New type of rare-metal mineralization: Deposition of metals in high-temperature vapor system of Kudriavy volcano, Iturup Island, Kuriles, Russia

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Fumarolic fields of the Kudriavy volcano represent that part of modern ore-forming system where deposition of ore minerals is now taking place directly from vapor phase. Different temperature regime and rugged topography of these fields allow to study matter precipitated within wide temperature range (up to 870ºC). There are four high-temperature fumarolic fields on the top of the volcano with different temperature of gases and geochemical specialization of sublimates: “Rhenium” (300-560ºC), Re–Cd–Zn–In; “Molybdenum” (400-650ºC), Mo–Zn; “Main” (700-870ºC) Mo; “Dome” (400-730ºC) Mo–Zn–Cd–In. Pb–Bi–S and pyrite mineralization is widespread excepting Molybdenum field.

Our data on zoning, mineral associations and phase compositions of the high-temperature fumarole products let us assume volatile chlorides (halogenides), oxychlorides and oxide compounds as predominant carriers of metals. Ppb-level amount of metals in gas (according to ICP-MS analyses of condensates) is enough to form individual mineral phases by means of vapor transport. Sublimate minerals in general occur as euhedral crystals, as well as skeletal, plate, needle crystals and their morphology reflects growth from low-dense medium.

Three new minerals of rare metals have been found among sublimates of the Kudriavy volcano to date: rheniite ReS_2 (Znamensky et al., in prep.), cadmoindite $CdIn_2S_4$ and kudriavite $(Cd,Pb)Bi_2S_4$.

Molybdenite, earlier concerned to crystallize separately from rheniite at higher temperatures, was found as epitaxial growth on rheniite. Micron-sized particles of native gold were determined among crystals of this molybdenite.

Metallogenic specialization of the mineralization in some aspects is close to Cu–Mo porphyry and Mo–W skarn deposits of ancient vapor-hydrothermal systems.

Reference

Znamensky et. al., in preparation

Transport of metalloids by low-density hydrothermal fluids: Insights from X-ray absorption spectroscopy

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Metalloids such as As, Sb, Si, and Ge are ubiquitous components of hydrothermal systems. They often accompany precious metals and may serve as geochemical tracers of hydrothermal and volcanic processes. However, the behavior and chemical forms of these elements in low-density fluids and vapor-brine systems are still poorly known.

The present contribution summarizes our recent X-ray absorption spectroscopy studies of As, Sb and Ge speciation and solubility in supercritical aqueous fluids. Our experiments were conducted using a new X-ray cell allowing simultaneous *in situ* measurement of both metal local atomic structure (XANES and EXAFS spectra) and its total dissolved concentration to 500°C and 1 kbar. Results show that in both neutral vapors and moderately-saline solutions (< 2 mol NaCl), As(III), Sb(III) and Ge(IV) form hydroxide complexes whose structures change little in a wide range of temperature (20-500°C) and fluid density (1-0.1 g/cm^3). In acid chloride-rich brines and HCl-bearing vapor (> ~0.05 mol HCl) in contrast, chloride species appear to be the dominant form of Sb at temperatures below 400°C. At higher temperatures and lower acidities corresponding to the conditions of most porphyry deposits, however, our data indicate that antimony chloride species are less important compared to the hydroxide $Sb(OH)_3$. Our X-ray cell allowed, for the first time, an *in situ* measurement of Sb vapor-brine equilibrium fractionation at the two-phase boundary of the H_2O-NaCl-HCl system.

Both solubility patterns of Sb(III) and Ge(IV) oxides in low-density aqueous fluids and vapor-brine partition coefficients of As, Sb and Si are directly related to the fluid density in a wide range of conditions. This implies that water-solute interaction is a key factor controlling the metalloid transfer by vapour-like fluids in the Earth’s crust. Our new findings allow quantitative prediction of the vapour-liquid distribution patterns and vapor-phase transport of metalloids in magmatic-hydrothermal environments.