

**NEW CONSTRAINTS ON ARCHEAN  $p\text{CO}_2$  FROM CALCIUM ISOTOPE MEASUREMENTS IN MARINE CARBONATES.** C. L. Blättler and J. A. Higgins, Princeton University (Department of Geosciences, Guyot Hall, Princeton, NJ 08544, USA; blattler@princeton.edu).

Very few constraints exist on Archean seawater chemistry, leaving huge uncertainties on the boundary conditions for the evolution of life and a habitable environment. Ancient carbonate chemistry, which is intimately related to oceanic pH and atmospheric  $p\text{CO}_2$ , remains particularly uncertain, despite its importance for understanding environments and temperatures on early Earth. Using a new application of high-precision calcium isotope measurements, we present data from the Tumbiana Formation (2.7 Ga, Western Australia) that allows us to place constraints on carbonate chemistry in the Archean.

The calcium isotope system has been shown to undergo Rayleigh distillation in evaporitic sulfate deposits, producing constraints on the sulfate to calcium ratio ( $\text{SO}_4/\text{Ca}$ ) in the Phanerozoic [1]. Similar behavior is expected in carbonate minerals, depending on the ratio of dissolved inorganic carbon to calcium ( $\text{DIC}/\text{Ca}$ ). Under high  $\text{DIC}/\text{Ca}$  conditions, such as in Mono Lake, California, extreme volatility in calcium isotope ratios is observed [2]. Conversely, low  $\text{DIC}/\text{Ca}$  conditions are expected to result in stable calcium isotope ratios within marine carbonate sequences. Analysis of carbonates from the Tumbiana Formation yields a limited range of calcium isotope ratios, implying relatively low  $\text{DIC}/\text{Ca}$  at 2.7 Ga. These data place limits on the possible states of the carbonate system, which has implications for Archean  $p\text{CO}_2$ , the strength of the silicate weathering feedback, and solutions to the problem of the Faint Young Sun.

**References:** [1] Blättler C. L. and Higgins J. A. (2014) *Geology*, 42, 711–714. [2] Nielsen L. C. and DePaolo, D. J. (2013) *Geochimica et Cosmochimica Acta*, 118, 276–294.