

The role of mantle fluid in formation of modern oceanic sulfide ore: Os isotope evidences

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Great potential of Re-Os isotope system as a tool for hydrothermal sulfide ore study and searching of the metal sources has already been demonstrated (Ravizza *et al.*, 1996; Brüggemann *et al.*, 1998; Gannoun *et al.*, 2003; Sharma *et al.*, 2000; Cave *et al.*, 2003). It was shown that the main sources for Os and Re in submarine hydrothermal systems are seawater, rocks of hosted oceanic crust (sediments, basalts, ultramafics), hydrothermal fluid and extraterrestrial dust. But, the data about pristine plume component with prominent mantle-like signatures are very limited (Cave *et al.*, 2003; Sharma *et al.*, 2000) and lacks further investigation in order to find out the true significance of this source in the process of oceanic ore formation. The main goal of the present investigation was to study behavior of Re-Os isotope system in the process of modern hydrothermal sulfide formation and to determine the role and share of mantle substance in this process. To solve these problems we choose modern (active from 7 thousand years ago till nowadays) Ashadze hydrothermal field developed over ultramafic basement and represented by different types of sulfide formations – from massive sulfides and smokers (up to 7-10 m high) to secondary Fe-Mn and hydrogenic crusts. The Ashadze hydrothermal field as a whole is located on the western slope of the MAR rift valley at 13°N, 44°50'W. Re and Os concentration and Os isotope composition of 15 hydrothermal sulfide samples and 14 host rocks were determined by NTIMS using a Finnigan MAT-262 and TRITON (for Os) and ICP-MS Neptune (for Re) at the IPGP. The chemical separation procedure has been described elsewhere (Birck *et al.*, 1997). Osmium isotope composition in the studied sulfides from the Ashadze hydrothermal field varies in a wide range of values ¹⁸⁷Os/¹⁸⁸Os from 0.2261 to 1.9709 and is higher than the known isotope estimations for the similar modern oceanic fields. At the same time, isotope composition of the host peridotites and gabbro-norites - 0.1234-0.2325 and 0.3062-0.5664, correspondingly, and can be compared with the data for the Logatchev and Rainbow hydrothermal fields, developed over ultramafic basement. There is no correlation between the types of hydrothermal sulfides – zonal, massive, fine-layered chimneys or massive high-temperature sulfides, and osmium composition, which evidence to a more complicated character of hydrothermal process than ordinary mixing of mantle fluid with oceanic water. It also points to the presence of material with high-radiogenic osmium composition in the ore forming process.

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Voltammetry of chalcogenide nanoparticles; The preconcentration mechanism at Hg⁰ surfaces

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Methods for detecting synthetic chalcogenide (MeX, X = S, Se, Te) nanoparticles at trace levels in the environment are of interest in view of possible large-scale commercialization of nanotechnology (1). Natural aquatic metal sulfide nanoparticles already have been observed (2). Nanoparticles composed of several metal sulfides sorb strongly at Hg⁰ electrodes (2-4), where cumulative deposits can be quantified by cathodic scans (MeS → Me⁰ amalgam). Thus Hg⁰ electrodes can serve both for preconcentration and for determination of chalcogenide nanoparticles. Detection at <10⁻⁶ M (as Me_T) has been demonstrated and lower limits are probably feasible.

Understanding the preconcentration mechanism is the key to optimizing detection of chalcogenide nanoparticles. In a detailed study of semi-spherical, copper sulfide (Cu_xS) aggregate particles having mean diameters of 5-20 nm, a three-step mechanism is required to explain preconcentration. The first step involves Brownian diffusion of particles to the Hg⁰ surface. When both the electrode and particles have negative surface potentials, this process resembles charge-impaired coagulation, obeying the Schulze-Hardy rule in various electrolytes. The second step involves atomic reordering of Cu_xS, probably to Cu_xS adlayers. A very significant (~0.3 V) negative shift in the Cu_xS reduction potential results, owing to a free energy decrease from release of the nanoparticles' surface energy and from favorable chemical interactions between Cu_xS adlayers and Hg⁰. The third step, which competes with the second, involves size-dependent, reductive loss of electroactive Cu_xS prior to the cathodic scan. This loss is greatest for the smallest particles with greatest surface free energy.

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