

ues range between -14.63 and -11.97 while $\log f\text{Te}_2$ values fluctuate between -13.70 and -11.04 . At temperatures as high as $400\text{ }^\circ\text{C}$ an increase in $f\text{S}_2$ (between -7.85 and -5.00) and an increase in Te_2 fugacity (between -7.17 and -4.31) is required.

The bismuth telluride inclusions trapped within bismuthinite may have formed in equilibrium with the Bi-sulfide. It is also possible that bismuthinite was the first mineral to crystallize followed by the bismuth telluride inclusions formation that may have been triggered by a slight S_2 fugacity decrease or even more likely by a Te_2 fugacity increase, possibly as a result of tellurium-rich magmatic vapor plumes.

The above data indicate that the stability fields for both mineral assemblages at a given temperature are rather similar, specially the $\log f\text{S}_2$ values. The main difference between the NW area and SE area may not be a change in S_2 and Te_2 fugacity but a function of Pb and Cu concentration in the hydrothermal fluid. This hypothesis is consistent with the fact that galena was only found in the NW area along with cosalite but only minor chalcopyrite. On the other hand, chalcopyrite is abundant in the SE area while cosalite is rarely found and galena is absent.

It is necessary to conduct a detailed fluid inclusion study in order to constrain the temperature of formation and consequently improve the thermodynamic model. By the end of this project we hope to include all other minerals in order to make a detailed thermodynamic modeling for San Francisco de los Andes ore deposit.

References

- Afifi A.M., Kelly, W.C., Essene E.J.* Phase relations among tellurides, sulphides and oxides: I. Thermochemical data and calculated equilibria; II. Applications to telluride-bearing ore deposits // *Economic Geology*. 1988. Vol. 83. P. 377–404.
- Barton, P., Skinner, B.* Sulfide mineral stabilities // In: Barnes, H.L. (Eds.), *Geochemistry of Hydrothermal Ore Deposits*. New York, 1967. P. 236–333.
- Barton, P., Skinner, B.* Sulfide mineral stabilities // In: H.L. Barnes (Eds.), *Geochemistry of Hydrothermal Ore Deposits*. New York, John Wiley, 1979. P. 278–403.
- Cardo, R., Segal S., Korzeniewski, L., Palacio, M., Chernicoff, C.* Estudio metalogenetico de brechas hidrotermales portadoras de mineralizacion de Bi-Au-Cu en el ambito de la Cordillera Frontal, Provincia de San Juan // *Serie de Contribuciones Tecnicas, Recursos Minerales N 31. SEGEMAR*, 2008. P. 3–28 [in Spanish].
- Craig, J., Barton, P.* Thermochemical approximations for sulfosalts // *Economic Geology*, 1973. P. 493–506.
- Frikken, P.H., Cooke, D.R., Walshe, J. L., Archibald, D., Skarmeta, J., Serrano, L. and Vargas, R.* Mineralogical and Isotopic Zonation in the Sur-Sur Tourmaline Breccia, Rio Blanco-Los Bronces Cu-Mo Deposit, Chile: Implications for Ore Genesis // *Economic Geology*, 2005. Vol. 100. № 5. P. 935–961.
- Garrals, R.M., Christ, C.L.* Solutions, minerals, and equilibria. San Francisco. CA: Freeman, Cooper. New York, 1965. 450 p.
- Krauskopf, K. B., Bird D.K.* Introduction to geochemistry. 3rd edi. McGraw-Hill, New York, 1995. 647 p.
- Llambias, E., Malvicini, L.* The Geology and Genesis of the Bi-Cu Mineralized Breccia-Pipe, San Francisco de los Andes, San Juan, Argentina // *Economic Geology*, 1969. Vol. 64. P. 271–286.
- Robie, R.A., Waldbaum D.R.* Thermodynamic properties of minerals and related substances at 298.15 K (25.0 C) and one atmosphere (1.013 bars) pressure and at higher temperatures // US Government Printing Office, 1968. 256 p.

G.A. Tret'yakov

Institute of Mineralogy UB RAS, Miass, Russia, genatret@yandex.ru

EXTRACTION OF METALS FROM THE SEDIMENT BY THE HEATED SEAWATER: A PHYSICAL-CHEMICAL MODELING

Выполнено физико-химическое моделирование взаимодействия нагретой морской воды, осадка впадины Гуаймас и океанического габбро при соотношениях порода–морская вода (R/SW) от $1 \cdot 10^{-5}$ до 10. Установлено, что максимальная экстракция железа из габбро происходит при минимальном рН и соотношении R/SW=0.007, а меди и никеля при 0.03. Кондуктивное

охлаждение раствора, отделившегося от габбро (R/SW=0.03), в зоне разгрузки приводит к осаждению руд, богатых халькопиритом, а прореагировавшего с осадком – пирротинном. При R/SW=0.007 в осадочной системе отлагается пирит в этих условиях.

The physical-chemical and experimental modeling of the sediment-related hydrothermal systems is dedicated to the various problems of interaction of the heated seawater and organic-rich sediments. The interest to such studies is caused by discovery of the hot vents located on the sediment-covered ridges like Guayamas basin, Escanaba and Okinawa troughs or Middle Valley in Juan de Fuca ridge [Gieskes et al., 1988; Koski et al., 1988; et al.]. The massive sulfides from these systems are characterized by abundant pyrrhotite and hydrothermal vents contain oil distillates. However, the former works give the contradictory data on the extractive ability of the fluid and the metal source for the sediment-hosted sulfide edifices. Some researchers consider that metals were extracted from the sediments [Thornton and Seyfried, 1987; Seewald et al., 1990; Cruse, Seewald, 2001] in contrast to the metal extraction from the underlying basalts [Goodfellow and Franklin, 1993, Butterfield et al., 1994].

In order to estimate the extraction ability of the sediments, we model the interaction between the heated seawater, bottom diatomaceous sediments from the Guaymas basin in the Gulf of California, and oceanic gabbro, which average composition (n 250) was taken from the PetDB (<http://www.petdb.org>). The modeling was implemented in the Selector computer program and was based on a multisystem formed and debugged previously [Tret'yakov and Melekestseva, 2008]. The primary composition of sediment was taken from [Thornton and Seyfried, 1987, p. 1998, table 1] and seawater, from [Encyclopedia..., 2008].

Preliminary, Ba, Sr, and Cr contents in the composition of sediment were recalculated into oxides, Fe₂O₃ was converted to FeO (because the sediment is reduced), an organic carbon and a part of H₂O were recalculated into fulvic acid (C₁₃₅H₁₈₂O₉₅N₅S₂), O, N, and S were added in accordance to the formula, and contents of all elements were reduced to 1 kg. First, the gabbro-seawater interaction was modeled for the various rock-seawater (R/SW) ratios in order to reveal the maximum of extraction of Ba, Co, Cu, Fe, Ni, Pb, Si, and Zn (Fig. 1). Further, the mineral precipitation from the fluid was modeled at a temperature decrease based on the subsequent reactor method for the R/SW ratios of 0.007 and 0.03 (Fig. 2). The parameters of temperature and pressure for calculations were based on P-T-conditions of the hydrothermal systems from the Guaymas basin and Mid-Atlantic Ridge. Seawater reacted with gabbro or sediment at 350 °C and 250 bars and then the equilibriums were calculated with a step of 20 °C at decreasing temperature. The solution was separated from the solid phases at each step and moved into the following reservoir that corresponds to the conductive cooling of the fluid and mineral precipitation and imitates, with some assumptions, the growth of the sulfide mound on the sea floor.

It was found that R/SW interaction at 350 °C and 250 bars leads to the onset of mineral assemblages, which are similar to those from natural hydrothermally altered rocks. At low R/SW ratios (≤ 0.0001) under oxidized conditions, the solid phases include hematite, anhydrite, chlorite, chrysotile, and brucite in contrast to quartz, talc, montmorillonite, seladonite, amesite, pyrrhotite, cubanite, millerite, pyrite, and jaipurite under reduced conditions and R/SW ratio of >0.0001 . Additionally, minerals typical of the altered sediments in the hydrothermal fields (clinoamphibole, actinolite, albite, illite, sphalerite, and galena) are formed at R/SW of ≥ 0.06 .

It was established that cooling of the solutions produces the ore mineral assemblages. No mineral precipitation occurs at the gabbro/seawater ratio of 0.007 (maximum of Fe extraction from the seawater) in the high-temperature area (>250 °C, Fig. 2c). The quartz + pyrite + chalcopyrite + fahlore assemblage is deposited at temperature of <250 °C and chalcocite and barite, at temperature of <100 °C. In the sediment, pyrite and a few amount of vaesite precipitate at the same ratio and temperature of <250 °C (Fig. 2a) admixed by quartz, covellite, cattierite, barite, galena, and sphalerite at decreasing temperature. The greater diversity of minerals is observed at R/SW ratio of 0.03. At high temperature, gabbro contains chalcopyrite and small amount of minerals of the linnaeite-polydymite group; the decrease in temperature leads to the formation of major quartz and pyrite and occasional greenockite, vaesite, and chalcopyrite. Sphalerite, galena, and barite appear at low temperatures. Pyrrhotite is the major mineral of the sediment at high temperature and minerals of the linnaeite-polydymite group, chalcopyrite, and millerite are secondary in abundance. At lower temperatures, pyrite alternates pyr-

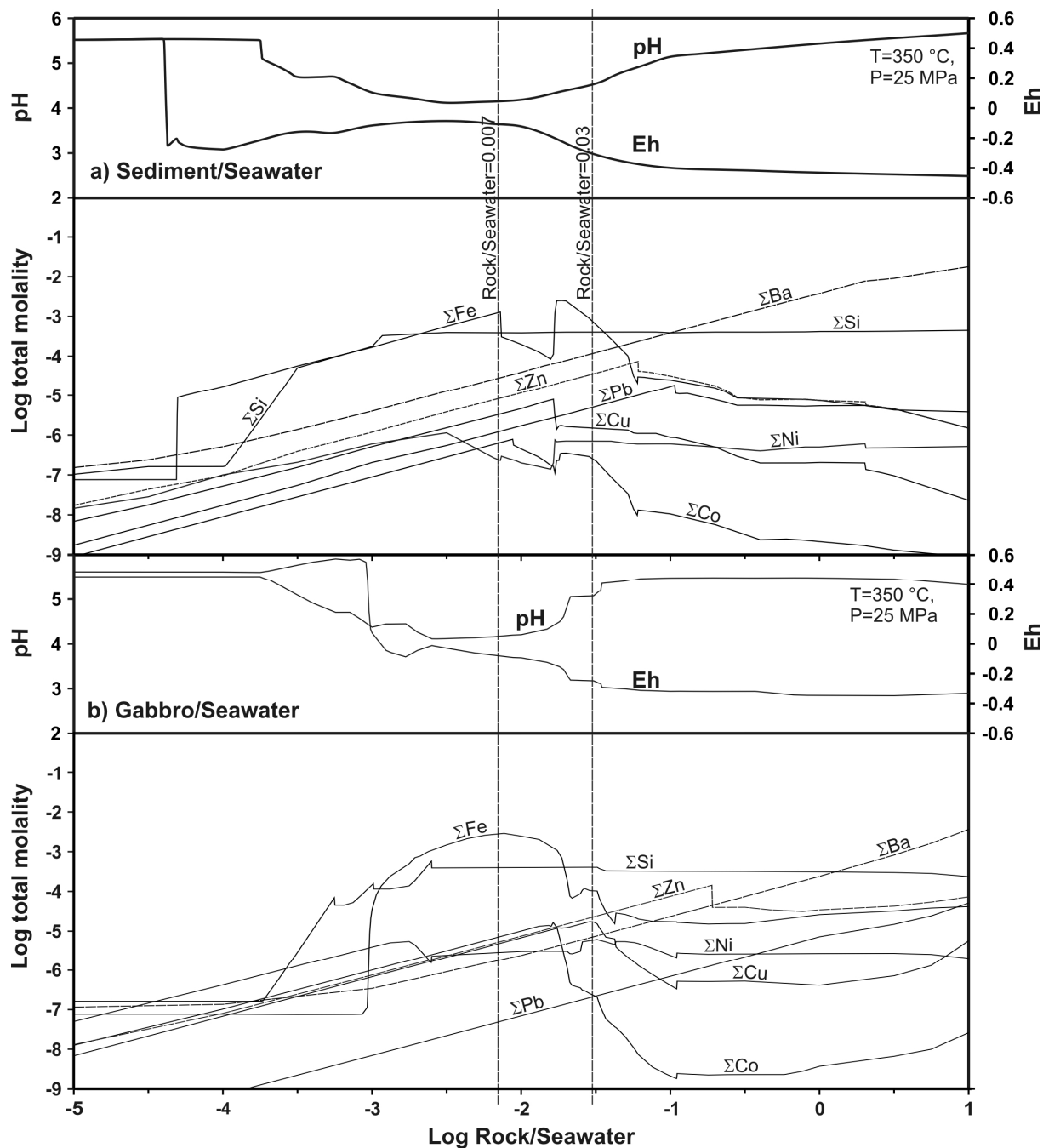


Fig. 1. Plots of Eh, pH, and total contents of metals extracted from the sediment (a) and gabbro (b) with the heated seawater at different R/SW ratios. The mineral assemblages precipitated from the fluid at decreasing temperature are calculated for the R/SW ratio of 0.007 and 0.03 (vertical dotted lines) (see Fig. 2).

rotite and Ni-minerals disappear. Quartz with subordinate pyrite, sphalerite, and galena dominate in a range of 270–150 °C.

The modeling has shown that the maximum amount of Fe is extracted at minimum pH (see Fig. 1) that completely corresponds to the chemical direction of the R/SW interaction. Our estimations of R/SW ratios for the extractive fluid ability are somewhat lower than experimental sediment-seawater ratios of 0.25 [Seewald et al., 1990] and 0.625–1 [Cruse and Seewald, 2001].

Thus, our calculations are in agreement with suggestion that sediments, serving as a basement for the massive sulfide mounds on the seafloor, could be the source of metals. The composition of massive sulfides mostly depends on the rock-seawater ratio in the interaction zone and also on the style of discharge of the hydrothermal fluid on a seafloor.

The work is supported by the program of Presidium of Russian Academy of Science no. 23 (project no. 12-II-5-1003).

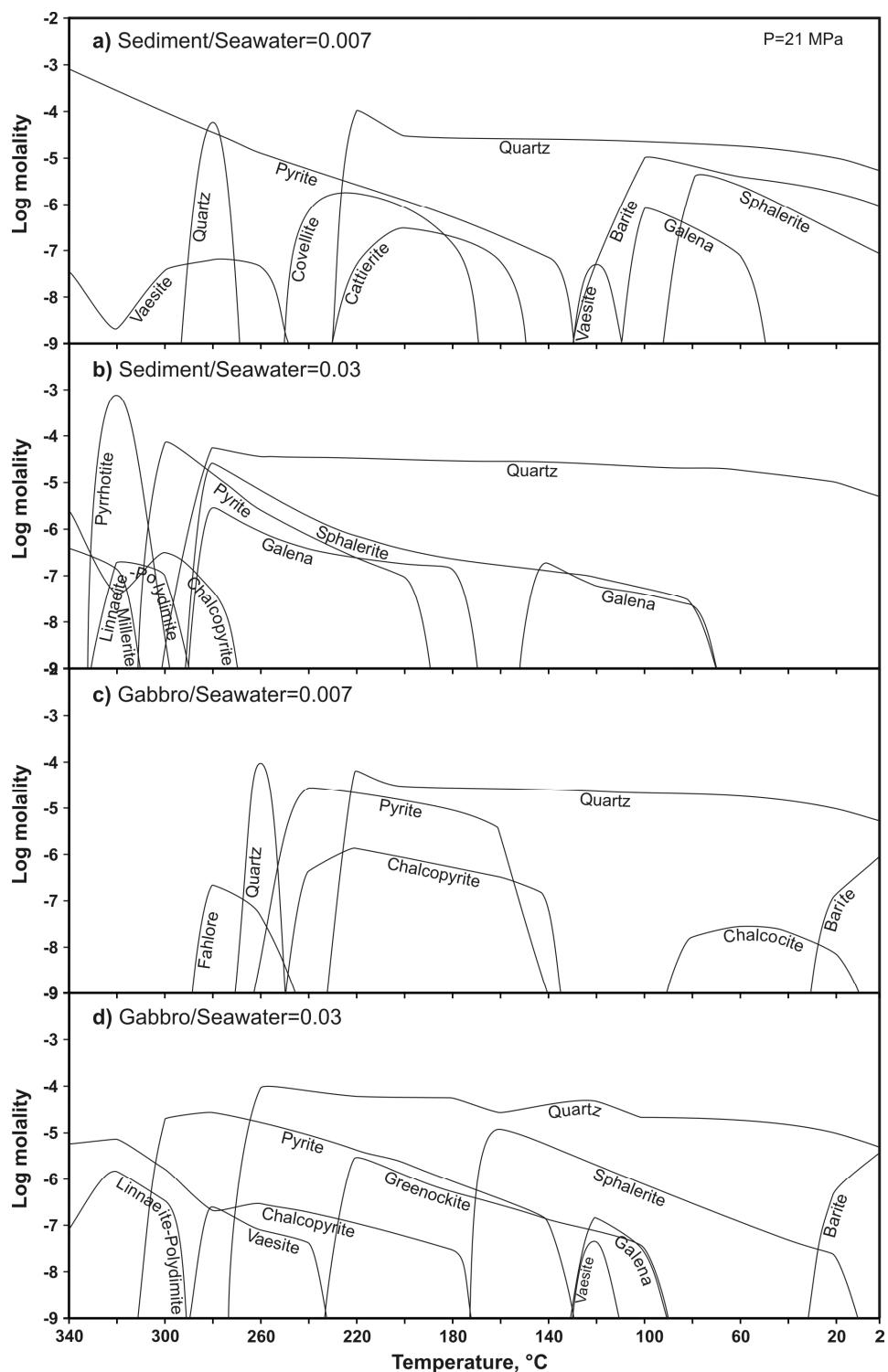


Fig. 2. Mineral assemblages precipitated from the fluid at its cooling from 350 to 2 °C at R/SW ratios of 0.007 and 0.03. These ratios were chosen owing to the maximum extraction of Fe (0.007), Cu, and Ni (0.03) at gabbro-seawater interaction (see Fig. 1).

References

- Butterfield, D.A., McDuff, R.E., Franklin, J., Wheat, C.G.* Geochemistry of hydrothermal vent fluids from Middle Valley, Juan de Fuca Ridge // Proc. of the ODP, Sci. Results. Eds. Mottle M.J., Davis E.E., Fisher A.T., Slack J.E. 1994. Vol. 139. P. 395–410.
- Cruse, A.M., Seewald, J.S.* Metal mobility in sediment-covered ridge-crest hydrothermal systems: Experimental and theoretical constraints // Geoch. et Cosmoch. Acta, 2001. Vol. 65. P. 3233–3247.
- Gieskes, J.M., Simoneit, B.R.T., Brown, T., Shaw, T., Wang, Y.-C., Magenheimer, A.* Hydrothermal fluids and petroleum in surface sediments of Guaymas Basin. Gulf of California: a case study // Can. Min., 1988. Vol. 26. P. 589–602.

Goodfellow, W.D., Franklin, J.M. Geology, mineralogy, and chemistry of sediment-hosted clastic massive sulfides in shallow cores, Middle Valley, northern Juan de Fuca Ridge // *Econ. Geol.*, 1993. Vol. 88. P. 2037–2068.

Encyclopedia of ocean sciences (second edition). Appendix 7. Estimated mean oceanic concentration of the elements // Editors: Steele, J.H., Turekian, K.K., Thorpe, S.A. 2008. P. 386–388.

Koski, R.A., Shanks, W.C., III, Bohrsen, W.N., Oscarson, R.L. The composition of massive sulfide deposits from the sediment-covered floor of Escanaba Trough, Gorda Ridge: implication for depositional processes // *Can. Min.*, 1988. Vol. 26. P. 655–673.

Seewald, J.S., Seyfried, W.E., Thornton, E.C. Organic-rich sediment alteration: an theoretical study at elevated temperatures and pressures // *Appl. Geoch.*, 1990. Vol. 5. P. 193–209.

Thornton, E.C., Seyfried, W.E. Jr. Reactivity of organic-rich sediment in seawater at 350°C, 500 bars: Experimental and theoretical constraints and implications for the Guaymas Basin hydrothermal system // *Geoch. et Cosmoch. Acta*, 1987. Vol. 51. P. 1997–2010.

Tret'yakov, G. A., Melekestseva, I.Yu. Serpentinization of ultramafic rocks and the source of metals for Co-bearing massive sulfide deposits // In: *Metallogeny of ancient and modern oceans-2008. Ore-bearing complexes and ore facies.* Ed. V.V. Zaykov and E.V. Belogub. Miass, Institute of mineralogy UB RAS, 2008. P. 26–30.

Udachin V.N.^{1,2}, Weiss D.J.^{3,4}, Aminov P.G.^{1,2}, Spiro B.⁴, Williamson B.J.^{4,5}

¹*Institute of Mineralogy Urals Branch of RAS, Miass, Russia, udachin@mineralogy.ru*

²*National Research South Ural State University, Chelyabinsk, Russia*

³*Department of Earth Science and Engineering, Imperial College, London, UK*

⁴*Department of Mineralogy, Natural History Museum, London, UK*

⁵*Camborne School of Mines, University of Exeter, Cornwall, UK*

ISOTOPIC GEOCHEMISTRY OF TRACERS FOR MINING AND SMELTING ACTIVITIES IN LANDSCAPE ENVIRONMENT IN THE SOUTHERN URALS

Приведены результаты использования радиометрических трассеров для характеристики горнопромышленного техногенеза Южного Урала. С применением изотопов ²¹⁰Pb и ¹³⁷Cs оценены скорости озерной седиментации в условиях природных и природно-техногенных ландшафтов подзоны южной тайги. При пирометаллургии меди важным индикаторным признаком являются низкие отношения стабильных изотопов свинца ²⁰⁶Pb/²⁰⁷Pb для объектов окружающей среды (металлургические пыли, атмосферный аэрозоль, донные отложения озер доиндустриального периода и верхние интервалы гумусово-аккумулятивных горизонтов почв).

The South Ural area has been heavily affected by mining activities, which include mining, transportation, storage, beneficiation and smelting of metaliferous ores. These cause the atmospheric and aqueous transport accumulation, transformation and reactions of trace – toxic elements in this area. These cause a perturbation of the major environmental systems: atmosphere – soil, atmosphere – water surface, water – lake sediments. The most common effects of mining activity and ore processing of massive sulphide deposits are the dispersion and accumulation of chalcophile elements. In this areas, the technogenic industrial elements are added to the already high natural background levels of trace elements in rocks, soils and plants. This enrichment in technogenic constituent elements is largely caused by atmospheric transport of fine particles from the locations of exploitation, wastes, tailings and copper smelters, in particular of copper ores. Native landscapes are modified to natural-industrial landscapes with formation of geotechnogenic systems in and around the locations of mining and ore processing.

A series of geochemical isotopic methods was used to identify the effects of mining and processing. This series of methods includes the use ¹³⁷Cs and ²¹⁰Pb as chronological indicators for the dating of lake sediments and the determination of their sedimentation rate. It includes also the ²⁰⁶Pb/²⁰⁷Pb isotopic ratio for the evaluation of chalcophile elements transport and cycling in these