Calcium isotope evidence for environmental change before and across the K-Pg extinction

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The Cretaceous-Paleogene (K-Pg) mass extinction dramatically changed the composition of life on Earth. Release of CO_2 from the Deccan Traps eruption and the Chicxulub impact may have perturbed the C cycle during this time; however, the duration and intensity differed between the two events[1]. Rapid CO_2 injection causes transient decreases in seawater pH, [CO_3^{2-}], and carbonate mineral saturation states. These effects, collectively known as ocean acidification (OA), also impact the Ca cycle. On timescales shorter than the residence time of Ca in seawater, Ca isotope ratios ($\delta^{44/40}$Ca) are hypothesized to respond to OA through input/output flux imbalances [2], as well as changes in the carbonate fractionation factor [3].

To test for OA signals through the K-Pg, we used a high-precision TIMS method [4] to measure $\delta^{44/40}$Ca of well-preserved aragonitic mollusk shells that were previously analyzed for Δ_{47} [5]. The samples are from the López de Bertodano Formation on Seymour Island, Antarctica and span the late Maastrichtian to early Danian (~67-65.5 Ma [6]). $\delta^{44/40}$Ca values range from -1.89‰ to -1.57‰ (ASW). Below the K-Pg, a series of positive to negative to positive isotope shifts inversely correlate with carbonate weight percent (Wt%$_{carb}$) in deep sea sediment cores. A final negative shift initiates ~50 kyr before the K-Pg and continues across the boundary, while Wt%$_{carb}$ in some cores decreases but other sedimentological indicators suggest increased carbonate preservation [1].

Mass-balance modeling precludes flux imbalances as the primary explanation for the trends. The combined body of isotopic and sedimentological evidence suggests that the molluskan fractionation factor is sensitive to OA, however, the mechanism of $\delta^{44/40}$Ca fractionation in the process of biomineralization is incompletely understood.

[1] Henehan et al., 2016 Phil. Trans. R. Soc. B; [2] Fantle and DePaolo, 2005 EPSL; [3] Du Vivier et al., 2015 EPSL; [4] Lehn et al., 2013 IJMS; [5] Petersen et al., 2016 Nat. Comm.; [6] Tobin et al., 2012 PPP