

## Periodic formation of organic haze in the Neoproterozoic atmosphere

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Photochemical models of the evolution of atmospheric redox on the early Earth suggest that a collapse in reductants (e.g., methane) was equally important to (if not required for) the rise in O<sub>2</sub> associated with the GOE [e.g., 1]. We present geochemical records directly linking changes in atmospheric chemistry with periodic increases in methane concentrations in the Neoproterozoic atmosphere. We have generated a multi-proxy dataset of ocean and atmospheric redox from sediments deposited on the Campbellrand-Malmani platform of South Africa from ~2.65-2.5 Ga, on the run-up to the GOE. Trends in Fe speciation and major sulfur isotope ratios ( $\delta^{34}\text{S}_{\text{pyrite}}$ ) provide evidence for oxygen production in microbial mats and localized oxygenation of surface waters. At the same time, minor sulfur isotope values ( $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ ) preserve mass-independent fractionations (S-MIF) indicative of a reducing atmosphere. Most significantly, changes in the character of S-MIF signals occur in several distinct sedimentary intervals correlated with areas of highly <sup>13</sup>C-depleted organic matter. These correlations extend to other datasets, implying a global trend between methane in the biosphere and variations in atmospheric S-MIF signals. We hypothesize that these signals record the periodic formation of a hydrocarbon haze at high CH<sub>4</sub>:CO<sub>2</sub> ratios [e.g., 2], which could have altered S-MIF signals, either through shielding or by changing the redox chemistry of S species in the atmosphere. These results suggest that carbon-bearing compounds played an important role in regulating the redox state of the Neoproterozoic atmosphere, and support arguments that the GOE would have required (and/or could have been caused by) a concomitant decrease in the biological flux of methane.

[1] Zahnle et al. (2006) *Geobiology* **4**, 271-283. [2] Domagal-Goldman et al. (2008) *Earth and Planetary Science Letters* **269**, 29-40.

## Volumetric properties of KCl-NaCl and CaCl<sub>2</sub>-NaCl binary aqueous solutions at elevated temperatures and pressures

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Modeling and understanding of geochemical processes involving aqueous fluids requires knowledge of thermodynamic properties of such solutions. Aqueous solutions in the upper crust are typically mixtures of electrolytes, thus the properties of an aqueous fluid cannot be approximated by a single-electrolyte model (e.g., NaCl-H<sub>2</sub>O) accurately. The properties of multi-electrolyte mixtures are largely unstudied at elevated temperatures, and at pressures above the vapour pressure saturation curve. Namely, data on volumetric properties that would characterize the pressure-dependencies are essentially in-existent. These data are of particular importance in hydrothermal and geothermal fluid-related modeling, petroleum and geothermal reservoir engineering, processing and utilization of industrial brines and CO<sub>2</sub>. We have undertaken a detailed study of the volumetric properties of multicomponent electrolyte solutions over a wide range of temperatures, pressures, and compositions.

This experimental study provides the volumetric properties of KCl-NaCl and CaCl<sub>2</sub>-NaCl aqueous electrolyte solutions at temperatures up to 300 °C and pressures up to 400 bar for ionic strengths up to 5.8 and 12 m, respectively. A vibrating-tube densimeter was used to measure the relative density of aqueous solutions containing mixtures of alkali and alkali earth chlorides. Pressure, temperature and composition dependence of the density of binary mixtures were constrained. Mean apparent molar volume of the electrolyte solutions were calculated from the experimental data. A model based on a Pitzer-type equation was used to approximate the apparent molar volume of solutions and evaluate the partial molar volumes of dissolved components. The latter were compared to other mixing models predicting the properties of mixture of electrolytes from the properties of pure end-member electrolyte solutions.

The pressure- and concentration- dependence of the apparent molar volume may also provide important information about the structure of a solution and ionic interactions occurring in aqueous liquids. The pressure dependence of activity coefficients of dissolved components can be revealed from the variable pressure series of density measurements. Ultimately, 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 geochemically relevant systems.