

## Ge isotope fractionation during adsorption processes onto the surface of Fe oxy(hydro)oxides

XUEFANG LI AND YUN LIU\*

State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China (\*correspondence: Liuyun@vip.gyig.ac.cn)

Fe oxides and oxyhydroxides, such as goethite, hematite, ferrihydrite and so on, are ubiquitous in forms of secondary minerals in soils and sediments, and also are major components of ferromanganese crusts and nodules in oxic ocean environments. Because of their strong adsorption characteristics, Ge and Ge isotope distributions in natural environments are partly controlled by such adsorption processes [1, 2]. However, molecular level mechanisms of these processes are elusive so far. This study investigates Ge isotope equilibrium fractionation during the surface adsorption processes by using high-level quantum chemistry methods.

The possible adsorbed Ge complexes on Fe (III)-oxyhydroxides surfaces are carefully verified by comparing their energies and geometries with known experimental evidences. The Bigeleisen-Mayer formalism has been used to calculate the Ge isotope fractionation factors. The electronic structures and frequencies of the Ge species are obtained at B3LYP/6-311+G (d, p) level.

Our results show that the Ge adsorption structures onto Fe (III) ferrihydrite mainly are bidentate corner-sharing type, e.g. tetrahedral Ge is bonded to two corners of two adjacent octahedral Fe atoms. The fractionation between the bidentate corner-sharing complex and  $\text{Ge}(\text{OH})_4$ , which is dominant species in natural waters, is around -1.7‰, light Ge isotopes prefer to be adsorbed. This fractionation will profoundly affect the Ge isotope compositions of rivers, groundwater and hydrothermal fluids, even is responsible for the enrichment of heavy Ge isotopes in seawater.

[1] Galy *et al.* (2002) *GCA* **66**, A259. [2] Pokrovsky *et al.* (2006) *GCA* **70**, 3325–3341.

## Authigenic and biogenic minerals in volcanic hot springs of Kamchatka, Russia

YILIANG LI\* AND SANYUAN ZHU

Department of Earth Sciences, the University of Hong Kong (\*correspondence: yiliang@hku.hk)

The volcanic hot spring deposits from Kamchatka, Russia were examined by scanning electron microscopy and transmission electron microscopy equipped with energy dispersive spectroscopy. Those hot springs include Burlyashii, Oil pool, Zavarzin, Thermophile and Jen's vents, which were previously reported for microbial ecology and mineralogy. Opal A spheroids are common in all hot spring sediments with particle size from <20 nm to 50 nm. Euhedral single quartz nanoparticles of ~700 nm crystallized from Opal-A can be observed scattered on the surface of anhedral sediments. Authigenic kaolinite of sharp faces can be observed in all hot springs with Si, Al and O as major compositions and having flaky- and scale-like structures. Iron sulfides are common with a wide spectrum of crystal sizes and morphologies. Small pyritic iron sulfides have octahedral shape with crystal size around ~20-80 nm; while pyrite crystals of ~200 nm to 500 nm and these >1  $\mu\text{m}$  have cubic structure. The small pyrite crystals are also observed assembled to bigger cubic shapes, showing an Ostwald ripening process. There are also spheroidal shaped, ~1  $\mu\text{m}$  size pyritic aggregates with rough surface which showed a sulfate-reducing bacteria mediated formation of iron-sulfides. Fibrous and tabular gypsum crystals can be observed coexisting with sulfides, indicating local oxidation condition. Euhedral crystals of element sulfur of ~30  $\mu\text{m}$  can also be observed. Magnetic minerals are abundant in Jen's vents, however, no magnetite can be detected, implying the existence of magnetic iron sulfides though thermophilic iron-reducing bacteria were isolated from some springs. Detrital quartz and silicates of larger sizes can be observed in some hot spring, showing water-rock interaction induced corrosion structures. The high abundance of iron sulfide minerals and the high percentage of menaquinones in sinter deposits indicated highly reduced conditions. The common existences of submicro- to nano-meter authigenic minerals, the abundant bacteria filaments, biofilms and diatoms indicate microbial mediation is a significant factor in the mineralization of those minerals in the hot springs.