

S isotope investigation of a redox-stratified system dominated by chemotrophic sulfide oxidation

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Anoxic and sulfidic conditions seem to have been common in parts of stratified Precambrian oceans. The fate of sulfide in these systems would presumably have depended on the availability of oxidants and the depth of the redox interface. Before widespread oxygenation of the surface oceans, sulfide in shallow waters reaching the photic zone would have been oxidized by anoxygenic phototrophs. Increasing oxygenation of surface waters would have driven the redox interface deeper into the ocean (and eventually into the sediments), where chemotrophic oxidation utilizing newly available oxidants (e.g., O₂ and NO₃⁻) would have taken over. We are using multiple S isotopes to examine S cycling processes and resulting isotope signatures in biofilms dominated by chemotrophic S-oxidizing organisms in the sulfidic Frasassi cave system (central Italy). Fractionations between sulfide and S⁰ in these biofilms are larger than those previously measured in the laboratory, and vary with stream chemistry, with larger fractionations occurring at higher O₂/H₂S. Mass balance models of sulfate, sulfide, and S⁰ isotope values point to a complex sulfur cycle within the biofilms. Fractionations between sulfate and sulfide plot outside the range of δ³⁴S vs Δ³³S published for natural systems dominated by sulfate reduction, and could provide a fingerprint for oxidative S cycling in modern (and potentially ancient) environments.

Density and apparent molar volume of binary electrolyte aqueous solutions at elevated temperatures

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Essentially all aqueous fluids encountered in geothermal and hydrothermal environments represent multicomponent electrolyte mixtures. Quantitative modeling of geothermal reservoir processes therefore requires thermodynamic properties of such solutions. While experimental data are available for most pure electrolyte solutions, the properties of multi-electrolyte solutions are largely unstudied at elevated temperatures and pressures above the vapour pressure saturation curve. This lack of experimental data precludes the derivation of accurate pressure dependencies in thermodynamic models of excess thermodynamic properties of aqueous species in geothermal fluids.

We present the results of an experimental study on the volumetric properties of binary electrolyte solutions at temperatures up to 300 °C and pressures up to 400 bar over a wide range of compositions and ionic strengths. We used a vibrating-tube densimeter to measure the relative density of aqueous solutions containing mixtures of alkali and alkali earth chlorides. Pressure, temperature and composition dependence of density and other derived properties of binary mixtures were constrained. Mean apparent molar volumes of the electrolyte solutions were calculated from the experimental data and compared to various mixing models from the literature. The data will be used in the ongoing development and/or parameterization of models for the calculation of excess thermodynamic properties (Hingerl *et al.*, this conference). The results of this study will permit a quantitative modeling of the properties of complex aqueous solutions and simulation of fluid-rock interaction processes occurring in geothermal systems.