Biogeochemical sulfur cycling in meromictic Fayetteville Green Lake, NY

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Green Lake (GL) is a small, permanently stratified freshwater lake located approximately 2 km northeast of Fayetteville, NY. The input of sulfate-rich groundwater at depth sustains density stratification and results in high sulfate concentrations (12 – 15 mM) and the build-up of hydrogen sulfide in bottom waters. As such, GL represents a high-sulfate contrast to low-sulfate systems currently being studied as Precambrian ocean analogues, and could be appropriate in thinking about euxinic systems that have been proposed for more recent Phanerozoic oceanic anoxic events occurring after an initial rise in marine sulfate. We measured concentrations of major sulfur species and S isotope values ($\delta^{34}S$ and $\Delta^{33}S$) of sulfur compounds in the GL water column in November 2007 and October 2008, in an attempt to quantify the major biological and inorganic processes controlling sulfur cycling in the system. Sulfide concentrations are at or near the detection limit above the chemocline (< 20 m depth), but increase to > 1.5 mM in bottom waters. A peak in total zero valent sulfur (up to ~30 μM S^0) occurs at around 20.5 m, coincident with a peak in turbidity representing a dense community of phototrophic S-oxidizing bacteria. $\delta^{34}S$ values of sulfide and sulfate in the GL water column are consistent with previous studies (increasing slightly with depth), with the important exception that we measure a *decrease* of ~4 ‰ in the $\delta^{34}S$ of sulfide with increasing depth across the chemocline (from 20 – 22 m). This trend suggests that inorganic oxidation of sulfide to ^{34}S-depleted sulfur intermediates (e.g., thiosulfate) is controlling the isotopic composition of sulfide in the chemocline, rather than phototrophic oxidation to S^0, which is enriched in ^{34}S by ~6 ‰ (consistent with the predominance of polysulfides). Additionally, mass balance models of $\delta^{34}S$ and $\Delta^{33}S$ values at depth indicate that both sulfate reduction and sulfur compound disproportionation metabolisms are contributing to the isotopic composition of sulfide in the deep waters.

Modeling of fluid phase equilibria for H_2S-H_2O mixtures to 400°C

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Hydrogen sulphide plays an important role in the complexation and transportation of metals, notably gold, in hydrothermal liquids. As a result of numerous experimental studies, this role is relatively well understood, and data are available that permit satisfactory quantitative modelling of ore-forming processes involving H_2S-bearing liquids. However, in magmatic hydrothermal systems, vapour can be an important and even dominant fluid and, as H_2S partitions strongly into the vapour, it is therefore important that we also develop a capacity to model ore-forming processes involving this phase. Unfortunately there is a dearth of data for H_2S-H_2O gas-liquid mixtures at elevated temperature and pressure. Furthermore, most of the experimental PVTx data available for this system, were obtained at low temperatures and partial pressures of H_2S. Consequently the equations of state that have been developed from these data are inaccurate in predicting phase relationships for H_2O-H_2S mixtures at high temperature and elevated partial pressures of H_2S.

The goal of our study was to collect the experimental data required for a detailed description of vapour-liquid equilibria in the H_2S-H_2O system for a wide range of partial pressures of H_2S at temperatures up to 400°C and pressures up to 300 bar. Experiments were performed in a titanium-alloy constant-volume cell equipped with a sapphire pressure sensor. The sensor was connected to the cell through a custom-made mercury-filled transducer equipped with a titanium membrane, permitting accurate measurement of pressure at the temperature of the experiments.

The new VLE model developed using the data collected employs an asymmetric γ-φ approach, i.e., the fugacity of the vapour is described using fugacity coefficients obtained from an equation of state and the fugacity of the liquid is derived from thermodynamic data and an appropriate activity coefficient model. The properties of the vapour were calculated using the Stryjek-Vera modification of the Peng-Robinson cubic equation of state. Binary interaction parameters for the mixture of water and hydrogen sulphide were fitted to a set of high-temperature experimental data.

The resulting model provides the framework required for reliable future modelling of two phase hydrothermal systems such as those responsible for the formation of porphyry and epithermal mineral deposits.