Application of multiple S-isotope studies to understanding early Earth environments and biology

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The use of multiple sulfur isotopes to study biological signatures on the early earth has been a relatively recent development in geochemistry. This approach relies on the information about sulfur cycling that comes from determinations of $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$. During sulfate reduction, variations in $\delta^{34}S$ values arise because less energy is required to break sulfate bonds involving ^{32}S than to break bonds involving ^{34}S. Variations for $\Delta^{33}S$ and $\Delta^{36}S$ arise because of mixing and unmixing that occurs during metabolic processing by organisms such as dissimilatory sulfate reducers. On an early Earth, variations for $\Delta^{33}S$ and $\Delta^{36}S$ also were produced by mass independent processes. A key feature of measurements that include $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ is the prospect of disentangling mass dependent biological processing from mass dependent and mass independent abiological processing.

Several approaches have been developed in the past few years to tackle the issue of biological signatures in the sulfur isotope record. These include the use of paired sulfate – sulfide evaluated using sulfur cycle models; the use of microanalytical data provided by SIMS and nanoSIMS measurements; the experimental study of isotope effects produced by pure and mixed cultures of Bacteria and Archaea; and novel approaches that tie variations in isotopic compositions to specific depositional settings.

Work to date has provided evidence for sulfate reducers in the Paleoarchean, and it is not inconceivable that evidence from more ancient rocks will be forthcoming in the future. Recent work has also suggested that sulfate reducers played an important role in the Neoarchean, and may have expressed large fractionations that were masked by the processes associated with pyrite formation. Evidence for sulfur metabolisms in addition to sulfate reduction have been proposed in the early Archaean and Neoarchean. Work to understand, and disentangle, the role and importance of different types of sulfur metabolizing microbes on the early earth represents an important challenge that faces scientists today.

Experimental investigation of CO_2-water-rock interactions under simulated fresh-water aquifer conditions

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The geochemical effects of supercritical CO_2 (sc-CO_2) injection on a targeted fresh-water storage site [1] located in the Surat Basin, Queensland, Australia, were investigated using experimental reactions at simulated basin conditions. Samples from a potential reservoir, Precipice Sandstone, and from two overlying formations, Evergreen Formation and Hutton Sandstone, were mineralogically and petrographically characterised prior to submersion in purified water and exposure to sc-CO_2 at 12 MPa and 60 °C conditions for 16 days.

Fluids were sampled periodically and analysed for major and trace elements to deduce CO_2-water-rock interactions. These data were related to changes to pre-experiment sample mineralogy and texture, as observed using scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS).

Incremental fluid concentrations show an initial increase in most major (e.g., Fe, Ca, Mn, Mg, Si) and trace (e.g., Sr, Ba, Zn) elements over time, indicating dissolution of minerals during reaction. Increasing dissolved Ca, Mn and Sr (± Mg, Fe) are partly attributed to the dissolution of carbonate minerals, with higher concentrations observed in carbonate-rich samples; extensive carbonate dissolution in calcite-cemented samples is also observed in SEM-EDS.

Relative concentrations of analytes for incremental samples from the Precipice Sandstone experiments are generally considerably lower than those from the overlying Evergreen Formation and Hutton Sandstone, excluding Al and Si, reflecting the relatively clean mineralogy of the Precipice Sandstone. Small decreases in concentrations of several major elements (e.g., Fe, Ca, Mn, Al, Na) within the Evergreen Formation and Hutton Sandstone effluents towards the end of the experiments suggest the onset of mineral precipitation, which is supported by equilibrium modelling of geochemical reactions using the Geochemist's Workbench.

[1] Farquhar, Dawson, Esterle & Golding (2013), *Australian Journal of Earth Sciences* **60**, 91–110.

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