Iron sulfide formation under low pH conditions in sulfate reducing enrichment cultures obtained from acidic pit lake sediments

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Dissimilatory sulfate reduction often plays a key role in bioremediation systems treating acid mine drainage as it leads to alkalinity generation and precipitation of metal ions. However, both, microbial sulfate reduction and metal sulfide formation, are pH dependent and are inhibited under low pH conditions. The aim of this study was to investigate iron sulfide formation under sulfate reducing conditions in systems mimicking low pH environments. Experiments were performed at 18°C with indigenous sulfate reducing populations originally enriched from sediments of an acidic pit lake. The artificial pore water media contained elevated concentrations of sulfate (20 mM), Ca (6 mM), Fe^{II} (5 mM), Al (4 mM), and Mg (1 mM) and a H_2/CO_2 gas mixture was used as electron donor/carbon source. The pH was initially set to pH 3.3, 3.8, 4.8, and 5.9. Over an incubation time of 12 weeks, pH, concentrations of soluble Fe(II), sulfate, and sulfide, and partial pressures of H_2 and CO_2 were monitored. In the less acidic systems (pH 4.8 and pH 5.9), sulfate reduction started shortly after inoculation. In the systems with an initial pH of 5.9, immediate precipitation of iron kept the concentration of free sulfide very low (< 30 µM), whereas in the systems initially set at pH 4.8, free sulfide concentrations built up to 300 µM during iron precipitation. In the more acidic systems, sulfate reduction occurred after a lag phase of 20 – 40 days but it proceeded at a much higher rate than in the less acidic systems. A decrease of soluble Fe(II) was only observed at pH > 4.3 when the amount of sulfate reduced exceeded 5 mmol per ml of culture medium. The results show that iron sulfides form at low pH when high concentrations of free sulfide are present. Sulfate reducing prokaryotes thriving under these conditions need not only to be acidotolerant but must also tolerate high concentrations of free sulfide. Different cell morphologies revealed by microscopic observations as well as microbial community analysis based on 16S rRNA gene amplicons suggest that different sulfate reducing species were enriched. Mineral precipitates formed in the different system will be characterized by electron microscopy (SEM/TEM). Geochemical equilibrium modeling will be used to calculate saturation indices and predict iron-rich mineral formation in the various systems.

Determination of siderophile and chalcophile elements in peridotites by sector field ICP-MS

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Obtaining complete and accurate data sets on all highly siderophile elements in peridotites and related rocks is challenging because of digestion issues, low abundances and the monoisotopic nature of Au and Rh. Similarly, moderatelly siderophile and chalkophile elements such as Mo, Ag and Cd are poorly constrained in such rocks, again because of digestion issues, low abundances and a wealth of interferences in ICP-MS. Here, we report initial results on highly siderophile elements including Rh and Au and a new approach for the precise analyses of some moderately siderophile and chalkophile elements. Analyses are carried out at the Freie Universität Berlin using a Thermo Element XR sector field ICP-MS equipped with an Aridus desolvating system, glass spray chambers and microconcentric nebulizers.

The analysis of PGEs, Re and Au follows a modification of previously published protocols (Meisel *et al*., 2003, JAAS 18, 720-726). Up to two g of powdered samples are digested in inverted aqua regia using carius tubes or a high pressure asher. Osmium is separated by solvent extraction and analyzed by TIMS, the other PGEs and Re are separated from the rock matrix in 0.2 M HCl using cation exchange resin. Rhenium and all PGEs except Rh are quantified by isotope dilution (ID). Rhodium is quantified relative to Ir by using the Ir abundance from the ID analyses and a response factor derived from a Rh-Ir calibration solution.

Gold abundances have been determined by the standard addition method for two samples, a serpentinized lherzolithe reference material (UB-N) and a Al-rich peridotite (TUR-7) from France. Four rock powder aliquots were spiked with 0, 2, 4 and 6 ng Au before carius tube digestion. Prior measurement, the samples were centrifuged and diluted with 0.5M HCl to a solution weight 50 times the initial sample weight. During the analysis, drift was compensated for by internal normalisation to sample Ir. Very good correlations were obtained despite the independent digestions for each aliquot, which suggests that Au and Ir are homogeneous at the 2g sample scale and that the digestion method is reproducible. The Au abundance in UB-N and TUR-7 was found to be 1.49 (+0.04; -0.05) and 1.34 (+0.11; -0.20) ng/g at the 95% confidence level.

The abundances of many moderately siderophile and chalcophile elements are poorly constrained in the Earth's mantle. To obtain high precision data, we started to prepare enriched isotope spikes and developed a chemical separation protocol for Cu, Zn, Ga, Mo, Ag, Cd, In, Sn, Te, W and Tl.