

Pr, Dy, Sm, and Gd in all ore types. In spite of considerable amount of cyrtolite, ferrithorite, and yttrifluorite, they are of secondary importance.

**The Sarysai tantalum-niobium-rare-earth deposit** is an example of ore mineralization hosted in carbonatites related to syenites. The deposit is composed of the Devonian, Carboniferous, and Permian terrigenous-carbonate sedimentary rocks. The intrusive rocks include Early Permian granites, rapakivi granites, and Late Permian alkali rocks of the Kaichin intrusive pluton, whose satellite, the Sarysai intrusive body, hosts Ta-Ni and rare-earth mineralization (Fig. 2). The latter is composed of the rocks of three consecutive phases of alkali magmatism: lujavrites and pulaskites of the first phase, leucocratic alkali syenites of the second phase, and intrusive aegirine-calcite carbonatites of the third phase. The veins of metasomatic carbonatites branch from the Sarysai stock.

All three stages underwent ore-bearing metasomatism and autometasomatism, which led to formation of fenites, albitites, and carbonate metasomatic rocks. The ore metasomatites of all stages form the combined ore zones.

The content of rare earth elements in metasomatites are 0.01–0.05 % for Yb and about 0.05 % for each of Ce, La, Y, and Nb. The Nb/Ta,  $\Sigma\text{REE}/\text{Y}$ , and  $\text{Y}_2\text{O}_5/\text{TR}_2\text{O}_5$  ratios in different ore bodies are approximately 10:1, 4:1, and up to 1:4, respectively.

The quartz-feldspar-aegirine ore veins are zonal: the central parts include leucocratic fenites, rarely with aegirine, and the marginal parts are composed of carbonatites with variable content of calcite. The aegirine-amphibole-feldspar metasomatites are the intermediate varieties. All of them are the products of metasomatic facies of the carbonatite process. The radioactive pyrochlore (hatchettolite), euxenite, xenotime, rare earth carbonates and products of their alteration, ilmenorutile, zircon, and thorite are economically valuable minerals. Sulfides include galena, pyrite, pyrrhotite, and molybdenite. Supergene minerals are iron and manganese hydroxides.

According to the geologic position, ore-bearing metasomatites, and ore mineralization, the closest analogues of the Sarysai deposit are the deposits of the carbonatite-related aegirine-albite type with hatchettolite and zircon [Solodov, 1987]. The high content of Y group elements is untypical of this type of the deposits. Probably, this is caused by involvement in ore formation both of carbonatites (intrusive and metasomatic), syenites, and derivatives of the granite magma.

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## HYDROTHERMAL VENT FAUNA IN THE URALS VMS DEPOSITS: CRITERIA FOR OCCURRENCE

Рассмотрены критерии появления, фоссилизации и сохранности пригидротермальной фауны в рудах колчеданных месторождений Урала и других колчеданоносных регионов. Показано, что для появления фауны благоприятными являются колчеданообразующие системы черных курильщиков, формировавшихся на базальтовом и риолит-базальтовом основаниях. Установлено, что черные курильщики, обогащенные Fe, Sn, Te, Co являются спутниками сульфид-

ных тафоценозов. Менее перспективными являются гидротермальные системы серых курильщиков, формирующие колчеданно-полиметаллические месторождения на субстрате, сложенном кислыми вулканитами. Показано влияние подрудных черных сланцев на вероятность появления пригидротермальной фауны. Рассмотрены геохимические особенности пригидротермальной биоты, включающие данные ЛА-ИСП-МС и изотопного состава серы. Установлено, что вероятность сохранности оруденелой фауны уменьшается в ряду от сульфидных холмов к пластообразным продуктам их разрушения.

The finding of very well preserved sulfidized fauna was one of the numerous surprises in the Urals. Previously, the fauna was found in the Silurian Yaman-Kasy, Krasnogvardeyskoe and Middle Devonian Sibai, Yubileinoe and Saf'yanovka VMS deposits [Ivanov et al., 1949, 1960; Maslennikov, 1991; Zaykov, 1991]. This fauna represents the most ancient known taxonomical hydrothermal vent community [Buschmann, Maslennikov, 2006; Maslennikov, 2006; Zaykov, 2006; Maslennikov, 1991, 1999, 2006; Little et al., 1997, 1999]. The most samples of fossil hydrothermal fauna are stored in the depository of the Institute of Mineralogy UB RAS in Miass and some samples were presented by authors to the Vernadsky Geological Museum in Moscow, TU Bergakademie in Freiberg, and Natural History Museum in London. The recent recognition of potentially vast, unexplored biomineralization associated with modern and ancient VMS deposits yielded the new material for mineralogical and biogeographic investigation. In last years, the sulfidized vent fauna was revealed in the Blyava, Molodezhnoye, and Valentorka VMS deposits. The recent study of new samples has given a novel data on peculiarities of the unexplored sulfidized fauna from the Urals VMS deposits in comparison with fauna from the modern and other ancient vent sites. The ore facies mapping, analyses of mineral assemblages, LA-ICP-MS and sulfur isotope analyses, and fluid inclusion study are the main methods of the research.

The oldest known and most taxonomically diverse hydrothermal fauna has been recovered from the Early Paleozoic basalt-rhyolite-hosted Yaman-Kasy VMS deposit located in the central part of Orenburg district, South Urals, and confined to the Sakmara marginal paleobasin. The sulfide body has a mound shape. The vent chimney relics, sedimentary reworked sulfides, and ferruginous sediments (gossanites after Maslennikov et al., 2012) indicate a seafloor hydrothermal origin of massive sulfides [Zaykov et al., 1995]. The sulfidized fauna is covered with colloform pyrite and the inner walls of the moulds are incrustated with drusy marcasite, sphalerite, pyrite, chalcopyrite, quartz, and barite. The fragments of sulfidized fauna in clastic sulfides are the signatures of the seafloor fossilization processes similar to the modern vent sites [Avdonin, 1996, Maslennikov, 1999]. The pyrite tube moulds both of the large tube worm *Yamanlasia refeia*, which is similar to the modern vestimentifera *Riftia pschiptilla*, and small worm tube *Eoalvinellodes annulatus* display widespread entombment of fossil filamentous and rod-like microorganism [Little et al., 1997; Maslennikov, 1999; Buschmann, Maslennikov, 2006]. The most researchers have suggested that the trophic chain of the Yaman-Kasy paleocommunity was obviously established by chemoautolithotrophic bacteria, which are the primary producers in the modern hydrothermal vent community. The extremely large sizes of the thergomian mollusk *Termoconus shadlunae* and giant lingulate brachiopod *Pyrodiscus lorraineae* are indicative of more prolific nutritional source in ancient hydrothermal vent habitat [Little et al., 1999; Kuznetsov, Maslennikov, 2000; Buschmann, Maslennikov, 2006].

The Silurian vent fauna is widespread in other Urals VMS deposits. Small pyrite tube worms in clastic sulfides were found in the drill core from the Komsomolskoye VMS deposit located at the same district, as well as Yaman-Kasy deposit [Pshenichny, 1981]. Similar well preserved tube worms were found by authors in the damp of the Blyava VMS deposit and recently in the Valentorka VMS deposit, North Urals. The latter is referred to the Baimak VMS type or is considered as intermediate member in a range from the Baimak to the Urals type. Single sample of the pyrite tube worm was collected by Gorocho A.V. in the Krasnogvardeiskoe VMS deposit in the Central Urals [Ivanov, 1959]. All deposits represent strongly degraded sulfide mounds and are similar to the Yaman-Kasy VMS deposit.

Diverse Devonian vent paleocommunity was found in the Sibai VMS deposit located in the inter-arc paleobasin. The deposit consists of four stacked massive sulfide lenses (mounds) enclosed in the bimodal mafic sequence. The fossils include the species of bivalvia (*Sibaya ivanovi* [Little et al., 1999]) and flanged worm tubes were formally described as *Tevidestus serriformos* [Shpanskaya et al., 1999], which are similar to the modern vestimentifera *Tevnia*. Much smaller annulated worm tubes resemble the modern near-vent polyhaetes. The same polyhaetes and other unexplored tube forms

were found in sulfide breccias around the sulfide mounds of the Molodezhnoe, Uzelga, and Talgan VMS deposits located in the East Magnitogorsk arc paleobasin. All of these VMS deposits are accompanied by ferruginous sediments, indicating oxidation conditions. In other hand, the sulfidized fauna in the Urals was also found in the Saf'yanovka deposit (East Uralian zone, Central Urals), which was formed under anoxic conditions expressed in the black shale and felsic sequence. Numerous worm tube samples were collected from the strongly destroyed sulfide mound and were formally described as *vestmentiferas* or *polyhaetes* [Maslennikov, 1999]. The problematic tube fossils were found at the Ishkinino, Oktyabr'skoe, Buribai, Barsuchiy Log, Levikha and other Urals VMS deposits, which merit further research.

Thus, the vent fauna is widespread at some VMS deposits in the Urals, Pontides, Cyprus, and California relative to other VMS districts in spite of the same degree of careful ore facies and mineralogical mapping. The petrologic, ore facies, mineralogical, and geochemical criteria of the vent fauna occurrences in the VMS deposits are reviewed herein.

The petrologic background includes the geological setting and composition of the host rocks. The most of the cast fossilized vent fauna occurs in the VMS deposits associated with mafic (Cyprus type) and bimodal mafic (Urals type) sequences. This is in agreement with an idea that hydrothermal systems developed in these sequences are characterized by the highest reduction potentials. The high reduction potential is a major factor for the development of the vent community based on chemosynthesis during bacterial consumption of the reduced gases such as  $H_2S$ ,  $CH_4$ , and  $H_2$  as a main source of energy. In the other hand, VMS deposits located in bimodal felsic and felsic sequences are commonly barren of sulfidized fauna. The most famous examples are Kuroko and Altai types of VMS deposits devoid of obvious sulfidized vent fauna. It is suggested that the hydrothermal systems from these deposits were depleted in reduced gases but enriched in  $SO_2$  and  $CO_2$ , representing the higher state of fluid oxidation and, therefore, the lower potential for the bacterial chemosynthesis. One of the known exceptions is the Saf'yanovka VMS deposit, where oxidation of fluids was prevented by foot-wall organic-rich sediments.

The interrelationship of ore facies may be an indicator of occurrence and preservation of the vent fauna. Several ore facies (ore types) were recognized at the VMS deposits. The abundance of the well preserved hydrothermal black smoker chimneys and diffusers, indicating the hydrothermal activity, is the most important factor for the vent fauna occurrence. However, the chimneys from the Kuroko, Altai and Baimak types of VMS deposits are not commonly associated with vent fauna. The vent fauna is minor during the waning stage of the hydrothermal system, when the seafloor weathering and reworking of sulfide mounds are the main processes of the clastic ore formation. Thus, the vent fauna is unlikely to be preserved, where sulfide turbidites are the main ore facies. In addition to weathering of the sulfide mounds, the hydrothermal alteration of the mound above the feeder zone play important role in recrystallisation of biomorphic textures. The proportion of hydrothermal activity and alteration periods depends on volcanic intensity. At intense volcanism, the catastrophic entombment of sulfide mounds may be the main reason of preservation of primary vent fauna features.

The mineralogical criteria are also related to the assessment of the reduction potential of the hydrothermal system. The best proxies for this research are the vent chimneys and diffusers as the best mineralogical indicators of the hydrothermal physicochemical condition. The chimneys from most Cyprus VMS deposits comprises abundant pyrite, pyrrhotite, isocubanite, and chalcopyrite and display lack of tellurides, arsenides and other rare mineral assemblages. The reason for that is low-S and low-Te conditions, which led to substitution of metals (Au, Co, Ag, Ni) and semimetals (Te, As, Se, Sb) in the lattice of main sulfides. These attributive features of the high reduction potential seem to be favorable for the vent fauna occurrence in association with the modern and ancient black smokers. In the Urals types of VMS deposits, the chimneys and diffusers display specific composition suggestive of low-S (low S fugacity,  $?S_2$ ) hydrothermal fluids. This means the low state of fluid oxidation or its high reduction potential. The mineral assemblages related to the low-S conditions include pyrrhotite or pseudomorphic pyrite after pyrrhotite, isocubanite, Fe-rich sphalerite, Fe-Co-arsenides, sulfoarsenides, and tellurides. The best indicator of low-S conditions is altaite (PbTe), which is widespread in chimneys associated with vent fauna. The chimneys and diffusers contain abundant colloform pyrite. In the other hand, the gray smoker chimneys from the Kuroko and Altai deposits include mostly barite, sphalerite, and stoichiometric chalcopyrite or bornite and galena. Native gold, galena, and fahlores are most important rare indicative mineral of high-S conditions or high state of fluids oxidation. The low reduction potential of the hydrothermal systems of the Kuroko and Altai deposits may be an important reason of vent fauna defi-

ciency. The intermediate type between bimodal mafic and felsic types of VMS deposits are Pontide and Baimak type, which is associated with bimodal felsic sequences. The vent fauna in these deposits is absent or extremely poorly preserved owing to the deficiency in colloform pyrite coating because of the general lack of Fe-rich minerals. The best preserved samples of sulfidized vent fauna are commonly associated with colloform pyrite, which is abundant mainly in the Cyprus and Urals types of VMS deposits.

The geochemical criteria are also consistent with maturation and reduction potential of the hydrothermal systems. The Se, Te, Co-, and Fe-rich massive sulfide ore are indicative of immature hydrothermal system with high reduction potentials. In opposite, the Zn-, Pb, Tl, Ba, and Sb-rich massive sulfide ores testify to the mature hydrothermal system with low reduction potential. The contents of trace elements in hydrothermal sulfides are most important indicators of physicochemical parameters of hydrothermal systems. The content of trace elements in sulfides may be high due to inclusions of rare minerals or substitution in lattice of sulfide structures. In the first case, the Pb/Te and Ag/Te ratios display telluride and fahlore-electrum-rich assemblages. The detection of second phenomena is most important instrument for physicochemical reconstructions. The chemical peculiarities of the hydrothermal chalcopyrite, which seals the conduits of the vent chimneys, are most interesting. The Se-, Te-, Co-, and Sn-rich chalcopyrite, which is typical of the black smokers in the Cyprus and Urals types of VMS deposits, is the best indicator of highly reduction potential. In the other hand, Se-poor chalcopyrite enriched in Ag is suggestive of high state of fluid oxidation unfavorable for the vent fauna occurrence. This chalcopyrite is characteristic of gray smokers in the Kuroko and Altai types of VMS deposits. The same situation is observed for the Fe-, Co-, and Sn-rich sphalerite associated with vent fauna. In contrast, Fe-, Co-, Sn-poor and Cd- and Mn-rich sphalerite is a constituent of the gray smokers, which are less favorable for association with plentiful vent community. It is less known on the relationship between vent fauna occurrence and substitution of trace elements in other sulfides. In general, Co-rich pyrite is most important for fertile vent ecosystems relative to Ni-rich varieties, because the first one is characteristic of low-S conditions in contrast to the second one. The sulfur isotopic composition of biomorphic sulfides may be indirect criteria to distinguish fertile and barren VMS deposits in regard to vent fauna. The values of  $\delta S^{34}$  from  $-2$  to  $+2$  ‰ [Lein et al., 2004] are the most common for the vent chimneys and near vent fauna formed in the black smoker systems of the Urals VMS type. The  $\delta S^{34}$  for chimneys from the Kuroko deposits is somewhat higher ( $+2$  to  $+6$  ‰) that suggests involving of seawater sulfate into reduction of sulfur during sulfide formation. This process may decrease the reduction potential of the hydrothermal system. The diagenetic sulfidized fauna display much wider  $\delta S^{34}$  variation.

The promising data may be obtained by gas chromatography analyses of the fluid inclusions. The first results display  $CH_4$  enrichment of quartz and barite in chimneys associated with vents fauna. However, we should be careful with these data, because influence of organic-rich sediments located in the footwall of the hydrothermal system on composition of the hydrothermal fluids and vent fauna occurrences is an unresolved problem.

Thus, petrologic, ore facies, mineralogical, and geochemical research has shown that Cyprus and Urals types of the VMS deposits display the highest reduction potential of the hydrothermal fluids, yielding abundant vent community and, therefore, plentiful sulfidized fauna versus Altai and Kuroko deposits. We suggest that VMS deposits of Pontides and Baimak types occupy intermediate position in a range of these bimodal mafic and bimodal felsic types of VMS deposits. The long-term research of VMS deposits allows exploration of linkages between formation conditions and near vent biosphere. Such approaches may provide significantly new information to resolve the problem of life origin.

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## **MINERALOGY AND CHEMISTRY OF MODERN AND ANCIENT BLACK AND GRAY SMOKER CHIMNEYS AND DIFFUSERS**

Показано минералогическое и геохимическое разнообразие сульфидных труб черных и серых курильщиков, формировавшихся в современных и древних колчеданоносных гидротермальных системах. Первые связаны с офиолитовыми и риолит-базальтовыми формациями, вто-