The structure of REE aqua and chloroaqua complexes in hydrothermal fluids

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Our understanding of the association of rare earth ions with ligands common in the Earth's crust (e.g. chloride, fluoride, phosphate, and carbonate ions) at elevated pressures (P) and high temperatures (T) is incomplete. Data on the stability and structure of REE ion complexes at elevated P-T conditions are necessary in order to understand fully the geochemistry of hydrothermal rare earth mineralization. We discuss structural data for several rare earth ions measured using synchrotron x-ray absorption spectroscopy (XAS) in aqueous solutions under elevated P-T conditions on the PNC-ID 20 beam line at the Advanced Photon Source, Argonne National Laboratory. Analysis of XAS spectra measured from Eu^{3+}, Gd^{3+}, and Yb^{3+} ions, at concentrations ranging from 0.006 to 0.07 *m* in 0.16 *m* HNO_3 aqueous solutions, shows that the number of H_2O ligands of the Gd^{3+} aqua ion decreases at a rate (0.41/100 ^oC) which is roughly one half of the rate of H_2O-ligand reduction for the Yb^{3+} aqua ion (0.84/100 ^oC) and for the Eu^{3+} aqua ion (0.77/100 ^oC) over the 25 to 500 °C temperature range. These results suggest that the Gd^{3+} aqua ion is more thermodynamically stable than the Yb^{3+} and Eu^{3+} aqua ions. We conjecture that this may be due to the tetrad effect, as evidenced in a strengthening of the bonding of aqueous ion complexes derived from enhanced quantum mechanical interelectronic repulsion energy of the half-filled 4f electronic shell configuration of the Gd^{3+} ion. XAS measurements of Nd^{3+}, Gd^{3+}, and Yb^{3+} ions, at concentrations ranging from 0.006 to 0.1 *m* in low pH chloride (0.02 – 0.3 *m*) aqueous solutions reveal that significant association between these REE ions and the chloride ligand occurs in the 300 to 500 °C temperature range forming stepwise inner sphere chloroaqua complexes of the type $REE(H_2O)_{\delta\ -\ n}Cl_n^{+3-n}$, where $\delta \approx 7 - 8$ and the number of Cl^- ligands (n) increases steadily with temperature from an average of roughly 0.5 to a value close to 2. This demonstrates that chloride species may be important for transport of REE in low pH chloride-bearing hydrothermal fluids at elevated temperatures (300 to 500 °C). Our results are found to have negligible pressure dependence for the pressure range of this study. The structural results for the REE chloroaqua complexes under elevated P-T conditions are discussed in terms of variability (or lack thereof) across portions of the REE series.

Identifying sources of riverine sulfate by combining hydrological, chemical and isotopic approaches

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A series of case studies will be presented in which sulfate in surface water systems was sampled frequently, $\delta^{34}S$ and $\delta^{18}O$ values were obtained, and interpreted in conjunction with hydrological and chemical data. Using this approach in selected forested headwater catchments in New Hampshire, New York, and Vermont (USA), it was demonstrated that a significant portion of stream water sulfate during base flow was derived from weathering of bedrock, particularly in catchments with sulfur-rich lithology. During storm events after a dry summer season, sulfate concentrations in stream water increased significantly and $\delta^{34}S_{sulfate}$ decreased to minimum values in some catchments. This suggests that sulfate derived from oxidation of sulfide minerals, e.g. in wetland areas or the hyporheic zone, contributed to the increased sulfate load in these streams following storm events. Monitoring of stream water during spring snowmelt events at the Sleepers River Research Watershed (Vermont, USA) revealed elevated contributions of sulfate from pedospheric sources, but little direct contribution of sulfate from the melting snowpack.

Investigations in two large watersheds in the Rocky Mountains of Alberta (Canada) indicated that riverine sulfate in headwaters was mainly derived from evaporite dissolution. In the agriculturally dominated downstream portions of the watersheds, oxidation of pyrite in tills was identified as an additional source of riverine sulfate evidenced by increasing sulfate concentrations and decreasing $\delta^{34}S$ values. Using a combination of hydrological, chemical and isotopic approaches, it was also demonstrated that urban centers, such as Calgary in southern Alberta, had a significant impact on riverine sulfate loads that was evident from the distinct isotopic composition of sulfate released from the waste water treatment plant.

In watersheds with forested, agricultural and/or urban land use, there are a variety of natural and anthropogenic sources of riverine sulfate. The relative contributions of these sources to sulfate in rivers and streams can vary significantly depending on hydrological conditions that have distinct seasonal patterns. To identify these different sources and to assess their relative contributions, it is essential to determine the isotopic composition of sulfate from spatially distributed sites along headwater creeks, rivers or streams under different hydrological regimes. These isotopic data, when combined with hydrological and chemical results, provide information that can be used to markedly improve the quantification of riverine sulfate sources.