Ivanov, S.N. Study experience of geology and mineralogy of the Sibay massive sulphide deposit // Akademia Nauk SSSR, Uralskiy Filial, 1947. Vol. 2. P. 1–109 [in Russian].

Ivanov, S.N. A discussion of some actual questions in formation of massive sulphide deposits in the Urals // Problems of geology and origin of massive sulfide deposits in the Urals. Sverdlovsk, 1959. P. 7–78 [in Russian].

Ivanov S.N., Kuritzyna G.A., Hodalevich N.A. New data about genesis of massive sulfide deposits of Urals // Genetic problems of ores. Moscow, 1960. P. 100–105 [in Russian].

Kuznetzov, A.P., Maslennikov, V.V. Hystory of the ocean hydrothermal fauna. Moscow, VNIRO, 2000. 118 p. [in Russian].

Lein, A.Yu., Maslennikov, V.V., Maslennikova, S.P., Spiro, B. Isotopes of carbon and sulfur in biomorphic ore facies from black smockers of the Uralian Paleoocean *// Geochemia*, 2004. No. 7. P. 770–785 [in Russian and English].

Little, C.T.S., Herrington, R.J., Maslennikov, V.V., Morris, N.J., Zaykov, V.V. Silurian high-temperature hydrothermal vent community from the Southern Urals, Russia // Nature, 1997. V. 385. №. 9. P. 146–148.

Little, C.T.S., Maslennikov, V.V., Morris, N.J., Gubanov, A.P. Two Palaeozoic hydrothermal vent communities from the Southern Ural mountains, Russia // Palaeontology, 1999. No. 6. P. 1043–1078.

Maslennikov V.V. Sedimentogenesis, Halmyrolysis and Ecology of massive sulphide-bearing vent fields. Miass, Geotur, 1999. 348 p. [in Russian].

Maslennikov, V.V. Lithogenesis and massive sulfide deposits forming processes. Miass, IMin UB RAS, 2006. 384 p. [in Russian].

Maslennikov, V.V. Lithological control of copper massive sulfide ores (after the example of Sibai and Oktyabrskoye deposits, Ural). Sverdlovsk, UB AN USSR, 1991. 139 p. [in Russian].

Maslennikov, V.V., Ayupova, N.R., Herrington, R.J., Danyushevskiy, L.V., Large, R.R. Ferruginous and manganiferous haloes around massive sulphide deposits of the Urals // Ore geology reviews, 2012. Vol. 47. P. 5–41.

Pshenichnyi, G.N. Texture and structure of the ore of VMS deposits of the Southern Urals. Moscow, Nauka, 1984. 207 p. [in Russian].

Shpanskaya A.Yu., Maslennikov V.V., Little, C.T.S. The tubes of Vestimentifera of early Silurian and middle Devonian hydrothermal biota of Ural paleoocean // journal of Paleontology, 1999. №. 3. P. 21–30.

Zaykov, V.V. Volcanism and sulfide mounds in paleooceanic margins. Moscow, Nauka, 1991. 206 p. [in Russian].

Zaykov, V.V. Volcanism and sulfide mounds in paleooceanic margins. Moscow, Nauka, 2006. 428 p. [in Russian].

Zaykov, V.V., Shadlun, T.N., Maslennikov, V.V., Bortnikov, N.S. Sulphide deposit of Yaman-Kasy – ancient black smockers of the Uralian paleoocean // *Geologia rudnich mestorogdeniy,* 1995. P. 511–529 [in Russian and in English].

S.P. Maslennikova[1], V.V. Maslennikov[1], R.R. Large[2], L.V. Danyushevsky[2], V.A. Kotlyarov[1], A.Yu. Lein[3], Yu.A. Bogdanov [3], R.J. Herrington[4], D. Ishiyama[5], T. Urabe[6], K. Revan[7], A.S. Tseluiko[1], B.Buschmann[8]

[1] Institute of Mineralogy UB RAS, Miass, Russia
[2] University of Tasmania, CODES, Hobart, Australia
[3] Institute of Oceanology RAS, Moscow, Russia
[4] Natural Hystory Museum, London, UK
[5] Akita University, Akita, Japan
[6] University of Tokio, Tokio, Japan
[7] Department of Mineral Research and Exploration, General Directorate of Mineral Research and Exploration (MTA), Ankara, Turkey
[8] Freiberg Mining Academy, Freiberg, Germany

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-

рые – с базальт-риолитовыми и андезит-риолитовыми. Выявлено, что в ряду от офиолитовых комплексов к риолитовым в сульфидах труб уменьшаются содержания Co, Ni, Se, Te и увеличиваются содержания Pb, Bi, Tl, Hg, Au и Ag. Установлены признаки гидротермально-осадочной дифференциации элементов-примесей при формировании минеральной зональности гидротермальных труб, свидетельствующие о единстве процессов формирования сульфидных труб современных и древних черных курильщиков. Показано влияние подрудных углеродистых отложений на появление черных курильщиков.

The study of rare mineral assemblages and trace elements in the hydrothermal chimneys yields a lot of information to resolve genetic problems of ore-forming processes in modern and ancient seafloor sulphide-bearing hydrothermal systems. Previous research has provided limited combined data on mineralogy and chemistry of modern and ancient black smoker chimneys. The first semi-quantitative data from Butler and Nesbitt (1999) illustrated the power of LA-ICPMS analysis by documenting the non-random distribution of V, Ag, In, Te, Ba, Au, and Pd within the chalcopyrite wall of an immature black smoker chimney from the Rainbow vent field (29° 10′N, MAR). In previous paper, we focused on mineralogy and the LA-ICPMS investigation of diverse Silurian-Devonian vent chimneys recently collected in the Urals VHMS deposit [Maslennikov et al., 2009; 2012]. Recently, we studied mineral assemblages and trace element concentrations in pyrite, chalcopyrite, and sphalerite of the chimneys from the Urals (Yaman-Kasy, Alexandrinskoye, Octyabrskoye, Tash-Tau, Yubileynoye, Saphyanovskoye, Molodezhnoye, Uzelga, Valentorskoye), Rudny Altai (Zarechenskoye, Nikolayevskoye, Artemyevskoye), Pontides (Lakhanos, Killik, Kutlular, Chaely, Kizilkaya, Kure), and Hokuroko (Mazumine, Mazuki, Ezury, Furutobe, Hanawa, Ainay, Kosaka Uchinotay and Kosaka Motoyama) VMS deposits in comparison with black, gray and white smoker chimneys from hydrothermal fields of Atlantic (Rainbow, Broken Spur, TAG, Lucky Strike, Menez Gwen, Snake Pit) and Pacific (EPR 9°N; Axial Seamount, Galapagos, North Manus, East Manus and Lau) oceans.

A preliminary mineralogical study of the chimneys was followed by scanning electron microscopy (REMMA-2M SEM equipped with energy dispersive X-ray detector and JEOL JXA 733) at the Institute of Mineralogy, Russian Academy of Sciences. Further mineral analyses were obtained in several laboratories equipped with CAMEBAX SX-50 and JEOL-JXL-8600 (Natural History Museum, London), Cameca SX-100 (University of Tasmania, Australia) and JEOL JXA 8900RL (Freiberg Mining Academy, Germany).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) offers enormous potential in advancing trace element studies of sulfides through significantly improved detection limits for in situ analysis [Norman et al., 1998]. Many important innovations, including preparation of new glass standards, which enable improved quantitative LA-ICPMS analysis of sulfides, have been made over the last ten years at the Centre for Ore Deposit Research, University of Tasmania [Danyushevsky et al., 2003, 2010]. The LA-ICP MS is used for detection of trace elements substitution and rare mineral inclusions in sulfides.

In general, the chimneys show decreasing amount of Fe-rich sulfides and increment of barite-galena-sphalerite-fahlore assemblages in the range from ophiolite to rhyolite-rich associations. Abundant Ni-Co sulfides, rare Co-Fe arsenides and very rare tellurides are characteristic of mineral assemblages in modern black smokers formed on ultramafic basements. The deficient rare minerals are found in modern and ancient chimneys situated on basalt units (Cyprus, MOR). The heighest contents of Se and Te are substituted in chalcopyrite.

Tellurium-bearing minerals are generally rare in chimney material from mafic and bimodal felsic volcanic hosted massive sulfide (VMS) deposits, but are abundant in chimneys of the Urals VMS deposits located within Silurian and Devonian bimodal mafic sequences [Maslennikov et al., 2013]. High physico-chemical gradients during chimney growth result in a wide range of telluride and sulfoarsenide assemblages including a variety of Cu-Ag-Te-S and Ag-Pb-Bi-Te solid solution series and tellurium sulfosalts. A change in chimney types from Fe-Cu to Cu-Zn-Fe to Zn-Cu is accompanied by gradual replacement of abundant Fe-, Co-, Bi-, and Pb- tellurides by Hg-, Ag-, Au-Ag telluride and galena-fahlore with native gold assemblages. Decreasing amounts of pyrite, both colloform and pseudomorphic after pyrrhotite, isocubanite (ISS), and chalcopyrite in the chimneys is coupled with increasing amounts of sphalerite, quartz, barite or talc contents. This trend represents a transition from low to high sulfur conditions, and it is observed across a range of the Urals deposits from bimodal mafic- to bimodal felsic-hosted types: Yubileynoye → Yaman-Kasy → Molodezhnoye → Uzelga → Valentorskoye → Oktyabrskoye → Alexandrinskoye → Tash-Tau → Jusa. Ag-, Au-, Bi- tellurides are described in the rhyolite hosted chimneys from bimodal mafic sequences of Two Brothers seamount. Tellurobismutite has been found by our research in dacite hosted chimneys from bimodal mafic basement of Eastern Manus basin. In Pontides, chimneys contain rare inclusions of Ag-, Bi tellurides in association with native gold, galena and sulfosalts. This type can be considered as intermediate member in the range between bimodal mafic and bimodal felsic VMS deposits. Gold-barite-galena-tetrahedrite assemblages are typical of bimodal felsic and felsic series in Paleozoic (Rudniy Altay) and Cenozoic (Hokuroko, Okinawa) ensialic arc basins. In Hokuroko, the chimneys exhibit specific mineral and trace element zonation which is broadly comparable with those studied in modern black or gray smokers with exception lack of evidence for the former initial pyrrhotite, isocubanite and anhydrite. Several types of zoned chimneys are subdivided into three varieties by different outer wall composition: 1) sphalerite-galena-pyrite, 2) sphalerite-barite-galena and, 3) barite-hematite varieties. The inner walls of the chimneys are usually incrusted by drusy chalcopyrite or bornite, tennantite, galena which shows elongate dendritic or bladded growth features. The axial conduit zones of the chimneys are often filled with sphalerite, tennantite, galena and barite. Hokuroko chimneys show depletion in Fe-rich sulfides and elevation in barite, galena and fahlores in comparison with typical black smokers from MOR but they are very similar to black and gray smokers from the modern West Pacific, Paleozoic Uralian and Mesozoic Pontides ensimatic arc basins. The major differences are the lack of tellurides and sulphoarsenides and the predominance of fahlore-bornite-galena-electrum assemblage. This assemblage is typical of barite-rich chimneys from the Paleozoic Rudniy Altay ensialic arc. The laser-ablation ICPMS study has shown the systematic trace element distribution patterns across chimneys. In the outer wall, colloform and euhedral pyrite has elevated concentrations of Mn, Tl, Ni, Mo, Se and Te. Coarse-grained chalcopyrite layers in the central conduits are relatively low in most of trace elements with exception of Bi and Sn. Sphalerite is enriched in Au, Ag, As and Sb. In general, the grades of trace-elements in the Phanerozoic black smokers depend on composition of host suites: ultramafic – high Se, Sn, Co, Ni, Au, and U, mafic – high Co, Se and low Bi and Pb, bimodal mafic – high Te and Bi, Co, and moderate Se. The chimneys associated with bimodal felsic suites, like Hokuroko and Rudniy Altay, are characterized by elevated contents of As, Sb, Mo, Pb, Bi, Tl, Ag, W, and Hg and much lower grades of Co, Te, and Se.

The study has commonly shown systematic trace element distribution patterns across chimneys. Coarse-grained layers of chalcopyrite in the central conduits are relatively high in Se and Sn, but are low in other elements. Chalcopyrite at the margins of such layers is enriched in Bi, Co, Au, Ag, Pb, Mo, Te, and As which reside in microinclusions of tellurides and/or sulfoarsenides or sulphosalts galena and native gold. Sphalerite in the conduits and the outer chimney wall contains elevated Sb, As, Pb, Co, Mn, U, and V. Sb, As, and Pb reside in microinclusions of a galena-fahlore assemblage, whereas Co and Mn likely substitute for Zn^{2+} in the sphalerite structure. The highest concentrations of most trace elements are characteristic for colloform pyrite within the outer wall of the chimneys, and likely result from rapid precipitation in high temperature-gradient conditions. The trace element concentrations in the outer wall colloform pyrite decrease in the following order, from the outer wall inwards: Tl> Ag> Ni> Mn> Co> As> Mo> Pb> Ba> V> Te> Sb> U> Au> Se> Sn> Bi, governed by the strong temperature gradient. In contrast, pyrite in the high- to mid-temperature central conduits exhibits the concentration of Se, Sn, Bi, Te, and Au. The zone between the inner conduit and outer wall is characterised by recrystallization of colloform pyrite to euhedral pyrite, which becomes depleted in all trace elements except for Co, As, and Se. The iron hydrooxides covering outer wall of the chimneys have elevated contents of U, V, Ba, and Mn.

The mineralogical and trace element variations between chimneys are likely due to increasing fO_2 and decreasing temperature caused by mixing of hydrothermal fluids with cold oxygenated seawater. Average values of Se decrease in the order from black to gray and white smoker chimneys are in correlation with general increase of barite and sphalerite. The medium-temperature association (Te, Bi, Co, Mo, and Au) is typically present in the gray smoker chimneys. The Zn-rich chimneys are depleted in most elements except for Ag, Tl, Te, Sb and As, probably due to the dilution of the vent fluid by seawater which penetrates into deeper parts of the hydrothermal system. U and V are concentrated in the outer wall of most chimneys due to their extraction from seawater associated with the more reduced fluids of black and gray smokers.

The peculiarities in rare mineral assemblages and trace elements concentrations are consistent with a mineralogical type of the chimneys and also depend on general composition of host rocks. The hydrothermal chalcopyrite is the best subject for this research.

This study of trace element distribution in the chimneys has contributed to our understanding of the wide range of physico-chemical processes and conditions of seafloor sulfide mineralization. The trace element patterns described above are considered to result from temperature and redox gradients across the section of the chimneys, and the variation in temperature associated with black, gray and white smoker type chimneys.

The combination of data on chimneys from modern and ancient massive sulfide deposits allows to understand general peculiarities of trace elements changes in the range from ultramafic to basaltic and felsic sequences. In colloform pyrite, contents of As, Au, Sb, Tl, Pb, Bi, and Ni subsequently increase with growth of felsic volcanite amount. In euhedral pyrite, the contents of Co decrease, but the Ni and Se increase in the same range. In chimneys from felsic association, sphalerite has elevated contents of Hg, Ag, and lower contents of Co and Fe. In the same range, chalcopyrite loses Se and Co, Te with increase in Bi, Ag, As, Sb, and Pb. Maximum concentrations of Te, Bi, and Au have been detected in chalcopyrite of chimneys from ancient bimodal mafic sequences which occupy the middle part of the range. Nevertheless, the gold also displays concentration in chalcopyrite of chimney from ultramafic sequences and in sphalerite of chimney from felsic bimodal sequences. The high gold content is not typical of basalt hosted chimneys. However, in "mature" hydrothermal systems (TAG, Galapagos, Menez Gwen) gold can be occasionally found in concentration above 1–150 ppm. The gold is associated with barite- and bornite-rich chimneys similar to chimneys from felsic bimodal sequences. The influence either of composition of volcanic rocks, maturation of hydrothermal system or magmatic contribution of the trace element concentration is considered as a cause of trace elements concentrations.

The general trend encloses decreasing of Fe and Co and increasing of volatile elements such as Sb, As, Au, and Ag in the range of chimneys from ultramafic to felsic sequences. This is consistent with increasing of magmatic contribution in the hydrothermal system with increase in amount of felsic volcanic rocks. However, these data are not in contradiction with recycling seawater hydrothermal system in terms of increase in this "maturity" independently of primary composition of the host rocks. Some elements concentrations (Se and Te) are probably independent of composition of the host rocks, but reflect fluid oxidation state. The high concentration of Ni in pyrite of chimneys associated with felsic volcanic rocks depends on the fugacity of S_2 increase [Maslennikov, 2009].

Thus, the mineral and trace element patterns described herein are considered to result from temperature and redox gradients across the section of the chimney, and the variation in temperature associated with black, gray, and white smoker chimneys formed in different host rock environments. The grades of trace elements in chalcopyrite of the Phanerozoic vent chimneys depend on composition of host suites: ultramafic – high Se, Sn, Co, Ni, Au, and U, mafic – high Co, Se and low Bi, and Pb, bimodal mafic – high Te and Bi, Co, and moderate Se, bimodal felsic – high As, Sb, Mo, Pb, Bi, elevated Ag, W, and lower Co. In chalcopyrite of the chimneys studied, the contents of Ba, Bi, Pb, Ag, Sb, Mo, W versus Se and Co increase in the range from ultramafic and mafic to bimodal felsic series.

This research was supported by the Program of Presidium RAS no. 23 (project 09-П-5-1023 Urals Branch of RAS). The mineralogical research was supported by several collaborative projects with Natural History Museum (London) and Freiberg Academy, LA-ICPMS analyses were carried out during a visiting program (2006, 2009) funded by the ARC Centre of Excellence grant to CODES, University of Tasmania.

References

Butler, I.B., Nesbitt, R.W. Trace element distributions in the chalcopyrite wall of black smoker chimney: insights from laser ablation-inductively coupled plasma-mass spectrometry (LA–ICP–MS) // Earth and Planetary Science Letters, 1999. P. 335–345.

Danyushevsky, L.V., Robinson, P., Gilbert, S., Norman, M., Large, R., McGoldrick, P., Shelley, J.M.G. A technique for routine quantitative multi-element analysis of sulfide minerals by laser ablation ICP–MS // Geochemistry: Exploration, Environment, Analysis, 2010. Vol. 11. P. 5–60.

Danyushevsky, L., Robinson, P., McGoldrick, P., Large R., and Gilbert S. LA–ICP MS of sulfides: Evaluation of an XRF glass disc standard for analysis of different sulfide matrixes. Goldschmidt Conference, Japan // Geochimica et Cosmochimica Acta, 2003. Vol. 67 (18), A73 Suppl.

Maslennikov, V.V., Maslennikova, S.P., Large, R.R., Danyushevsky, L.V., Herrington, R.J., Stanley, C.J. Tellurium-bearing minerals in zoned sulfide chimneys from Cu-Zn massive sulfide deposits of the Urals, Russia // Mineralogy and Petrology, Special Issue: Ore deposits of the Urals, 2013. Vol. 107 (1). P. 67–99.

Maslennikov, V.V., Maslennikova, S.P., Large, R. R., Danyushevsky, L.V. Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanic-hosted massive sulfide deposit (Southern Urals, Russia) using LA–ICP MS // Economic Geology., 2009. Vol. 104 (8). P. 1111–1141.

Norman, M.D., Griffin, W.L., Prearson, N.J., Garcia, M.O., O'Reilly, S.Y. Quantitative analysis of trace element abundances in glasses and minerals: a comparison of laser ablation inductively coupled plasma mass spectrometry, solution inductively coupled plasma mass spectrometry, proton microprobe and electron microprobe data // Journal of Analytical Atomic Spectrometry, 1998. Vol. 13. P. 477–483.

I.Yu Melekestseva[1], V.V. Maslennikov[1], S.P. Maslennikova[1], R.R. Large[2], L.V. Danyushevsky[2]

[1] Institute of mineralogy UB RAS, Miass, Russia, melekestseva-irina@yandex.ru

[2] CODES ARC Centre of Excellence in Ore Deposits, University of Tasmania, Hobart, Australia

TRACE ELEMENTS IN SULFIDES FROM THE SEMENOV HYDROTHERMAL CLUSTER, 13°30?N, MID-ATLANTIC RIDGE: LA-ICP-MS DATA

Установлен типохимизм сульфидов гидротермального узла Семенов (13?30′ с.ш., САХ). Ранние генерации пирита обогащены большинством элементов-примесей (в том числе, золотом) относительно поздних, что свидетельствует об истощении последних порций растворов микроэлементами. Дисульфиды железа, отлагавшиеся на поверхности морского дна, обогащены элементами-примесями по сравнению с метасоматическим пиритом, что говорит о более эффективной экстракции элементов-примесей в момент смешения гидротермального раствора с морской водой. Главным концентратором невидимого золота в Cu-Zn рудах поля Семенов-2 является ковеллин.

It is well known that ores from the continental massive sulfide deposits contain a series of economically important trace metals, including Au and Ag. Because of the future potential of the modern massive sulfide fields, it is necessary to understand the distribution of trace elements in sulfides. In this work, we examine the trace element composition of sulfide minerals from the Semenov hydrothermal cluster (13?31?N, MAR) using a LA-ICP-MS analysis, which became an effective instrument of mineral investigations during the recent years.

The Semenov hydrothermal cluster was discovered in 2007 by Russian R/V *Professor Logatchev* by Polar Marine Geosurvey Expedition and VNIIOkeangeologiya (St-Petersburg) [Beltenev et al., 2007]. It is situated in the western slope of the rift valley at the depths of 2400–2950 m on a seamount 10 km long and 4.5 km wide. The seamount is composed of basalts, gabbro, ultramafic rocks, and plagiogranites [Ivanov et al., 2008]. The hydrothermal cluster consists of five hydrothermal fields. Our study is based on the samples from the Semenov-1, -3, -2 and -4 fields directly obtained on board of the research vessel in 2007.

The massive sulfides from the Semenov-1 (13°30.87?N, st. 186 and 292) and Semenov-4 (13°30.24?N, st. 145) fields are the products of low-temperature (<250 °C) diffuse venting on the flanks of sulfide mounds and are characterized by fine-crystalline, nodule-like, porous, colloform, zonal, framboidal, and coarse-grained structures. Barite, pyrite, marcasite are major minerals, sphalerite, quartz and hematite are less abundant, and galena, chalcopyrite, pyrrhotite are minor. The fine-grained, porous, and massive sulfides from the Semenov-2 field (13°31.13?N, st. 287) are resulted from the high-temperature (>300 °C) venting inside the sulfide mound. Isocubanite, chalcopyrite, wurtzite, and opal are major minerals; sphalerite, marcasite, pyrite, covellite, and barite are widespread; and galena, pyrrhotite, native gold, and silver telluride are occasional. The clastic sulfides from the Semenov-3 field (13°30.70?N, st. 294) are composed of major marcasite, pyrite, barite, quartz, abundant chalcopyrite and hematite, and accessory sphalerite, pyrrhotite, bornite, covellite, jarosite. The stringer-disseminated massive sulfides in strongly altered basalts with major quartz and pyrite,