### References

Buchachenko, A.L., Galimov, E.M., Ershov, V.V., Nikiforov, G.A., Pershin, A.D. enrichment of isotopes, the induced magnetic interactions in chemical reactions // Doklady Akademii Nauk USSR, 1976. Vol. 228 (2). P. 379–381 [in Russian].

Buchachenko, A.L. New Isotopic in Chemistry and Biochemistry. Moscow, Nauka, 2007. 189 p. [in Russian].

*Galimov, E.M.* Nuclear spin isotope effect – a new type of isotope effect // Geochemistry International, 1979. No. 2. P. 274–284 [in Russian].

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# **BARITE FROM THE ANCIENT VMS-DEPOSIT AND MODERN HYDROTHERMAL** SULFIDE FIELDS: A COMPARISON OF FORMATION CONDITIONS

В работе изложены результаты изучения минеральных ассоциаций, химического и изотопного составов, термобарогеохимических характеристик флюида, образовавшего барит из серноколчеданных колломорфных и обломочных руд палеозойского Сафьяновского месторождения (Средний Урал) и кайнозойских гидротермальных полей Семенов-1 и Семенов-3 (САХ).

В результате проведенных исследований установлены черты сходства и отличия процессов образования баритсодержащих минеральных ассоциаций в различных текстурных типах руд из разновозрастных колчеданных построек. В брекчиях, в отличие от колломорфных и тонкозернистых руд, отмечается сходство минеральных ассоциаций баритов. Отличия выявлены в содержании микропримесей, изотопном составе и параметрах флюида, образовавшего барит.

Barite is one of the widespread gangue minerals both in on-land volcanogenic-hosted massive sulfide deposits and submarine hydrothermal sulfide vent systems. The different formation conditions of barite are recorded in its morphology, chemical and isotopic composition, and fluid inclusions [Paytan et al., 2002], thus it may serve as an indicator of formation conditions of accompanying massive sulfides. This work presents the comparative study of barite from low-metamorphoused Devonian Saf'yanovka VMS-deposit in the Central Urals and Cenozoic Semenov-1 and Semenov-3 hydrothermal sulfide fields in the Mid-Atlantic Ridge. The mineral assemblage, chemical and isotopic composition, and fluid inclusions were analyzed in barite from colloform, fine-crystalline and clastic sulfides.

The barite-bearing ore samples from the Saf'yanovka deposit were collected from the main orebody in the operating open pit. The deposit hosted by rhyolitic-dacitic-andesitic-basaltic volcanic complex [Yazeva et al., 1991]. Based on the detail ore-facial mapping, the major subvertical triangle-shaped ore lens was reconstructed as a destroyed sulfide mound [Maslennikov, 2006]. The colloform pyrite ores with barite and quartz in the top of the sulfide body represent the fragments of seafloor hydrothermal slabs. The sulfide breccias and sandstones with clasts of massive and colloform ores and black smoker chimneys cemented by barite, quartz and, locally, by C-bearing silty sandstones are located in the southern flank of the main orebody.

Massive sulfides from the Semenov-1 and -3 hydrothermal fields were collected in the 30<sup>th</sup> cruise of the R/V *Professor Logachev* in 2007. The hydrothermal fields are the part of the large Semenov massive sulfide cluster [Beltenev et al., 2007]. The Semenov-1 field (13°30.87? N, 44°59.24? W) is situated near the seamount foot at a depth of 2570–2620 m. It represents a single mound or, more probably, a series of coalescent sulfide mounds and their destruction products [Ivanov et al., 2008]. The dredged samples included serpentinized ultramafic rocks, altered basalts, and massive sulfides, containing up to 20 vol % of barite. The Semenov-3 field (13°30.70? N, 44°55.00? W) is located on the northeastern slope of the seamount at a depth of 2400–2600 m and is associated with altered basalts [Beltenev et al., 2007]. Sulfide breccias with marcasite–pyrite clasts enclosed in the fine-grained sulfide–quartz cement were recovered from the seafloor.

The abundance of fine-crystalline, porous, nodular, banded, and colloform textures, predominant iron disulfides over Cu-Fe-Zn-sulfides and presence of barite and less abundant quartz bring together the Saf'yanovka and Semenov-1 colloform sulfides, indicating similar way of their formation. Barite crystals from both objects are large, tabular and form rosettes that is typical of hydrothermal barites [Paytan et al., 2002]. Barite from the Saf'yanovka colloform ores is associated with late quartz and was formed after major sulfides. The most part of barite from the Semenov-1 fine-crystalline massive sulfides is the earliest mineral precipitated before the sulfides. Less amount of barite was formed at the final stage of mineral deposition.

Barite from the Saf'yanovka and Semenov-3 pyrite breccias is a late mineral formed after destruction of the early colloform sulfides and their cementation by newly formed sulfides. Barite from the Saf'yanovka clastic ores is most likely postdiagenetic, because it develops after diagenetic pyrite framboids and metacrystals. Barite crystals, locally with stylilote boundaries, are deformed as a result of increasing pressure. The compact barite aggregates owing to the straitened crystallization conditions are similar in morphology with diagenetic barite from ocean sediments [Paytan et al., 2002]. Barite from the Semenov-3 field is a product of late hydrothermal input. It grew in the large cavities in clasts and cement, forming the typical radial aggregates of large tabular crystals and, locally, associating with late chalcopyrite.

Based on microprobe analysis, Sr is a major admixture in barite. Sr contents in barite from the Saf'yanovka deposit (0.00–0.83 wt %), Semenov-1 (0.31–4.45 wt %) and Semenov-3 (0.50–2.84 wt %) fields are typical of barite from many ancient VMS-deposits and modern hydrothermal sulfide fields. So, Sr content by itself could not be the reliable genetic indicator.

Different trace element distribution based on ICM-MS analysis is caused by different reasons. The increased Zn contents in barite from the Semenov-1 field and elevated Zn, Pb, As, Te, Hg and Bi contents in barite from the Saf'aynovka clastic ores reflect microinclusions of sphalerite (Semenov-1) and sphalerite, galena and various sulfosalts (Saf'aynovka). The elevated Co, Ni, Mn, and U contents in barite from the Semenov-1 field derived from seawater. The higher Cu, Ga, Ge, and Sb contents in barite from the Semenov-3 field may be attributed to the contribution of high-temperature hydrothermal fluid during coeval precipitation of barite and Cu-Fe-sulfides.

Increase in  $\delta^{34}$ S values in barite from the Saf'yanovka colloform (+25.5 ‰) and clastic (+27.0 ‰) ores relative to the  $\delta^{34}$ S values of the Silurian–Devonian seawater (+23...+24 ‰) [Claypool et al., 1980] is a result of bacterial activity that agrees with numerous relics of sulfidized near-hydrothermal fauna in colloform ores and their clasts in breccias. This fact also corroborates the presence of N<sub>2</sub>, CO, and CH<sub>4</sub> in gaseous mixture from fluid inclusions. Sulfur isotopic composition of the Semenov-1 barite (+21.0 and +21.3 ‰) completely corresponds to that of the contemporary seawater (+21.2 ‰) [Rees et al., 1978]. Little decrease in  $\delta^{34}$ S values in barite from the Semenov-3 breccia (+20.6 ‰) may indicate contribution of some portion of light sulfur isotope from the high-temperature hydrothermal fluid.

Barite in the Saf'yanovka colloform ores and Semenov-1 fine-crystalline sulfides was crystallized from relatively low- to medium-temperature and low-salinity fluids of compound composition:  $182-204 \,^{\circ}C$ ,  $1.5-4.5 \,$  wt % NaCl-eq., NaCl-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O and NaCl--NaHCO<sub>3</sub>-H<sub>2</sub>O (Saf'yanovka) and 83-224  $\,^{\circ}C$ ,  $0.6-3.8 \,$  wt % NaCl-eq., Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>-NaHCO<sub>3</sub>-H<sub>2</sub>O (Semenov-1). The hydrothermal fluid most likely underwent phase separation that is evident from low salinities. The presence of SO<sub>2</sub> and CO<sub>2</sub> in fluid inclusions in barite from the Semenov-1 field may indicate the magmatic contribution. Barite from clastic ores was formed from medium-temperature (150–190  $\,^{\circ}$ C), low-salinity (1.0–5.5 wt % NaCl-eq.) NaCl-dominant fluid at the Saf'yanovka deposit and hightemperature (270–340  $\,^{\circ}$ C), medium- to high-salinity (4.5–9.5 wt% NaCl-eq.) Na<sub>2</sub>SO<sub>4</sub>-NaCl-H<sub>2</sub>O fluid at the Semenov-3 field.

The results of our study have revealed similar formation conditions of hydrothermal barite from the ancient massive sulfide deposit and modern hydrothermal sulfide fields. Barite from the colloform ores was formed from the low-temperature low-saline fluid of compound composition in contrast barite from clastic ores, which was crystallized from moderate- to high-temperature higher saline NaCldominant fluid. Phase separation of the fluids played important role in formation of barites from colloform ores that may be deduced from one- and two-phase fluid inclusions and low salinity relative that of seawater. Some discrepancies in chemical composition, sulfur isotopic composition or fluid inclusion data reflect specific geological-mineralogical environments of barite formation. The high-temperature barite from the Semenov-3 clastic ores could incorporate some portion of light sulfur isotopes from the high-temperature hydrothermal fluid that was resulted in slightly decreased  $\delta^{34}$ S values. Increased sulfur isotopic composition of barite from the Saf' yanovka ores is a consequence of bacterial reduction that is in accordance with abundant fauna relics in the deposit. Barite from the Saf' yanovka ores was formed under more reducing conditions that is evident from the higher CO and  $CH_4$  contents in gaseous composition of fluid inclusions. High Cu content, higher homogenization temperatures of fluid inclusions and higher salinity of the fluid in barite from the Semenov-3 clastic ores are related to its precipitation from the high-temperature hydrothermal fluid in assemblage with late Cu-Fe-sulfides.

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#### References

*Beltenev, V., Ivanov, V., Rozhdestvenskaya, I. et al.* A new hydrothermal field at 13?30' N on the Mid-Atlantic Ridge // InterRidge News, 2007. Vol. 16. P. 9–10.

*Beltenev, V., Ivanov, V., Rozhdestvenskaya, I. et al.* New data about hydrothermal fields on the Mid-Atlantic Ridge between 11?–14?N: 32<sup>nd</sup> cruise of R/V Professor Logatchev // InterRidge News, 2009. Vol. 18. P. 14–18.

*Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I.* The age curves of sulphur and oxygen isotopes in marine sulphates and their mutual interpretation// Chem. Geol., 1980. Vol. 28. P. 199–260.

*Ivanov, V.N., Beltenev, V.E., Stepanova, T.V. et al.* Sulfide ores of the new hydrothermal fields at 13°31' N MAR // In: Metallogeny of ancient and modern oceans-2008. Ore-bearing complexes and ore facies. Miass, IMin UB RAS, 2008. P. 19–22 [in Russian].

*Maslennikov, V.V.* Lithogenesis and formation of massive sulfide deposits. Miass, IMin UB RAS, 2006. 383 p. [in Russian].

Paytan, A., Mearon, S., Cobb, K., Kastner, M. Origin of marine barite deposits: Sr and S isotope characterization // Geology, 2008. Vol. 30. No 8. P. 747–750.

*Rees, C.E., Jenkins, W.J., Monster, J.* The sulfur isotopic composition of ocean water sulfate // Geochim. Cosmochim Acta, 1978. Vol. 42. P. 377–381.

Yazeva, R.G., Moloshag, V.P., Bochkarev, V.V. Geology and ore parageneses of the Saf'yanovka massive sulfide deposit in the Central Urals back thrust // Geol. Ore Dep., 1991. Vol. 3

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## FORMATION CONDITIONS OF THE RIDDER-SOKOLNOE DEPOSIT, RUDNYI ALTAI, KAZAKHSTAN

Риддер-Сокольное золото-полиметаллическое месторождение является крупнейшим на Рудном Алтае. Формирование оруденения связано с раннедевонским (эмс) вулканизмом. Оруденение локализовано в депрессионной палеоструктуре, возникшей на склоне или подножье подводной вулканической гряды. Его размещение контролировалось зонами трещиноватости, служившими проводниками гидротермальных рудоносных растворов, отлагавших оруденение в придонной части морского бассейна и на путях их следования. Отчетливо проявлены признаки выноса рудного материала из подрудных пород месторождения.

The Ridder-Sokolnoe gold-polymetallic deposit is the largest deposit in the Rudny Altai. It is located in the Leninogorsk-Zyryanovsk subzone of the Rudny Altai metallogenic zone within the Leninogorsk graben bounded by the Ivanovsky (Obruchevsky) reversed fault in the south and Severny thrust in the west, north and northeast, which is alternated by the Bosyakovsky reversed fault in the southeast. The territory of the graben hosts the Leninogorsk ore field with Ridder-Sokolnoe and similar Kryukovskoe, Novo-Leninogorskoe, Obruchevskoe, and Dolinnoe deposits.