Calcium isotopic ($\delta^{44/40}$Ca) fractionation between inorganic calcite and water: implications for paleothermometry and seawater Ca isotopic composition

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Stable calcium isotopic composition ($\delta^{44/40}$Ca) of natural biogenic carbonates (calcite and aragonite) shows a positive correlation with the temperature of the ambient seawater [c.f., 1]. However, in addition to seawater temperature, growth rate, pH, as well as vital effects can also affect $\delta^{44/40}$Ca of biogenic carbonates. To further evaluate the efficacy of $\delta^{44/40}$Ca as a paleo-temperature proxy, we have conducted calcite precipitation experiments in a controlled laboratory environment at 5, 10, 20, 30, 40 and 50°C. All precipitated samples were characterized using XRD. $\delta^{44/40}$Ca of the precipitates were measured using a ^{43}Ca-^{48}Ca double spike technique on a Thermo Fischer Triton Plus TIMS at the Centre for Earth Sciences, IISc. External reproducibility of our measurements are better than ±0.1‰, estimated by multiple measurements of NIST standards SRM915a and SRM915b and seawater (NASS6). $\delta^{44/40}$Ca (w.r.t. SRM915a) of the calcite samples range from -0.50 to +0.20 ‰ with $\delta^{44/40}$Ca increasing with increasing water temperature. The $\delta^{44/40}$Ca of the 50°C-precipitate overlaps with that of the starting $CaCO_3$ used for precipitation. Our preliminary results suggest that the variation in $\delta^{44/40}$Ca is ~0.01 ‰/°C which is consistent with earlier studies on inorganic calcite [2], inorganic aragonite [3] precipitations, as well as coral (aragonite) culture experiments [1]. Variation in $\delta^{44/40}$Ca in natural corals (*porites sp.*) are however higher (~0.09 ‰/^{0}C) [c.f., 4]. The limited variability of $\delta^{44/40}$Ca with temperature, and its high concentration in carbonates, thereby reducing the possibility of diagenetic alteration, makes $\delta^{44/40}$Ca in inorganic carbonates a powerful tool for understanding the evolution of Precambrian seawater composition.

[1] Gussone et al., (2005) *Geochimica et Cosmochimica Acta* 69.18: 4485-4494. [2] Marriott et al., (2004) *Earth and Planetary Science Letters* 222.2: 615-624. [3] Gussone et al., (2003) *Geochimica et Cosmochimica Acta* 67.7: 1375-1382. [4] Mondal S., Chakrabarti R., Ghosh P., (2016). *Goldschmidt conference Abstracts #2131,2016, Japan.*