Short communication

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
www.limnolfwbiol.com

Hg minerals formed in the dispersion halos of mining waste (Western Siberia)

Myagkaya I.N.*, Gustaytis M.A.

V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Koptyug Avenue, 3, 630090, Russia

ABSTRACT. The article presents the specialties of Hg minerals formed in natural organic matter from the dispersion halos of tailings and in suspended particulate matters of snowmelt and river waters in the dispersion halos of mining waste. The results were obtained due to studying of mining wastes from Novo-Ursk and Aktash deposits of the Kuznetsk-Altai mercury belt. The formation of secondary Hg minerals of similar shape and size (sulfides and selenides; ternary and quaternary chalcohalides, presumably) were found in both objects. Minerals appear as complex thin intergrowths and that currently do difficult certain identification of them compositions.

Keywords: mercury belt, hypergenesis zone, mining waste, mercury, secondary minerals

1. Introduction

Knowledge about the occurrence forms (speciation or species) of potentially toxic elements (including Hg) in the environmental components is the key of understanding the special aspects of their migration and accumulation, as well as bioavailability under surface conditions, supposed the relevance of such studies. Information about the mineral species of elements is the basis confirming theoretical concepts about element's behaviour in the environment. Authigenic (secondary) minerals, i.e. those formed *in situ* due to precipitation at the water-rock interface (Novikov, 2020) provide data on the biochemical processes and geochemical conditions in the environmental components and are also used for paleoreconstructions (Glenn and Filippelli, 2007). Furthermore, authigenic minerals control the migration and toxicity of elements under hypergene conditions (e.g. in soils) (Smieja-Król et al., 2022). Usually the secondary minerals are found as the thin complex aggregated phases in the heterogeneous environments (soils, suspended particulate matters or bottom sediments). Research of these minerals is laborious and can be technically complicated due to the characteristics of the substance and phases themselves. Nevertheless, this research is increasing in scope and relevance (Smieja-Król et al., 2022). In Western Siberia, there is a natural source of Hg in the form of mercury zones are combined in the Kuznetsk-Altai mercury belt that is part of the Altai-Sayan mercury province (Obolensky et al., 1995). The study's aim is to identify the specialties of secondary Hg minerals in environmental components from the halo of tailings and mining wastes within the mercury belt.

2. Materials and methods

2.1 Study object

Studies were carried out on the example of two objects of the Kuznetsk-Altai mercury belt (Salair and Kurai mercury zones) (Obolensky et al., 1995). The first object is located within the Ursk plutonic and volcanic structure of the Salair Ridge (Kemerovo Region, Ursk settlement) in the area of the Novo-Ursk massive sulfide ore deposit. For the study, we used natural organic matter (NOM) from the tailings dispersion halo (Lazareva et al., 2019), which had been in contact ~ 100 years with Hg-containing drainage waters and mining wastes (Myagkaya et al., 2022a). This led to the formation of some secondary minerals, including Hg-containing ones (Myagkaya et al., 2020).

The second object is located within the Anuya-Chuya forearc trough and the junction of the Kadrin and Kurai branches of the Kurai deep fault in the Kurai mercury zone in the halo of the epithermal Aktash mercury deposit (Altai Mountains, Aktash settlement). The deposit mined by Aktash Mining and Metallurgical Enterprise (AMME) is situated on the bank of the Yarly-Amry River that flows into the Chibitka River (Gustaitis and Myagkaya, 2022; Myagkaya et al., 2022b). For the 2019 study, the following samples were taken: (i) snow suspended matter near AMME and along the Yarly-Amry valley; (ii) suspended matter from temporary

*Corresponding author.
E-mail address: i_myagkaya@igm.nsc.ru (I.N. Myagkaya)

Received: June 10, 2022; ***Accepted:*** June 21, 2022;
Available online: July 31, 2022

watercourses that are formed near mines when snow melts and (iii) suspended matter from the Yarly-Amry River near the AMME dispersion halo (1.4 km distance from AMME).

2.2 Methods

The composition and micromorphology of the tested substances from both objects were examined using a *MIRA 3 LMU* scanning electron microscope (Tescan Orsay Holding) with Aztec Energy/INCA Energy 450+ XMax 80 and INCA Wave 500 (Oxford Instruments Nanoanalysis Ltd) microanalysis systems that allow studying nanosized particles.

3. Results and discussion

There were several varieties of mercury minerals (Fig. 1A, B) in the NOM from the dispersion halo of the tailings dump in the Novo-Ursk deposit. The bulk of them was characterised by the formation of complex aggregates consisting of separate fine-grained individuals (from 100 nm to 1 μm). Their composition includes the Fe, Zn, Cu, Ag, As, S, Se, I, Br, and Cl admixtures in different proportions. As previously shown (Myagkaya et al., 2020), Zn sulfides (sphalerite group) form thin intergrowths with Hg sulfides (presumably metacinnabarite) with different amounts of Ag, Zn, Cu, Se, I, Cl, and Br. There were also Hg selenides (timannite), Ag iodides (iodargyrite) and Au^0.

Mercury and Hg-containing minerals in the ores of Siberian deposits are represented by native metals and intermetallics, arsenides and antimonides, halide compounds, sulfides, selenides, seleno- and sulfosalts, oxides, sulfates, and arsenates. The halide, oxyhalide, oxide and sulfate compounds of Hg are rare among the secondary minerals of the oxidation zones of the mercury deposits. The composition of sulfohalides is not constant and depends on the number and type of halide atoms in their crystal structure (Magarill et al., 2007; 2008). The sulfohalide varieties are closely coexistent with each other, with cinnabarite and metacinnabarite (Podgornykh and Vishnevsky, 2020).

We specified the composition of complex Hg sulfides in NOM, which contained Ag, Se, I, Cl, and Br admixtures, using triple diagrams (Hg – S+Se – Hal and Hg – Se – S systems, where Hal = the sum of I, Cl and Br) according to the data of possible Hg minerals in the oxidation zone (Fig. 2) (Magarill et al., 2007; 2008). Among the chalcohalides, there are ternary halides with the general formula $Hg_3(S,Se)_2Hal_2$ where *Hal = I, Br* and *C* that form a group of polymorphic compounds (grechishchevite, lavrentievite, arzakite, kenshuaite, and radkeite) and quaternary ones with the general formula *AgHgS(Hal)*, which also form the group of polymorphic compounds (perroudite, capgaronnite and iltisite) (mindat.org; webmineral.com; Magarill et al., 2007). Based on the Hg – S+Se – Hal and Hg – Se – S systems (Fig. 2), in the NOM samples show that the formation of Ag-Hg sulfohalides is possible

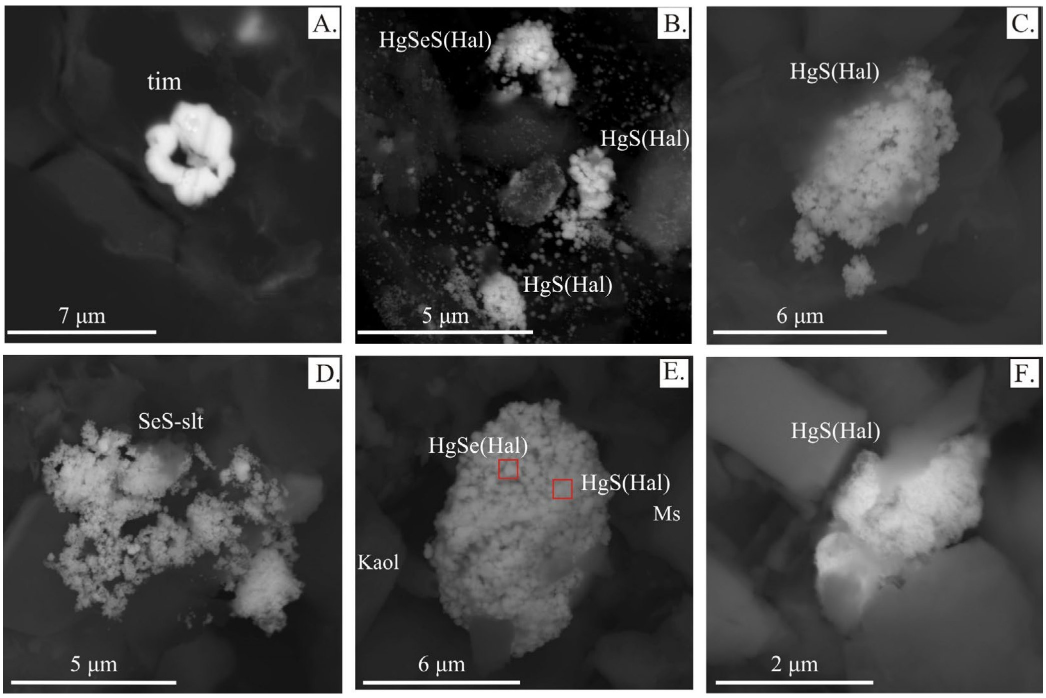

Fig.1. SEM images (BSE) of secondary Hg minerals in NOM from the dispersion halo of the Ursk tailings dump (A and B), in the snow suspended matter near AMME (C and D), in the suspended matter of temporary fluxes formed during snowmelt near the AMME mines (E), and in the suspended matter of the Yarly-Amry River sampled at a 1.4 km distance from AMME (F): A – cross section of the timmanite tube (tim); B – accumulation of globular and nodular Hg sulfide particles with Cu, Ag, I, and Cl (HgS(Hal)) in contact with Se-containing phases (HgSeS(Hal)); C – nodular aggregation of Hg sulfides containing Se, I and Cl admixtures; D – flocculated segregations of I-containing Hg seleno- and sulfosalts in muscovite; E – aggregations of Hg sulfide and selenide particles with Ni, Cu and Br admixtures; F – fine-grained aggregations of Hg sulfides with Ni, Cu and I admixtures.

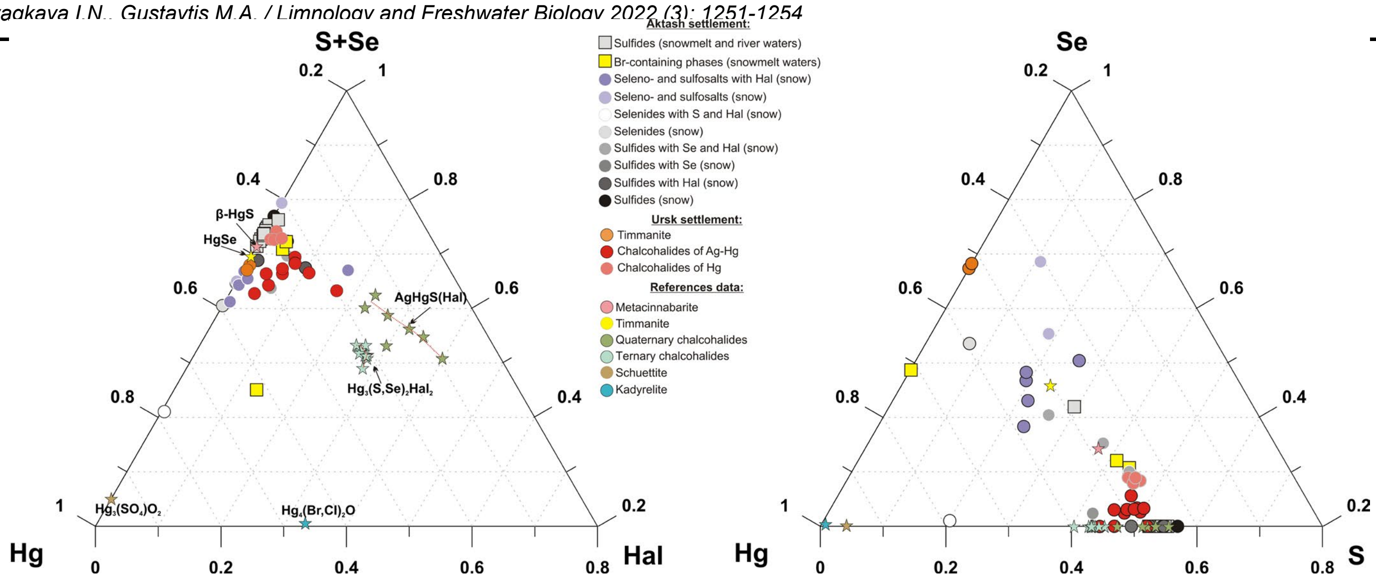

Fig.2. Triple diagram (Hg – S + Se – Hal and Hg – Se – S systems, where Hal = the sum of I, Br and Cl) of the composition of Hg minerals (atomic ratios) in the studied samples of the Salair (Ursk settlement) and Kurai (Aktash settlement) mercury zones according to reference data (stars mark the electronic mineralogical sources mindat.org and webmineral.com): Kadyrelite ($Hg_4(Br,Cl)_2O$); Schuettite ($Hg_3(SO_4)O_2$); Ternary chalcohalides with the general formula of $Hg_3(S,Se)_2Hal_2$ where Hal = I, Br and Cl; Quaternary chalcohalides with the general formula of AgHgS(Hal); Timmanite (HgSe), and Metacinnabarite (β-HgS).

and their composition are similar to perroudite ($Hg_5Ag_4S_5(I,Br)_2Cl_2$) common in oxidation zones (Hunt et al., 2016). There are also mercury phases without Ag and with a small Se content, which can be assigned to seleno- and sulfosalts (Fig. 2). However, it is rather difficult to make an accurate identification taking into account the size of the phases. Timmanite (HgSe) and metacinnabarite (β-HgS), having a miscibility gap between each other (Vasil'ev, 2011), are also identified among secondary mercury phases.

In the suspended matter of snowmelt and river waters near AMME, among secondary Hg minerals, there were Hg-containing phases (Fig. 1C-F) similar in shape and size to the minerals observed in NOM of the dispersion halo of the Novo-Ursk deposit (Fig. 1B). Comparison of the compositions of authigenic minerals in the area of the Kurai mercury zone (without Ag) with the compositions of the known phases (Fig. 2) suggests the presence of several varieties that form thin intergrowths: sulfides, selenides and compounds close to seleno- and sulfosalts in composition (ternary chalcohalides). Notably, secondary Hg minerals as considered are seasonal, i.e. appearing and disappearing periodically depending on the change in climatic and atmospheric conditions (Obolensky et al., 1995).

4. Conclusions

In summary, the presence of the Hg authigenic minerals (sulfides and selenides; ternary and quaternary chalcohalides) as complex thin intergrowths with a wide range of composition variations were found in both study objects. Among the seleno- and sulfosalts, those containing I and Cl predominate as well as Br to a lesser extent. Further research will be aimed at identifying the processes that promote the formation of these minerals and, in turn, control the Hg migration under surface conditions.

Acknowledgements

The authors are grateful to their colleagues: I.S. Kirichenko, PhD E.V. Lazareva (Geology and Mineralogy), V.I. Malov, and B.Yu. Saryg-ool.

This study was partly carried out within the framework of the IGM SB RAS State Project at the Analytical Centre for multi-elemental and isotope research of IGM SB RAS. The study of the composition of Hg phases for the substance from the dispersion halo of AMME was supported by the Russian Science Foundation (No. 18-77-10056).

Conflict of interest

The authors declare no conflict of interests.

References

Electronic mineralogical reference book. Accessed on 1 May 2022. URL: mindat.org

Electronic mineralogical reference book. Accessed on 1 May 2022. URL: webmineral.com

Glenn C.R., Filippelli G.M. 2007. Authigenic mineral formation in the marine environment: pathways, processes and products. Deep-Sea Research Part II. 11(54): 1141-1146. DOI: 10.1016/j.dsr2.2007.05.001

Gustaitis M.A., Myagkaya I.N. 2022. Features of the distribution of mercury in the hair of residents of the Aktash settlement (Altai Republic). Pochvy i Okruzhayuschaya Sreda [Soils and the Environment] 5(1): e165. DOI: 10.31251/pos.v5i1.165 (in Russian)

Hunt J., Lottermoser B.G., Parbhakar-Fox A. et al. 2016. Precious metals in gossanous waste rocks from the Iberian Pyrite Belt. Minerals Engineering 87: 45-53. DOI: 10.1016/j.mineng.2015.12.002

Lazareva E.V., Myagkaya I.N., Kirichenko I.S. et al. 2019. Interaction of natural organic matter with acid mine drainage: in-situ accumulation of elements. Science of the Total Environment 660: 468-483. DOI: 10.1016/j.scitotenv.2018.12.467

Magarill S.A., Pervukhina N.V., Borisov S.V. et al. 2007. Crystal chemistry and features of the structure formation of mercury oxo- and chalcohalides. Russian Chemical Reviews 76(2): 115-146. DOI: 10.1002/chin.200729196

Magarill S.A., Borisov S.V., Pervukhina N.V. et al. 2008. Characteristics of structure formation of rare mercury minerals and the role of crystal chemical analysis in studying the migration of heavy metals in natural and technogenic environments. In: Biodiversity, Environmental Problems of Gorny Altai and Adjacent Regions: Present, Past, Future, pp. 89-94. (in Russian)

Myagkaya I.N., Lazareva E.V., Zhmodik S.M. et al. 2020. Interaction of natural organic matter with acid mine drainage: authigenic mineralization (case study of Ursk sulfide tailings, Kemerovo region, Russia). Journal of Geochemical Exploration 211: 106456. DOI: 10.1016/j.gexplo.2019.106456

Myagkaya I.N., Gustaytis M.A., Saryg-ool B.Y. et al. 2022a. Mercury partitioning and behavior in streams and source areas affected by the Novo-Ursk gold sulfide tailings (West Siberia, Russia). Mine Water and the Environment 41(2): 1-21. DOI: 10.1007/s10230-022-00859-6

Myagkaya I.N., Saryg-ool B.Yu., Kirichenko I.S. et al. 2022b. Ecogeochemical assessment of the Yarly-Amry and Chibitka rivers located in the halo of the Aktash mercury deposit and its dumps (Gorny Altai). Izvestiya Tomskogo Politekhnicheskogo Universiteta [Bulletin of the Tomsk Polytechnic University, Geo Assets Engineering] 333(4): 7-26. DOI: 10.18799/24131830/2022/4/3273 (in Russian)

Novikov D.A. 2020. Hydrogeochemistry of authigenic mineral formation in Upper Jurassic sediments (the Nadym-Taz interfluve area, Arctic regions of Western Siberia). Applied Geochemistry 122: 104704. DOI: 10.1016/j.apgeochem.2020.104704

Obolensky A.A., Ozerova N.A., Vasiliev V.I. 1995. Natural sources of mercury in Siberia. Khimiya v Interesakh Ustoychivogo Razvitiya [Chemistry for Sustainable Development] 3(1-2): 11-22. (in Russian)

Podgornykh N.M., Vishnevsky A.V. 2020. «Ozaryonny Merkuriyem» Pamyati Vladimira Ivanovicha Vasilieva. [“Illuminated by Mercury” In memory of Vladimir Ivanovich Vasiliev]. V mire mineralov. Mineralogicheskiy almanakh [In the world of minerals. Mineralogical almanac] 25(2): 74-79. (in Russian)

Smieja-Król B., Pawlyta M., Gałka M. 2022. Ultrafine multi-metal (Zn, Cd, Pb) sulfide aggregates formation in periodically water-logged organic soil. Science of The Total Environment 820: 153308. DOI: 10.1016/j.scitotenv.2022.153308

Vasil’ev V.I. 2011. New data on the composition of metacinnabar and Hg-sphalerite with an isomorphous Cd admixture. Russian Geology and Geophysics 52(7): 701-708. DOI: 10.1016/j.rgg.2011.06.002