REE fractionation during the precipitation of hydrous ferric oxides from anoxic lake water

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An enrichment of LREE is characteristic for most of the acidic, iron and sulphate rich pit lakes and groundwaters in the lignite mining district of Lower Lusatia (Germany). One of these acidic lakes - the pit lake “RL 1223” - has a strong thermal and chemical stratification. The upper water layer (0 - 9 m) shows pH values of about 3 during all seasons. The monimolimnion (10 - 17 m) of the lake is anoxic and has pH values of about 7. The REE patterns of the upper layer are enriched in LREE (La_N/Yb_N: 1.6) whereas opposite patterns (depletion of LREE, La_N/Yb_N: 0.4) are found in the anoxic water of the monimolimnion.

Experiments were conducted to observe the behaviour of REE during the iron oxidation in water from the monimolimnion (depth 14 m). The sampled water was filled into plastic bottles, which were exposed to air in laboratory. The changing water chemistry was observed up to 40 weeks after the sampling day. Due to the initial anoxic, but acidic conditions almost all iron precipitated in the investigated water, and the pH value decreased from about 7 to 3 during the oxidation. The iron precipitates are identified as ferrihydrite which is transformed into goethite within the oxidation process. Stable pH conditions (pH 3.0) were reached after about 10 weeks of oxidation time. The original REE patterns of the investigated water are generally reflected in all collected iron precipitates at the beginning of the experiment as well as after 40 weeks of the oxidation. However, in the corresponding water samples a time dependent REE fractionation was observed. LREE were temporary enriched with a maximal La_N/Yb_N ratio of 1.0 after 6 weeks of the oxidation time (pH 3.8 - 4.9).

These findings lead to the conclusion that the LREE enrichment of acidic waters in the study area can be caused by the formation of secondary iron minerals due to oxidation processes in aquifers of the lignite mining dumps. At the actual oxidation state of the dumps, the iron precipitates (particularly ferrihydrite) tend to preferentially sorb HREE and MREE. Therefore, the typical dump groundwater with pH values of about 4 (passing through the mining dumps and filling the pit lakes) can be enriched in LREE.

Fractionation of sulfur and oxygen isotopes in sulfate produced by anaerobic photosynthetic sulfur bacterium

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Biomarkers for photosynthetic bacteria have been preserved in the geological record dating back more than 1.6 billion years. rRNA evidence shows photosynthetic bacteria having branched off close to the base of the tree of life. Therefore, anoxygenic photosynthetic oxidation of sulfide to sulfate may have been an important process in the formation of sulfate in the Archaean ocean. Investigating the isotope systemtics of sulfate produced during sulfide oxidation in modern photosynthetic bacteria might provide clues as to how sulfate may have formed in the geologic past. We have measured the $\delta^{34}S$ and $\delta^{18}O$ of sulfate produced by laboratory pure cultures of photosynthetic green and purple sulfur bacteria. From these measurements we have determined the sulfur ($\delta^{34}S_{SO4-H2S}$) and oxygen ($\delta^{18}O_{SO4-H2O}$) isotope fractionation effects to be ~0‰ and +5.6‰, respectively, for the purple sulfur abcterium, *Allochromatium vinosum*. Additional investigations of green sulfur bacteria are currently underway. Precise determination of these $\delta^{34}S_{SO4-H2S}$ and $\delta^{18}O_{SO4-H2O}$ values will permit more accurate interpretation of the $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values measured in modern envirinments, or preserved in the rock record, and whether they reflect a biological origin.