Phototrophic S oxidation in modern and ancient redox stratified ecosystems: A multiple S isotope perspective

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Phototrophic S-oxidizing organisms are the dominant anoxygenic phototrophs in redox-stratified environments where sulfidic waters intersect the photic zone. These organisms form dense and diverse communities at the redox interface of modern sulfidic systems [1], and sedimentary biomarkers chronicle their existence in ancient microbial communities as old as 1.6 Ga [2]. Despite the abundance and antiquity of these organisms, their past and present importance in carbon and sulfur cycling is not well constrained. We have undertaken a series of multiple S isotope studies of sulfur compounds associated with phototrophic S-oxidizing organisms (in both the laboratory and in the field) to determine: 1) the range of S isotope fractionations produced by this metabolism, 2) the environmental and physiological controls on these fractionations, and 3) the expression of these isotope signatures in modern and ancient redox stratified systems. Pairing of traditional sulfur isotope measurements ($\delta^{34}S$) with minor S isotope analyses ($\Delta^{33}S$ and $\Delta^{36}S$) allows us to constrain and quantify the flow of sulfur compounds at both the metabolic and ecosystem levels, providing insight into the physiology of phototrophic S oxidation and the contribution of phototrophs to biogeochemical sulfur cycling in natural systems.

[1] Overmann, Beatty, Hall, Pfennig & Northcote (1991) *Limnology & Oceanography* **36**, 846–859. [2] Brocks & Schaeffer (2008) *Geochimica Cosmochimica Acta* **72**, 1396–1414.

Experimental data and equation of state for modeling of PVTx properties of H_2O-H_2S mixtures

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Knowledge of the properties and behavior of H_2O-H_2S fluid mixtures is of great importance for a number of geochemical and engineering applications. For example, at elevated temperatures, this system has major significance for geological processes in many environments. However, at the conditions encountered in magmatic hydrothermal systems, the equations of state (EOS) and thermodynamic models of vapor-liquid equilibrium are inadequate to reliably predict the properties of H_2O-H_2S fluid mixtures due to a dearth of experimental data. Based on previous measurements of the properties of gas mixtures, we suggested a set of parameters for custom EOS applicable to temperatures <400 °C and high partial pressures of hydrogen sulfide [1]. We now present new experimental data on the PVTx properties of saturated aqueous mixtures of water and hydrogen sulfide which result in a notable improvement of the EOS at vapor-liquid equilibrium conditions.

Vapor and liquid phase compositions were determined at the liquid saturation boundary using a custom designed apparatus permitting direct sampling of the fluid at the temperature and pressure of the experiment. The constant-volume experimental cell was equipped with a sapphire pressure sensor which also allows direct measurement of pressure along the selected isotherms. Titanium oxide coatings of the surfaces which were in contact with the fluids ensured corrosion resistance of the cell. The data obtained from the experiments were used to select the best equation of state, fit the necessary adjustable binary interaction parameters, and facilitate the thermodynamic model describing the PVTx properties of fluids in both homogeneous vapor and vapor-liquid two-phase regions.

The results of this experimental study make it possible to reliably estimate volumetric properties of aqueous fluids containing hydrogen sulfide at temperatures up to 400 °C and high partial pressures of H_2S, i.e. for conditions commonly encountered in volcanic-hydrothermal systems. Using this same experimental method, we are also planning to conduct measurements of vapor-liquid element partitioning, which is one the potentially important applications of the direct sampling of two-phase fluids.

[1] Zezin D.Yu. Migdisov A.A. Williams-Jones A.E. (2009) *GCA* **73** (Supplement 1) A1501.