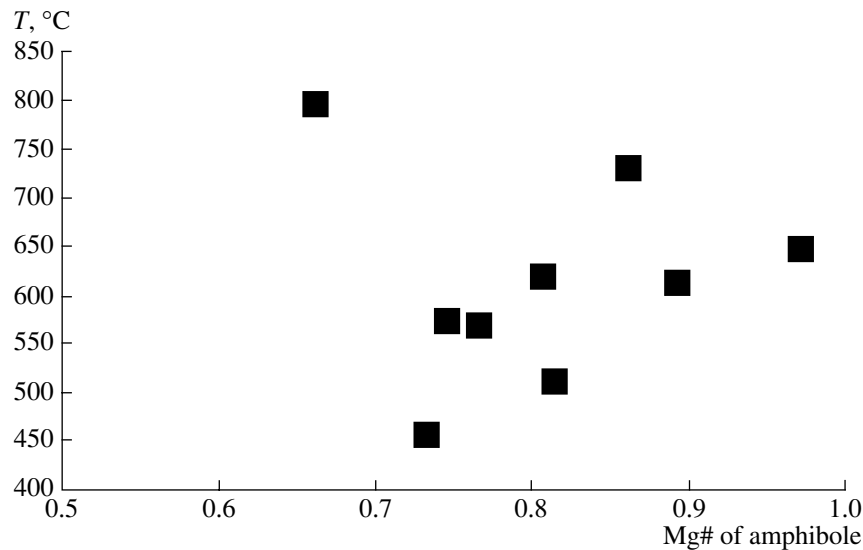


Fig. 5. Magnesium number of amphibole versus temperature of its formation estimated with the Hbl–Pl thermometer (Holland and Blundy, 1990).

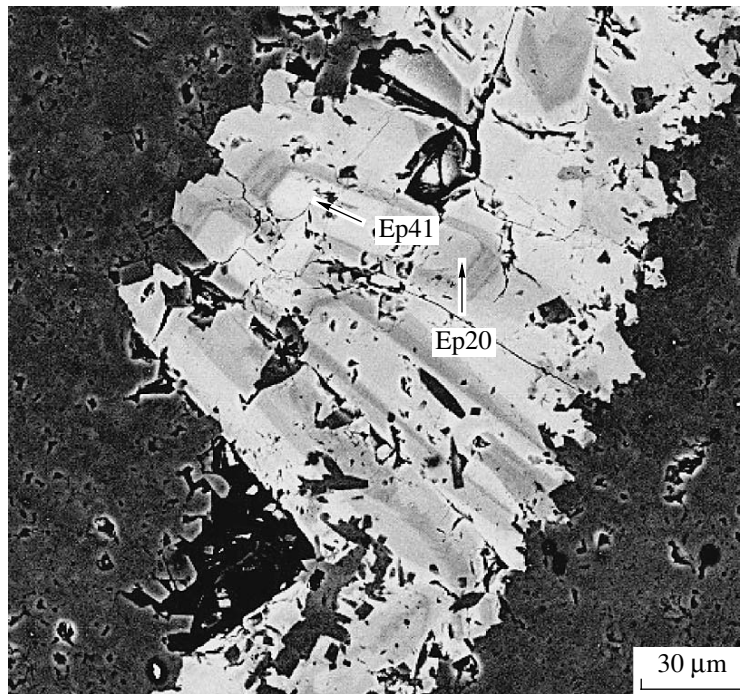


Fig. 6. Zonal epidote crystal in hydrothermally altered rock (image in reflected electrons). Arrows indicate the pistacite content, mol %, in particular areas of the crystal. The epidote crystal is replaced by prehnite (dark gray aggregate) along the margins. Scale bar, 30 μm .

ple L1163/62). All the studied chlorites belong to the daphnite–clinochlore series.

The early and late chlorites that replaced gabbroic rocks differ in composition. The late chlorite 2 formed together with prehnite is characterized by a low alumina content. The change in the chlorite chemistry may be explained by two schemes of isomorphism: $2\text{Al}^{\text{VI}} \rightarrow 3\text{Mg}$ and $4\text{Al}^{\text{IV}} \rightarrow 3\text{Si}$. A decrease in the

mole fraction of Al^{IV} in chlorite 1 is a result of a temperature drop (Kranidiotis and McLean, 1987; Cathelineau, 1988). The temperature of chlorite crystallization calculated with the methods proposed by these authors is 200–220°C for the early generation and 160–180°C for chlorite 2 in rodingites (Fig. 7). These temperatures seem to be underestimated. More reliable estimates of the temperature of prehnitization can be

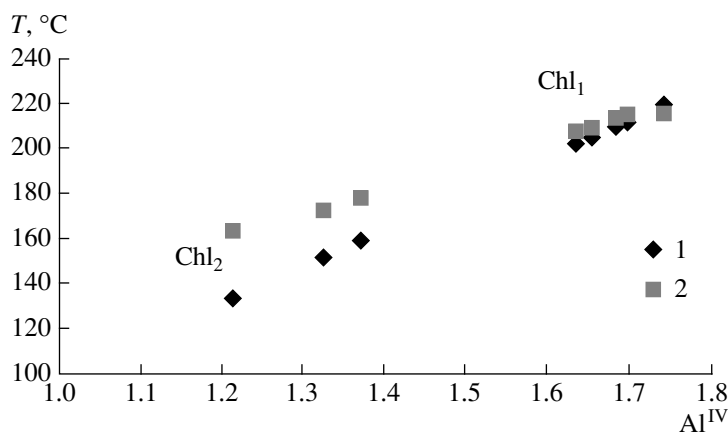


Fig. 7. Calculated temperature of hydrothermal chlorite formation versus Al^{IV} , f.u. Chl₁ is chlorite from the Amph–Chl–Ep–sulfide assemblage, and Chl₂ is chlorite from prehnite metasomatic rocks. The temperature was calculated using geothermometers elaborated by (1) Cathelineau (1988) and (2) Kranidiotis and McLean (1987).

obtained on the basis of the change of mineral assemblages $Ep + Trem \rightarrow Prh + Chl$ (Liou et al., 1987). At pressure of 0.5–1.0 kbar and $X_{Fe}^{Ep} = 0.3$ –0.2, this equilibrium is stable at 320–350°C. If this estimate is regarded as a reference, rocks of the epidote–actinolite–chlorite stage might have formed at a temperature of ~400°C.

Prehnite is characterized by insignificant fluctuations of chemical composition that correspond to 3–7 mol % of the end member $Ca_2FeAlSi_3O_{10}(OH)_2$ because, in the Ep–Prh assemblage, prehnite always contains less Fe^{3+} than coexisting epidote (Rose and Biord, 1987). The clinozoisite end member of epidote is replaced by prehnite without any appreciable gain or loss of components, whereas, when intermediate epidote compositions are replaced, iron is removed and fixed in hematite and/or chlorite.

Variations of Whole-Rock Composition

The studied samples are rocks that underwent hydrothermal alteration to a greater or lesser degree. The initial rocks are cataclastic and brecciated hydrothermally altered gabbro and gabbro-norites containing sulfide mineralization. Since prehnitization eliminates minerals of previous stages, the change in the whole-rock composition characterizes the gain and loss tendencies typical of rodingites. In order to trace this transformation, the concentrations of major and ore elements in rocks were determined with XRF at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, RAS. The results confirmed substantial mass transfer during metasomatic alteration.

The magnesium number ($Mg\# = Mg/(Fe + Mg)$) turned out to be the most sensitive index for estimating the intensity of hydrothermal alteration. In unaltered rocks, $Mg\# = 0.80$ –0.82, decreasing to 0.60 in the most

altered varieties, where Na, Si, and Mg contents decrease, while Ca, Fe, and S contents increase. The Cu and Zn contents rise with the degree of hydrothermal alteration. However, the behavior of ore components could hardly be interpreted unambiguously. First, as indicated above, ore minerals in rodingite are products of the preceding epidote stage. Second, rocks with sulfide mineralization were selected in the sampling, though prehnitized rocks are usually barren. Therefore, the observed trend, most likely, reflects a higher stability of ore minerals as compared with epidote and quartz when they were replaced by prehnite. The removal of major elements led to the secondary enrichment of rodingite in ore elements.

It is convenient to examine the changed composition of mineral assemblages using the Ca–Mg– Fe_{total} diagram (Fig. 8), where the fields $Ep + Act + Chl_1 + Ab \pm$ iron sulfide and $Pr - Chl_2$ are shown. As the metasomatic process develops, the composition of altered rocks shifts toward Ca (prehnite) while the Fe content remains almost unchanged and that of Mg decreases. The described changes must have occurred in the presence of fluid with a low content of carbon dioxide and sulfur because interaction of rocks with sulfate-bearing fluid leads to the formation of anhydrite (a mineral common for the setting of black smokers) instead of prehnite (Humphries et al., 1998) and only calcite would be stable if the CO_2 mole fraction in the fluid increased (Rusinov, 1988).

Thus, the obtained data indicate that metasomatism at the main stage of ore formation is characterized by the gain of Ca, Fe, and S, whereas its final stage proceeds in the presence of fluid with low S and CO_2 contents. According to the thermometric data, the main metasomatic alteration that accompanied ore formation started at a temperature of 800–450°C and proceeded further within the temperature interval 400–160°C.

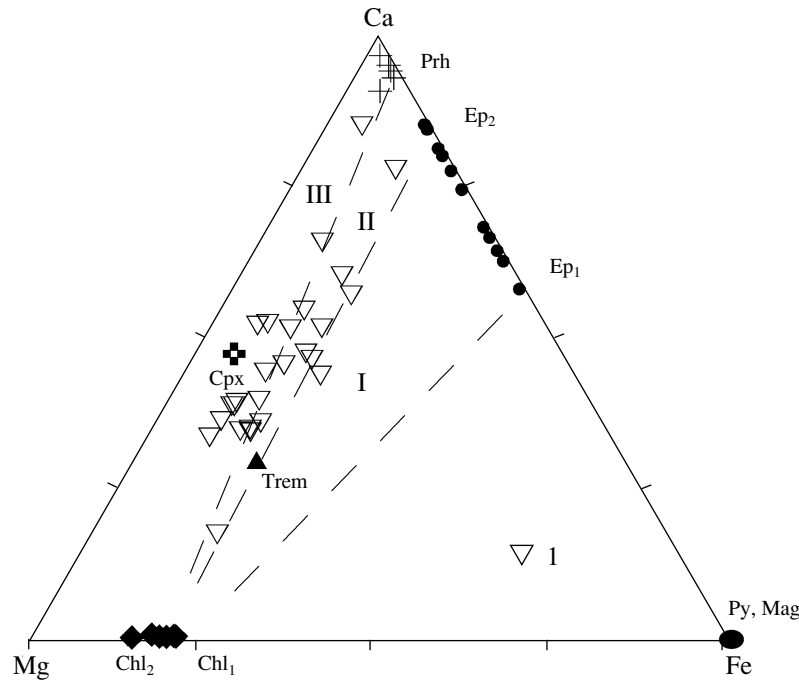


Fig. 8. Ca-Mg-Fe ($\text{Fe}^{+2} + \text{Fe}^{+3}$) diagram. (1) Whole-rock compositions of altered rocks. See text for explanation of tie-lines I-III.

FLUID INCLUSIONS

Fluid inclusions were studied in prehnite and epidote from metasomatic rocks with stringer-disseminated sulfide mineralization.

Prehnite contains abundant fluid inclusions of angular shape from 5 to 15 μm in size, which are uniformly distributed throughout grains of this mineral. At room temperature, the fluid inclusions differ in phase composition: single-phase inclusions predominantly consist of the gas phase, while multiphase inclusions contain liquid, crystalline phases, and a gas bubble. The latter usually moves within a vacuole, indicating a rather low temperature of fluid entrapment. No carbon dioxide was revealed in substantially gaseous inclusions. The coexistence of inclusions varying in phase composition may be regarded as evidence for crystallization of metasomatic minerals under conditions of phase separation of fluid. The presence of solid phases in fluid inclusions indicates that the mineral-forming solution was saturated with some minerals under certain conditions.

Two-phase fluid inclusions 5–15 μm in size (up to 25 μm in occasional cases) are abundant in prehnite as well. Some of these inclusions are spherical, but more frequently they are flattened and irregular in shape, with a rough surface. The inclusions are mainly located along healed fractures. However, in many cases, the fluid inclusions do not show an obvious relation to fractures and are classified as pseudosecondary and possibly primary. At room temperature, the inclusions are two-phase and contain transparent liquid and a gas bubble.

Microthermometric measurements have shown that, during cooling, the fill of inclusions freezes within the temperature interval from -35 to -43°C and the eutectic temperature varies from -24 to -27.5°C . This indicates that the salts dissolved in the captured fluid were dominated by NaCl, while KCl was contained in a minor amount. The melting temperature of the last tiny ice crystals varies from -3.0 to -4.1°C . Hence, the salt concentration in the fluid may be estimated as from 4.6 to 6.5 wt % NaCl equiv. When heated, the fluid inclusions were homogenized at a temperature of 172 – 238°C . To obtain the true temperature of crystallization, it is necessary to introduce a correction for pressure. If the pressure was equal to that of the water column at a depth of about 4200 m, prehnite crystallized at 202 – 270°C . Actually, the temperature could be higher because the ore veinlets were formed below the ocean floor.

In *epidote* from the groundmass, primary fluid inclusions up to 20 μm in size (5–15 μm , on average) and mainly tubular in shape are uniformly distributed and oriented in one direction. At room temperature, these inclusions are two-phase and contain a gas bubble incorporated into a transparent liquid. The results of microthermometric measurements turned out to be similar to those obtained for prehnite. The fluid in inclusions freezes within the temperature interval from -41.5 to -44.5°C , whereas the eutectic temperature is about -26°C ; hence, dissolved NaCl is predominant in the fluid, whereas KCl is contained in a minor amount. The melting temperature of the last ice crystals (-3.6 to -3.8°C) indicates that the concentration of salts in the fluid was 5.7–6.0 wt % NaCl equiv. When heated, these

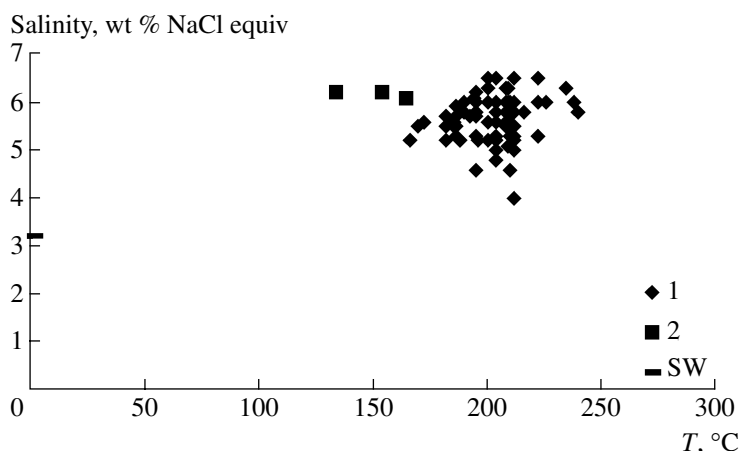


Fig. 9. Salinity of fluid inclusions versus temperature of their homogenization. (1) Inclusions in prehnite; (2) inclusions in epidote; (SW) seawater.

inclusions are homogenized at 138–248°C. Taking into account the correction for pressure (420 bars), the temperature of epidote formation is estimated at 168–280°C.

Fluid inclusions 5–10 µm in size, elongated or equant and angular, uniformly distributed or related to healed fractures, have been detected in epidote from microcavities. They are regarded as pseudosecondary and probably entrapped at the final stage of epidote crystallization. At room temperature, they are two-phase and contain a gas bubble and liquid. On cooling, the fluid in inclusions rapidly freezes at a temperature from –37 to –42°C. The appearance of the first portion of solution (eutectics) is observed at –23.5 to –24°C, indicating the predominance of NaCl among the dissolved salts; KCl occurs as a minor admixture. The melting temperature of the last ice crystals (about –3.9°C) corresponds to a salt content of approximately 6.2 wt % NaCl equiv, which is higher than in prehnite. The homogenization of fluid inclusions occurs at 134–164°C. Taking into account the correction for pressure, the true temperature of epidote crystallization is estimated at 165–196°C.

The above data imply that crystallization of epidote and prehnite started simultaneously at 270–280°C and further they crystallized under similar conditions. The minerals of the groundmass crystallized at a higher temperature (200–280°C) than the small crystals precipitated in microcavities (165–196°C).

The salt concentration in the mineral-forming fluid (4.6–6.5 wt % NaCl equiv) was somewhat higher than the salinity of seawater (3.47 wt % NaCl equiv). The coexistence of gaseous and liquid inclusions with solid phases indicates that gas and more concentrated aqueous fluids could simultaneously circulate in the mineral-forming system. The aqueous fluid could have arisen due to phase separation of supercritical fluid leading to the formation of fluid with a higher salinity as compared with seawater, up to brine (Fournier, 1987). In particular, this may occur when a fluid sepa-

rated from magma, having been mixed with seawater, reaches *PT* conditions of phase separation in the H₂O–NaCl system.

It should be noted that the temperature of mineral formation estimated for stringer–disseminated ore (Fig. 9) is lower (350–400°C) than that established for stockwork sulfide mineralization penetrated by Borehole 504B (Nehlig, 1991). It may be suggested that the dredged fragments of stringer–disseminated ore were formed at a certain distance from the channel along which high-temperature fluids ascended.

The above data indicate that the parameters of hydrothermal solutions in the Markov Deep and at the Rudny site do not show significant differences from results obtained previously (Mazarovich et al., 2001; Simonov et al., 2001) for fluid inclusions in samples dredged at Station S2234 in the Sierra Leone FZ (the salt content is 3.8–5.0 wt % NaCl equiv and the crystallization temperature is 205–226°C). In general, the temperature intervals of ore-bearing metasomatic alteration estimated from fluid inclusion study (280–170°C) are, to a great extent, coincident with the results of studying mineral assemblages (400–160°C). These data are consistent with the results obtained for fluid inclusions in minerals from sulfide mounds in the MAR (the Logachev, Rainbow, and Broken Spur hydrothermal fields) and in the Manus (Vienna Woods) and Woodlark basins, where the fluid salinity varies from 4.2 to ~26 wt % NaCl equiv and the homogenization temperature of fluid inclusions ranges from 102 to 398°C (Bortnikov et al., 2004).

ORE MINERALIZATION

The hydrothermally altered rocks dredged from the rift valley in the Markov Deep contain numerous quartz–sulfide and prehnite–sulfide veinlets (up to 15 cm in thickness), sulfide disseminations, and chalcopyrite–sphalerite–pyrite veins. The host cataclastic

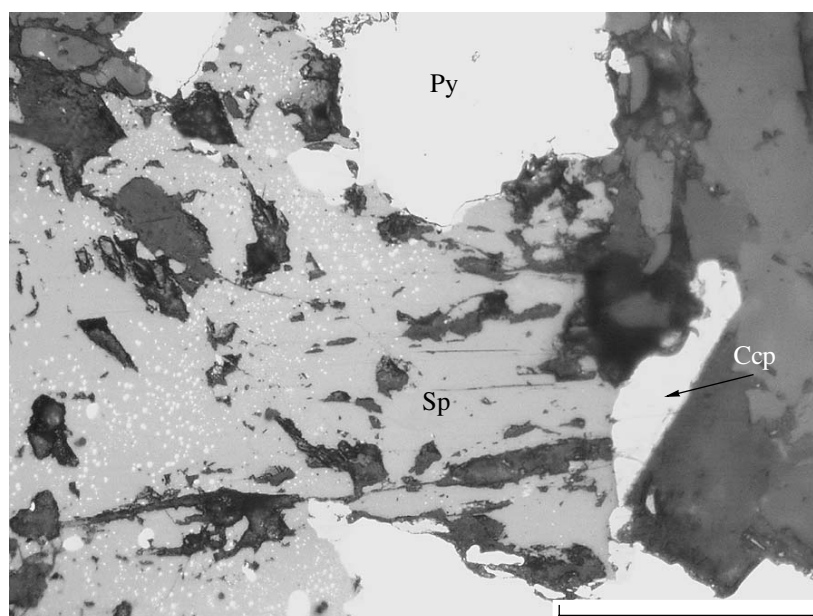


Fig. 10. Large pyrite grains (Py) cemented with chalcopyrite (Ccp) and crosscut by sphalerite (Sp) with chalcopyrite emulsion. Sample 3272. Scale bar, 0.2 mm.

gabbroids experienced a variable degree of hydrothermal metasomatic alteration. Small lenses of foliated gabbro and a relict porphyroclastic structure of rocks are retained locally. The porphyroclasts are composed of altered feldspar and pyroxene incorporated into a matrix consisting of quartz and chlorite with sporadic grains of pyrite, pyrrhotite, and chalcopyrite. The severely altered rocks have a fine-grained structure and are completely replaced by chlorite and epidote with sulfide, largely chalcopyrite, disseminations.

Brecciated and hydrothermally altered rocks with slickensides and fault gouge are composed of amphibole, epidote, chlorite, quartz, and barite. Brecciated quartz–chlorite rocks with sulfide disseminations and quartz–epidote veinlets with epidote selvages and quartz cores were dredged as well. The thickness of such veinlets, which in many cases have a cellular structure, is 1.0–1.5 cm. They contain disseminations of iron hydroxides, which likely replaced pyrite, and pores left behind by leached sulfides.

The strongly epidotized rocks contain prehnite–sulfide veinlets up to 15 cm thick, sulfide disseminations, and segregations of massive chalcopyrite–sphalerite–pyrite ore. Occasional open cavities contain pyrite and sphalerite crystals. Epidote pockets occur in prehnite veinlets.

Thus, the dredged samples are fragments of a stringer–disseminated ore zone controlled by a tectonic zone or channel that provided migration of high-temperature hydrothermal fluids.

Mineral Composition of the Ore Occurrence

Polished sections of samples from stringer–disseminated (Fig. 10) and vein (Fig. 11) ores have been examined. The ore veins largely consist of chalcopyrite and contain sporadic clinozoisite relics crossed by cracks filled with chalcopyrite. The dredged samples are considered to be fragments of relatively thick (10–15 cm) ore veins hosted in metasomatically altered rocks.

The mineral composition of stringer–disseminated ore is more complex. Pyrite, chalcopyrite, sphalerite, pyrrhotite, bornite, chalcocite, and digenite were identified. Prehnite is the main gangue mineral. Barite and opal occur sporadically. Titanomagnetite, rutile, siderite, apatite, atacamite, and native metals have been detected as well.

Chalcopyrite is the major ore mineral. In disseminated ore, it occurs as irregular grains often cementing crushed pyrite grains. The size of chalcopyrite grains varies from hundredths of a millimeter to 0.5 mm. In ore veins, chalcopyrite forms plates and grains irregular in shape, from hundredths of a millimeter to large plates 1.5 × 0.3 cm in size. Chalcopyrite contains 0.02–0.08 wt % Ni and Co and an unusual As impurity (about 0.15 wt %).

Pyrite is the second in abundance and occurs only in disseminated ore. In most cases, pyrite is observed as broken grains of irregular shape up to 0.2 mm in size in combination with occasional cubic crystals of the same size. In most cases, pyrite is entrapped or cemented by chalcopyrite. In a number of cases, pyrite crystals reveal oscillatory growth zoning, which reflects periodic dissolution and subsequent growth of crystals, as

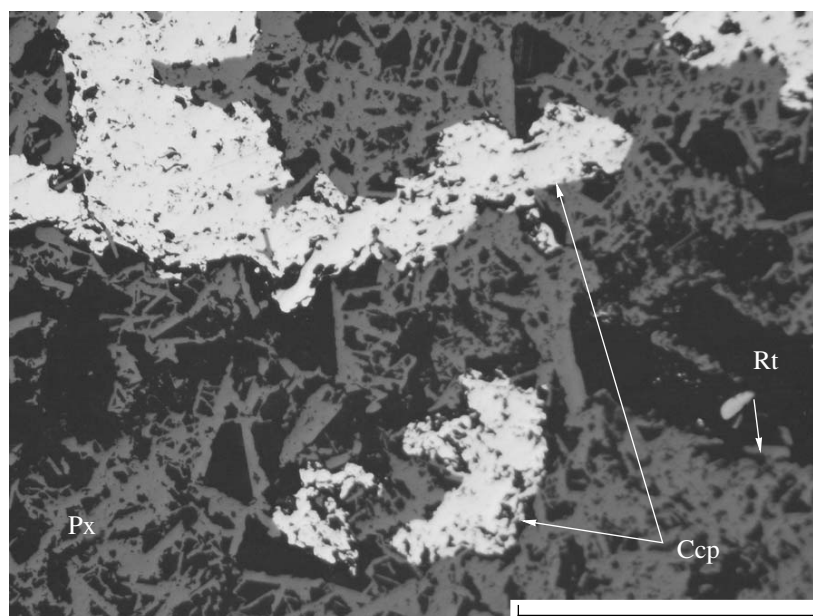


Fig. 11. Veined ore. Irregular chalcopyrite grains (Ccp) surrounded by pyroxene (Px) grains. A rutile (Rt) needle is observed. Sample 3275. Scale bar, 0.2 mm.

is confirmed by corrosion boundaries of growth layers in euhedral crystals.

Some samples contain microglobular segregations confined to the marginal parts of pyrite aggregates. It may be suggested that pyrite crystals begin to grow as nonequilibrium skeletal porous masses at the growth front, which are later filled to form monolithic crystals with relics of globular structure. The initial globular pyrite then recrystallizes. In the given case, the relics of globular structure gradually diminish and disappear with increasing degree of recrystallization. The microprobe results indicate that pyrite contains As (up to 0.18 wt %), Ni (up to 1.65 wt %), and Co (up to 0.14 wt %).

Sphalerite occurs as veinlets and isolated grains about 2.0 mm in size, corroding or cementing aggregates of chalcopyrite grains. At the Ccp–Sp contact, sphalerite always contains emulsion inclusions of chalcopyrite, which in some cases are confined to the growth boundaries of sphalerite grains. The Fe content in sphalerite varies from 2.0 to 5.2 wt % and decreases from the center toward the margins of grains. Sphalerite contains 0.53 wt % Cd, 0.2 wt % Hg, and 0.16 wt % Se. Cd is inversely correlated with Fe, and the Cd content increases from the center of crystals toward their periphery.

Bornite is a very rare mineral that occurs as discrete grains 0.01–0.03 mm in size or overgrows pyrite in the chalcopyrite matrix. Bornite most likely replaces chalcopyrite because bornite grains are not known separately from chalcopyrite.

Chalcocite is observed as narrow rims around chalcopyrite and emulsion inclusions of chalcopyrite in sphalerite.

Digenite is identified as isolated dendritic segregations. The size of dendrites reaches 50 μm . Digenite dendrites are always coated with chalcocite films.

Siderite rims pyrite and chalcopyrite grains, fills open cavities in sulfides and gangue minerals, and in some cases occurs as colloform crusts.

Titanomagnetite and *ilmenite* are identified as numerous fine grains (0.005–0.01 mm) within and between pyroxene grains, as well as by relics in rutile.

Atacamite occurs at the boundaries of chalcopyrite grains and in interstices in combination with epidote and prehnite crystals.

Sulfur Isotopes in Sulfides

The $\delta^{34}\text{S}$ value of sulfides from ore occurrences in the Markov Deep varies within a wide range, from +3.0 to +15.3‰ (Pushcharovsky et al., 2004), and, in the case of chalcopyrite, from +3.7‰ in disseminated ores to +13.6‰ in ore veins. These values are close to those established in sulfides hosted in serpentinized ultramafic rocks of the Rainbow and Logachev hydrothermal fields (Bogdanov et al., 2002) but differ from $\delta^{34}\text{S}$ of sulfides in black smokers in the TAG, Broken Spur, Lucky Strike, and Snake Pit hydrothermal fields at the MAR, which are associated with basalts (Shanks, 2001; Bortnikov and Vikent'ev, 2005). In these sulfide mounds, $\delta^{34}\text{S}$ varies from –5 to +8‰, mostly falling within the interval from +1 to +5‰.

DISCUSSION

Before discussing the results obtained, it is necessary to say a few words about igneous rocks of the Markov Deep, including those that host sulfide mineralization.

Structure and Alteration of the Oceanic Crust at the Studied Site in Connection with Ore Formation

According to the available data, the alteration of the oceanic crust in the considered segment of the MAR axis occurred under very dynamic conditions and frequently started immediately after solidification of igneous rocks, which still remained hot. While cooling, the rocks underwent brittle fracturing; seawater penetrated into fractures and induced overall low-temperature alteration under conditions of zeolite to epidote-amphibolite facies. Fracturing of the oceanic crust inevitably led to the formation of an intracrustal aquifer that resembles reservoirs of subsurface water in continents. When an active magmatic system comes into contact with such an aquifer, a circulating hydrothermal system arises, just like in volcanic provinces on land but in this case with participation of seawater.

The elevated salinity of hydrothermal fluids might have been caused by phase separation of supercritical fluid (see above) or low-temperature hydration of igneous rocks (amphibolization, serpentinization, chloritization, etc.). Thereby, salts originally contained in seawater accumulated in hydrothermal solution rather than entered secondary minerals.

The root zones of hydrothermal systems were characterized by metasomatic alteration of host rocks accompanied by ore deposition, whereas black or white smokers marked hydrothermal vents on the seafloor.

Sulfide Mineralization as a Product of Hydrothermal Metasomatic Processes

The hydrothermal alteration of the oceanic crust started immediately after solidification of igneous rocks and presumably proceeded within a temperature interval from 800 to 150°C. The same temperature interval was established in the Troodos ophiolites (Gillis and Roberts, 1998), in the altered gabbro and cataclastic rocks of the Romanche and Vema FZs adjacent to the Markov Deep (Talbi et al., 1999), and elsewhere in oceans (Silant'ev, 1998).

A similar scenario of hydrothermal alteration may likewise be suggested in our case. The early alteration, i.e., amphibolization of pyroxenes and albitization of plagioclase in igneous rocks, gave way to the low-temperature alteration of basic rocks with formation of the Hbl + sodic Pl + Ep + Ttn + Chl + Prh mineral assemblage within a temperature range from 800 to 200°C. A wide temperature interval of hydrothermal alteration does not always result in ore formation.

The ore mineralization in the Markov Deep is related to epidotization. This process is characteristic of massive sulfide ore deposition (Hannington et al., 1998) and regarded as an attribute of root ore-concentrating zones (Gillis and Robinson, 1988). It is suggested that ore components are leached by reduced fluid from solidified igneous rocks precisely in such root zones. Very illustrative in this respect are epidiosites from the Tonga Basin, markedly depleted in Cu and Zn as compared with unaltered basalts (Banerjee et al., 2000). The reduced character of fluids responsible for the formation of epidiosites follows from the epidote zoning (pistacite in the core and clinozoisite at the margins). The same zoning is established in epidiosites from the Markov Deep.

The deposition of massive sulfide ore in the TAG hydrothermal system was accompanied by argillic alteration and formation of secondary quartzites (Hannington et al., 1998; *Metasomatism...*, 1998). This alteration develops in the central part of the ore system that feeds the active channel of a smoker. Such altered rocks were not dredged from the Markov Deep (barite and anhydrite were identified only in heavy concentrates). It may be suggested that the upper mineralized body with a quartz core has been eroded and only the lower part of the hydrothermal system is exposed now on the seafloor. In this case, fragments of the scoured altered rocks must be found either by dredging or by sampling of loose sediments in the basin.

Another explanation infers that the ore-forming process was stopped by tectonic movements, which provoked cataclasis and breakup of rocks with concurrent prehnitization. Judging by the observed relationships, the formation of rodingite directly followed epidotization, leaving only a short time span between these alteration stages. Otherwise, rodingite would be superimposed on the low-temperature metasomatic alteration that completed the preceding stage. As judged from the temperatures of chlorite formation in epidiosite and rodingite, the difference in temperature between these stages was only 50–70°C. Such a minor though detectable drop in temperature could have been caused by rapid intake of seawater through the system of newly formed fractures and cataclastic zones. Seawater diluted the ore-bearing fluid, halting the ore-forming process and inducing replacement of the previously formed minerals by prehnite.

As was shown above, the metasomatic zoning developing thereby is characterized by loss of Si, Mg, and Na and gain of Ca and Fe. Evidently, such a (rodingite) type of alteration is characteristic of other hydrothermal systems on the ocean floor. This suggestion is supported by the composition of the Rainbow hydrothermal plume, where the youngest hot portions of the flow with positive buoyancy are distinguished by anomalously high concentrations of Si, Mg, Na, H₂S, and chalcophile elements and low concentrations of Mn, Ca, V, Y, and REE as compared with samples from

aqueous plumes with neutral buoyancy (Edmonds and German, 2004). Therefore, if the chemistry of an aqueous plume reflects the interaction of a hydrothermal flow with host rocks, then an analogy with chemical changes that give rise to rodingitization of metabasic rocks is evident.

Structure of the Ore-Bearing Zone in the Markov Deep

The proposed interpretation allows us to understand the vertical distribution of metasomatic rocks formed at different temperatures along the eastern wall of the rift valley in the Markov Deep (Bel'tenev et al., 2004b). The low-temperature leached rocks make up the upper part of the system, where hydrothermal fluids seep to the surface. The zone of hydrothermal alteration extends conformably with the main northwestern trend of faults that control the seafloor topography and steeply dips to the east. Thus, it becomes clear why the tract of altered rocks in the western hanging wall of the suggested ore-controlling zone is so thin (for instance, sample L1123, dredged 600 m west of this zone, yields unaltered rocks).

The sulfide, largely copper ore mineralization occurs in the zone of brecciation and cataclasis of hornblende gabbro affected by intense hydrothermal metasomatic reworking at a fairly low pressure (about 0.5–1 kbar) and temperature (170–280°C; possibly, up to 400°C). Judging by the S and Sr isotopic compositions (Pushcharovsky et al., 2004; Shatagin et al., 2006), seawater made a substantial contribution to the hydrothermal solutions. The metasomatic reworking of rocks might have been accompanied by leaching of ore components from sulfides and silicate minerals. As was mentioned above, gabbroic rocks in the Markov Deep contain small grains of primary copper sulfides and are frequently enriched in Pb and Zn.

As follows from the thermodynamic modeling of hydrothermal systems of oceans (Grichuk, 2000), sulfides are leached from host rocks at the early, oxidizing stage of metasomatism and subsequently precipitate as a result of metasomatic reactions in the reducing environment. Our data are consistent with this sequence. Indeed, the hydrothermal metasomatic alteration of rocks in the Markov Deep proceeded during two stages. The first stage corresponds to metamorphism under conditions of epidote-amphibolite facies and developed owing to the penetration of seawater into igneous rocks. The second, ore-bearing stage occurred in the reducing environment and comprised two phases; in the first phase, epidote and chlorite played the crucial role, whereas in the second phase prehnite became the major mineral. The hydrothermal alteration of the second stage was of local character and controlled by the permeability of rocks. After their formation, the ore-bearing metasomatic rocks were brought to the ocean floor owing to recent tectonic movements along the deep faults.

The dredged samples may be fragments of a stringer-disseminated ore zone with elements of vein mineralization. Such zones develop close to the conduits along which the high-temperature hydrothermal fluids ascend toward the ocean floor and, in many cases, are retained at lower levels of ancient massive sulfide deposits. However, no active black smokers or older analogues are known from the eastern wall of the Markov Deep. This indicates that we deal here with a new type of sulfide ore occurrences at the ocean floor, which is distinguished by deposition of ore matter at a depth rather than in the area of discharge of low-temperature hydrothermal solutions on the ocean floor. These solutions are responsible for the formation of ferromanganese crusts and enrichment of some seawater layers in Fe, Mg, Cu, and Zn (Pushcharovsky et al., 2004).

Thus, we suppose that the ore occurrence in the Markov Deep was formed in a fracture zone, which is marked by zones of cataclasis and mylonitization. Taking into account the inferred metasomatic zoning and the results of dredging, it may be suggested that the fracture zone dips to the east-northeast. The occurrence of high-temperature metasomatic rocks, which could not have been formed on the ocean floor, implies that the ore-bearing zone was uplifted after its formation. Judging by the occurrence of atacamite and the low degree of sulfide oxidation, this event happened quite recently, probably in the process of the ongoing evolution of the present-day Markov Deep.

Origin of Sulfide Mineralization in the Markov Deep

Like the majority of modern ore-bearing hydrothermal systems discharging on the ocean floor in the form of black smokers, the studied ore occurrence is located in the axial MAR zone and confined to the conduit of a similar system. According to generally accepted views, the sulfide mounds are formed by fluids that contain sulfur of different origin (Bortnikov and Vikent'ev, 2005). The mineral-forming fluid, obviously, contains sulfur of magmatic origin, with $\delta^{34}\text{S}$ varying from –2.3 to +0.4‰. The supply of heavy sulfur into the hydrothermal system is explained in different ways, by (1) reduction of sulfate sulfur of seawater and its non-equilibrium mixing with hydrogen sulfide of hot hydrothermal fluids; (2) mixing of mineral-forming fluid with seawater, simultaneous hydrogen sulfide oxidation, and reduction of sulfates with ferrous ion; (3) partition of sulfur isotopes between the coexisting sulfide and sulfate; (4) phase separation and boiling up of fluid; (5) hydrogen sulfide oxidation to sulfate; and (6) involvement of sulfur derived from sulfates or sulfides that fill veinlets in serpentinized rocks.

Another mechanism was proposed by Alt and Shanks (2003), who investigated the high-grade sulfide mineralization hosted in serpentinites of the MARK field, where secondary sulfides (millerite, pentlandite, pyrrhotite, and locally developed heazlewoodite and awaruite) replaced primary magmatic sulfides in

altered peridotites. The geochemical modeling carried out by these authors showed that development of ore mineralization was due to leaching of sulfides by seawater from adjacent gabbroids at 400°C and their redeposition in the process of serpentinization of peridotites at 300°C.

Thus, all proposed models require a complicated, largely speculative mechanism of heavy sulfur supply into the hydrothermal system and do not consider the obvious phenomenon of mixing of primary magma-derived fluid with seawater circulating through fractured rocks of the oceanic crust, as was suggested by Kelley and Delaney (1987). Such systems with a wide range of $\delta^{34}\text{S}$ values displaying different rates of mixing of magma-derived fluid with seawater are supposed to develop in slow-spreading ridges, where ancient brittle plutonic rocks have been brought to the surface.

Moreover, in a number of hydrothermal systems, the weighting of S isotopes was established at the final stages of their activity (Bogdanov et al., 2002), reflecting progressive dilution of the fluid with seawater. Such a succession of events in the Markov Deep is corroborated by replacement of the ore-bearing epidote mineral assemblage by the barren prehnite assemblage as an indicator of advanced dilution of magma-derived ore-bearing fluid with seawater.

It is suggested that a solidifying intermediate magma chamber (intrusive body) in the oceanic crust composed of a hydrous melt of the silicic Fe–Ti–oxide series was the major source of ore-bearing fluids. The study of melt inclusions in melanocratic troctolite belonging to this series has shown that the water content in the melt reached 1.24 wt %; even minute amounts of sulfides were detected in these inclusions (Simonov et al., 2007). The release of aqueous fluids from such magmas commonly occurs under a pressure of 1 kbar, where the solubility of water in silicate melts sharply declines (*Fluids...*, 1991), i.e., at a depth of 3–4 km, where the magma chamber is presumably located. The fluid spread from the roof of the solidifying magma chamber through the system of fractures, initiating development of the hydrothermal system, which progressively involved seawater from the sub-bottom hydrosphere.

The position of the ore-bearing zone is consistent with a shallow depth of the magma chamber. The zone developed at a depth of 4600–4400 m from the ocean surface, i.e., approximately 2.6–2.4 km below the ocean floor. As in layered intrusions, new portions of melt were periodically injected into the solidifying magma chambers, which served as traps for such injections (Sharkov, 2006). The shallow-seated magma chambers could have existed for a long time, supplying the hydrothermal systems with ore-bearing fluids and heat.

Melts of the silicic Fe–Ti–oxide series are enriched in precisely those ore components that are noted in the ore occurrence of the Markov Deep, and these melts could have been sources of both hydrothermal fluids

and heat. In addition, some amount of ore matter could have been leached from host gabbroids. The ore deposition stopped when the primary hydrothermal solutions were diluted with seawater below a certain limit.

In addition to development of hydrothermal systems, dehydration of melts of the siliceous Fe–Ti–oxide series may have another consequence. It is known that decreasing water content in melt brings about a rise in its liquidus temperature and, hence, its rapid crystallization at a depth. As a result, lavas of this series are rare on the ocean floor.

Two other potentially ore-bearing basins in the Sierra Leone site—the Rudny field and 5°46' N (Pushcharovsky et al., 2004)—have a similar geological structure. It may be expected that sulfide ore occurrences of metasomatic origin in the form of extended zones will be discovered in these basins.

The high-temperature hydrothermal activity that leads to the formation of hydrothermal plumes and massive sulfide ore of the black smoker type is unknown at the eastern slope of the Markov Deep. The hydrochemical anomalies above this slope are most likely related to the low-temperature hydrothermal activity controlled by zones of tectonic deformation and hydrothermal metasomatism, as supported by findings of ferromanganese crusts of hydrothermal origin. This activity is probably related to residual magma chambers left behind after recent magmatic events.

Thus, a new promising type of sulfide mineralization of hydrothermal metasomatic origin has been revealed in the axial MAR zone. The ore-bearing fluid probably had a mixed origin. At the initial stage, the fluid was released from water-saturated magma of the mantle–crustal silicic Fe–Ti–oxide series during its ascent toward the surface, afterward being diluted by seawater until it became completely depleted in ore-forming constituents. The study performed does not allow estimation of the scope of this ore occurrence. The main ore reserves may occur here below the ocean floor. Since the ore matter is not dispersed in seawater, as occurs in black smokers, the reserves may be significant.

CONCLUSIONS

(1) The results of dredging carried out during Cruise 10 of the R/V *Akademik Ioffe*, Cruise 17 of the R/V *Akademik Sergei Vavilov*, and Cruise 22 of the R/V *Professor Logachev* in the axial part of the MAR rift valley in the Markov Deep (Sierra Leone site) have shown that its walls over a large distance (>300 km) are composed of gabbroic and ultramafic rocks; basalts and dolerites are also exposed. A zone of cataclastic and metasomatically reworked gabbroids with high-grade sulfide mineralization was discovered in one of the rift valley segments (the Markov Deep, 6° N).

(2) Altered ultramafic mantle rocks (restites) and two associations of igneous rocks, each composed of plutonic, subvolcanic, and volcanic complexes, were

dredged from the slopes of the Markov Deep. These associations differ in mineral composition and geochemical features. The rocks are commonly altered to variable extents: ultramafics are intensely serpentinized, while gabbroic rocks are amphibolized; samples of both altered and fresh basalts with glassy crusts were carried up.

(3) The first association is composed of a cumulative series: dunite–troctolite (melanocratic and leucocratic)–olivine gabbro–gabbro–leucogabbro (gabbroanorthosite) in combination with dolerites and basalts close to N-MORB in petrography and geochemical signatures. Rocks of this primitive association are characterized by highly magnesian dark-colored minerals and high-Ca plagioclase. Minor amounts of primary copper sulfides are detected in gabbro and troctolites.

(4) The second (silicic Fe–Ti-oxide) association consists of norite, gabbro-norite, gabbroanorthosite, Fe–Ti-oxide gabbro-norite, gabbrodiorite, diorite, and plagiogranite. These rocks contain magmatic brown hornblende (Ti-pargasite) and Fe–Ti-oxides, as well as ubiquitous apatite, zircon, and baddeleyite. High-temperature pyroxenites and some lherzolites and harzburgites with relics of cumulative structures probably pertain to this association as well. Subvolcanic and volcanic rocks of this association are rare; they are composed of hornblende dolerite and pyroxene–hornblende and hornblende basalts with abundant submicroscopic grains of Fe–Ti-oxides.

(5) Almost all ultramafic rocks and a great deal of gabbroids have undergone high-temperature alteration related to ductile flow of the mantle material and lower crust in the process of spreading. At the subsequent stage, the cooling of rocks was accompanied by brittle fracturing with penetration of seawater through fractures and cavities into the crust and by regional metamorphism under conditions of zeolite to epidote-amphibolite facies with the appearance of the Act + Chl₁ + Ep mineral assemblage in basic rocks.

(6) Almost all igneous rocks of the ocean floor in the Sierra Leone site are enriched in Pb, Cu, U, Rb, Ta, Nb, Cs, and Rb and depleted in Th and Hf. A specific feature of rocks of the Fe–Ti-oxide series is their enrichment in Zn, Sn, and Mo and depletion in Ni and Cr.

(7) Zones of brecciated and cataclastic gabbroic rocks of the Fe–Ti-oxide series are locally affected by ore-bearing hydrothermal metasomatic alteration. The thickest and most mineralized zone strikes in the north-northwest direction along the foot of the eastern slope of the Markov Deep. Several mineral assemblages replace one another in the following order: Hbl + Pl ± Ilm + Mag → Ab + Trem + Chl → Czo + Chl + Prh → Ep + Qtz + Chl + sulfides → Prh + Chl → Prh. The ore-forming metasomatism developed in the reducing environment within the temperature interval from ~400 to 160°C; the initial stages of hydrothermal alteration took place at a temperature from 800 to 450°C. The ore mineralization is associated with epi-

dosites, which are subsequently replaced by prehnite. The ore minerals occurring in prehnite metasomatic rocks are relict and related to the preceding stage of hydrothermal mineral formation. The latest alteration is expressed in replacement of sulfides by iron hydroxides.

(8) The study of fluid inclusions in prehnite and epidote from ore samples showed that the salt concentration in hydrothermal solutions (4.6–6.5 wt % NaCl equiv) was higher than the salinity of seawater (3.47 wt % NaCl equiv). The temperature of the stringer–disseminated ore formation is estimated from fluid inclusion study at 170–280°C, which is consistent with the results of mineralogical thermometry.

(9) The ore mineralization comprises quartz–sulfide and prehnite–sulfide veinlets, sulfide disseminations, and chalcopyrite veins hosted in metasomatically altered rocks (fragments of these veins 10–15 cm thick were dredged). The stringer–disseminated ore consists of pyrite, chalcopyrite, sphalerite, pyrrhotite, bornite, chalcocite, and digenite. Native Cu (including the Zn-bearing variety), Pb, Zn, Au, and Sn, as well as intermetallics (isoferroplatinum, tetraferroplatinum), have been identified in addition to sulfides.

(10) The $\delta^{34}\text{S}$ value of sulfides varies within a wide range, from +3.0 to +15.3‰, testifying to the involvement of both primary magmatic sulfur and seawater sulfur in the hydrothermal fluid. The Sr and Nd isotopic compositions of hydrothermally altered rocks confirm this conclusion.

(11) It is suggested that hydrothermal ore-bearing fluids initially had a magmatic origin and then were progressively diluted with seawater penetrating into the sub-bottom hydrosphere of the ocean. The ore matter was derived from both hydrous melts of the Fe–Ti-oxide series during their solidification in shallow-seated magma chambers and from host gabbroic rocks.

(12) A new promising type of sulfide mineralization revealed in the axial MAR zone probably is a part of the system feeding black smokers.

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