Calcium isotope composition ($\delta^{44/40}Ca$) of bulk carbonate spanning Ocean Anoxic Event 2: kinetic effects or diagenesis?

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Calcium isotope ($\delta^{44/40}Ca$) records spanning Ocean Anoxic Event 2 (OAE2) show positive excursions on the order of 0.10‰-0.15‰[1]. Positive $\delta^{44/40}Ca$ excursions are consistent with a decrease in the magnitude of the carbonate fractionation factor due to decreased precipitation rates[1]. However, shifts to heavier $\delta^{44/40}Ca$ values may also represent early diagenetic alteration under fluid-buffered conditions[2,3]. To evaluate whether the excursions represent primary rate-dependent effects or secondary diagenetic alteration, we used a high-precision TIMS method[4] to generate Ca isotope data for two sections in the Western Interior Basin. We also measured carbon and oxygen isotope ratios ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$), as well as Sr/Ca ratios. Measurements for the Aristocrat-Angus-12-8 core capture a complete section leading into OAE2. DuVivier et al. (2015) previously reported $\delta^{44/40}Ca$ values for the USGS #1 Portland core. We analyzed the same samples for $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, as well as new samples for all four parameters.

The Angus Ca isotope record shows a positive excursion similar to the one documented for the Portland core[1]. Both excursions correspond with shifts to lower Sr/Ca ratios, which could reflect either decreased precipitation rates or diagenetic alteration. One sample from the Angus core has a $\delta^{13}C_{carb}$ value <0‰, but the corresponding $\delta^{44/40}Ca$ value is no higher than all other samples with $\delta^{13}C_{carb}$ values >0‰. Four Portland core samples with the highest $\delta^{44/40}Ca$ values correlate with $\delta^{13}C_{carb}$ values <0‰. These data, which DuVivier et al. (2015) excluded from consideration, may provide evidence for fluid-buffered diagenetic alteration. All other samples defining the positive $\delta^{44/40}Ca$ excursion have $\delta^{13}C_{carb}$ values >0‰, consistent with the range expected for primary carbonate deposited during OAE2. For the sections studied, we find that diagenesis manifests in discrete intervals and produces small $\delta^{44/40}Ca$ increases (0.10‰) that are resolvable with high-precision methods. Our results point to kinetic effects as the driver of the positive isotope excursions.

[1]DuVivier et al. (2015), EPSL [2]Higgins et al. (2018), GCA [3]Ahm et al. (2018), GCA, [3]Lehn et al., (2013), IJMS.