Sulfur and carbon geochemistry of carbonate-veined serpentinites from Liguria: A comparison to the Iberian Margin and Lost City

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Serpentinization processes at slow- and ultra-slow spreading ridges strongly influence S- and C-exchange between seawater and the oceanic lithosphere and play an important role in global marine bio-geochemical cycles. During the exposure of ultramafic rocks to seawater distinct opaque mineral assemblages as well as S- and C-isotopic signatures are produced, which reflect fluid fluxes, redox conditions and microbial activity that prevail during serpentinization and carbonate precipitation. In this study, carbonate-veined serpentinites from ophiolites in the Ligurian Apennines (Italy) were analyzed for their sulfur mineralogy, S and C contents, and S and C isotopic composition. These are compared to serpentinites from the Iberian Margin, an ancient peridotite-hosted hydrothermal system, and to the serpentinite basement of the Atlantis Massif, a modern, active hydrothermal system driving serpentinization processes near the Mid-Atlantic Ridge.

Total S contents of the Ligurian serpentinites are up to 1000ppm, and have strongly varying SO_4/S_{total}-ratios, with bulk rock S isotope compositions that are slightly to strongly depleted in ^{34}S. $\delta^{34}S$-values of the sulfides and sulfates provide constraints on oxidation processes and microbial activity during serpentinization. In particular, highly depleted $^{34}S_{sulfate}$-compositions are indicative of oxidation of microbially-produced sulfides. Furthermore, our studies suggest that high total organic carbon contents and depleted $^{13}C_{TOC}$-compositions reflect the presence of organic matter incorporated during serpentinization.

The opaque mineralogy of the Ligurian serpentinites is dominated by pyrite, pentlandite, millerite, magnetite, and hematite, reflecting generally oxidizing conditions during serpentinization, and is associated with high inorganic C-contents and the incorporation of seawater-carbonate. The relatively high f_{O2}-conditions found in Liguria are similar to those found at the Iberian Margin and at the southern wall of the Atlantis Massif, near Lost City. Furthermore, sulfur and carbon species strongly indicate the presence of microbial activity in active and ancient peridotite-hosted hydrothermal systems.

Organo-iodine formation in aquifer sediments at ambient concentrations

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Iodine (I), a biophilic element, and its long-lived isotope ^{129}I, a component of nuclear waste disposal sites, are considered to be highly mobile in the environment. Releases from nuclear waste disposal sites occur through groundwater aquifers, where migration depends on the species tendency to be retarded due to sorption and other reactions to aquifer materials. Since I mobility can vary greatly with I speciation, studies with aquifer sediments from the Savannah River Site were undertaken, which show that I interaction and mobility highly depend on the concentration added to sediment slurries, the time of equilibration, and the organic carbon (OC) content of these sediments. Particle-water partition coefficients (Kd) became an inverse power function of the iodide (I^-) concentration. Organo-I species that are released from sediments into solution after 1-2 weeks of equilibration with I^- make up a major fraction of total I at ambient concentrations of total I, but a decreasing fraction at increasing I^- concentrations. Because OC concentration can become limiting, experiments that are conducted at elevated I^- concentrations (e.g., mM) would miss the fact of significant organo-I formation and I retardation.

Furthermore, in the 2 weeks studies, the organo-I in the slurries appear to follow Michaelis-Menten kinetics. Results from studies of I speciation, variable OC content, and incubation times using microbial cells and exopolymeric substances at a Savannah River riparian site are contrasted to those from a glacial-fluvial site of the Glattfelden aquifer (water and soil samples courtesy of J. Beer, E. Hoehn, and S. Bollhalder, EAWAG).