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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,

widespread hematite, and occasional sphalerite, chalcopyrite, pyrrhotite were dredged from the Semenov-4 field (13°30.24'N, st. 153).

LA-ICP-MS data demonstrate that sulfides from different hydrothermal fields or different generations in the same station accumulate various trace elements.

Semenov-1 field. The early disulfides are high in concentrations of most trace elements in contrast to the late disulfides. The fine-grained pyrite-1 from st. 186 is enriched in most elements and is depleted in Ti, Hg and Tl relative to the crystalline pyrite-2. The early iron disulfides from st. 292 are also enriched in trace elements: framboidal pyrite-1 is enriched in Ti, V, Mn, As, Mo, Sb, Au, Hg and Tl relative to pyrite-2 and in most elements, except for Pb, relative to pyrite-3. In turn, pyrite-2 is enriched in Co, Cu, Cd, Sn, W, Pb and U relative to framboidal pyrite and in most elements, except for Mn, Au, Hg and Tl, relative to pyrite-3. The latter is depleted in most elements relative to framboidal pyrite and pyrite-2. Marcasite is depleted in most elements, except for Mn, Hg and Pb relative to pyrite-2 and for Mn, Au, Hg and Tl relative to pyrite-3. All varieties of iron disulfides from st. 292, except for the late pyrite, are enriched in trace elements compared to those from st. 186.

Semenov-2 field. Sphalerite contains the higher amounts of Mn, Co, Se, and Cd, moderate contents of Ga, Sn, and Te, and minor to trace amounts of Ni, As, Mo, Ag, In, Sb, Tl, Pb, and Bi. Chalcopyrite is enriched in Co, As, Se, and Ag and has moderate amounts of Ni, Mo, Cd, Sn, Sb, Te, and Tl, and minor to trace contents of Mn, Ga, In, Pb and Bi. Isocubanite is characterized by negligible amounts of Ni, Ga, As, Mo, In, Sb, Tl, Pb, and Bi, moderate contents of Mn, Cd, Sn, and Te, and elevated contents of Co, Se, and Ag. In comparison to chalcopyrite, isocubanite is depleted in trace elements.

LA-ICP-MS analysis has shown that covellite developed after sphalerite and chalcopyrite is distinct in amount of trace elements similarly to Au contents. In the first case, covellite is strongly enriched in most trace elements relative to sphalerite, both in “high-temperature” (Se, Mo, Sn, Te, Au, Bi) and “low-temperature” (As, Ag, Sb, Tl, Pb) elements. Some elements (Ga, Ni, In) show no significant variations or are lower than in sphalerite (Mn, Co, Cd), being removed during the replacement. This covellite is also strongly enriched in all trace elements relative to chalcopyrite, which replaces chalcopyrite.

Covellite developed after chalcopyrite has lower contents of most trace elements in comparison to chalcopyrite but is enriched in Au and “low-temperature” elements (Ag, Cd, Sb, Pb) relative to chalcopyrite. No considerable variations are observed for Mn, Ga, Se, In, Sn, and Te and contents of Co, Ni, As, Mo, and Tl are lower in covellite relative to chalcopyrite.

Semenov-3 field. The pyrite-1 and pyrite-2 from the clasts in sulfide breccia are also enriched in most trace elements (excluding Ti, Co, Ni, As and Se) in comparison to pyrite-3. In contrast, pyrite-4 contains the higher amounts of most elements, excluding Co, Au and Hg, compared to pyrite-1 and -2 and Co, As and Se compared to pyrite-3. Similarly to the Semenov-1 field, marcasite is depleted in most elements (except for Ti, V, Cr, Mn, Mo, Sb, Tl and U) in comparison to the clastic pyrite-1 and -2 and is enriched in most elements relative to pyrite-3. The newly formed pyrite-4, in its turn, is enriched in most elements in comparison to the earlier marcasite and has the highest Cu and Zn contents in comparison to other varieties of iron disulfides.

Semenov-4 field. The tendencies of trace element enrichment or depletion in iron disulfides of the Semenov-4 field are generally very similar to those from Semenov-1 and -3 fields with some exceptions. The pyrite-1 from st. 286 is high in most trace elements except for the “high-temperature” Co, Cu and Se in comparison to pyrite-2. Marcasite is enriched in trace elements compared to both pyrites, excluding Co, Zn, As, Se and U for pyrite-1 and Co and Se for pyrite-2. The massive crystalline pyrite from st. 145 is enriched in V, Cu, Mo, Sn, Hg and Tl in comparison to pyrite-1 from st. 286 and is depleted only in Co, Cu and Se relative to pyrite-2. The veined crystalline pyrite from st. 153 is depleted in all trace elements relative to massive crystalline pyrite from st. 145 and pyrite-1 and -2 from st. 286. Slightly elevated average Co and Sn contents in pyrite from st. 153 relative to pyrite from st. 145 and Sn and Ti contents relative to pyrite from st. 286 are insufficient and fall into dispersion.

Conclusions. The same generations of pyrite from the different fields, which are formed under similar formation conditions, are similar in enrichment in most trace elements relative to late pyrite. This points to the input of most trace elements from the primary hydrothermal fluid. The late crystalline pyrite was crystallized from the fluid depleted in most trace elements. The crystalline py-

rite, which deposited from the new fluid portions closely to chalcopyrite and sphalerite, are enriched in Cu and Zn. The iron disulfides, which were formed on the seafloor, are strongly enriched in trace elements relative to the subseafloor crystalline pyrite that most likely is related to the effective accumulation of trace elements, when the high-temperature hydrothermal fluid meets the cold seawater. Gold is concentrated in the early generations of pyrite and marcasite.

The main carrier of the invisible gold in the Semenov-2 massive sulfides is covellite in contrast to traditional pyrite, chalcopyrite, bornite or isocubanite [e.g., Bortnikov et al., 2000]. Covellite from the Semenov-2 massive sulfides contains 22.51–226.64 ppm Au that is much higher than Au content in sphalerite (0.00–0.01 ppm), chalcopyrite (0.11–0.22 ppm), and isocubanite (0.03–0.06 ppm). Covellite, which replaces sphalerite, is characterized by the higher Au contents. We suggest that gold in covellite is chemically bound because each of 11 analyses has stable gold content and Au and Cu contents in covellite directly depend on each other.

Similarly to Au, all identified elements have more or less stable contents in all analyses that does not favor microinclusions of minerals. However, direct correlation between Bi and Te may probably indicate presence of microinclusions of Bi-telluride. The source of most trace elements in covellite, which replace sphalerite, is problematic and the mechanism of their incorporation is still unclear. Some of trace elements (Mn, Co, Ga, Cd) were inherited from the replaced sphalerite and were removed during the replacement. In case of covellite, which is developed after chalcopyrite, most trace elements (Mn, Co, Ni, Ga, As, Se, Mo, In, Sn, Te, Tl, and Bi) derive from the host chalcopyrite.

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THE ALDAN-MAADYR ZONE, WESTERN TUVA, RUSSIA: FORMATION CONDITIONS OF GOLD-QUARTZ VEINS IN LISTVENITES, CONGLOMERATES, AND BERESITES

Установлено три стадии образования золото-кварцевых жил на месторождениях Алдан-Маадырской зоны в Западной Туве: высоко-, средне- и низкотемпературная (>350 °C, 270–180 °C и <180 °C). Отмечается понижение пробности золота от высоко- к низкотемпературной стадии. На основании близкого изотопного состава кислорода в кварце исследованных месторождений и валового состава флюидных включений сделан вывод о единой гидротермальной системе, образовавшей месторождения в лиственитах, конгломератах и березитах.

The gold-quartz deposits of the Aldan-Maadyr zone in the Western Tuva are worthy of interest because they are located in the common geological structure but are hosted in different kinds of rocks (listvenites, conglomerates, and beresites). Their formation is considered to be related to the Devonian granitic magmatism [Zaykov et al., 1981]. The aim of the present work was an identification of