Calcium isotope evidence for environmental variability before and across the Cretaceous-Paleogene mass extinction

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ABSTRACT
Carbon dioxide release during Deccan Traps volcanism and the Chixculub impact likely contributed to the Cretaceous-Paleogene (K-Pg) mass extinction; however, the intensity and duration of CO₂ input differed between the two events. Large and rapid addition of CO₂ to seawater causes transient decreases in pH, [CO₂²⁻], and carbonate mineral saturation states. Compensating mechanisms, such as dissolution of seafloor sediment, reduced biomineralization, and silicate weathering, mitigate these effects by increasing the same parameters. The calcium isotope ratios (δ⁴⁴/⁴⁰Ca) of seawater and marine carbonates are hypothesized to respond to these perturbations through weathering/carbonate deposition flux imbalances and/or changes in fractionation between carbonate minerals and seawater. We used a high-precision thermal ionization mass spectrometry method to measure δ⁴⁴/⁴⁰Ca values of aragonitic bivalve and gastropod mollusk shells from the K-Pg interval of the López de Bertodano Formation on Seymour Island, Antarctica. Well-preserved shells spanning the late Maastrichtian (ca. 67 Ma) to early Danian (ca. 65.5 Ma) have δ⁴⁴/⁴⁰Ca values ranging from −1.89% to −1.57% (seawater [sw]). Shifts in δ⁴⁴/⁴⁰Ca inversely correlate with sedimentological indicators of saturation state. A negative excursion begins before and continues across the K-Pg boundary. According to a simple mass-balance model, neither input/output flux imbalances nor change in the globally integrated bulk carbonate fractionation factor can produce variations in seawater δ⁴⁴/⁴⁰Ca sufficient to explain the measured trends. The data are consistent with a dynamic molluscan Ca isotope fractionation factor sensitive to the carbonate geochemistry of seawater. The K-Pg extinction appears to have occurred during a period of carbonate saturation state variability caused by Deccan volcanism.

INTRODUCTION
Debate persists about the causes of the Cretaceous-Paleogene (K-Pg) mass extinction. The bolide impact at Chixculub left a globally distributed iridium anomaly at the primary extinction horizon that is coincident with the rapid extinction of both terrestrial and marine organisms (Schulte et al., 2010; Lyson et al., 2011; Witts et al., 2016). Some propose that eruption of the Deccan Traps large igneous province (LIP) caused the extinction (Keller et al., 2009). Although LIP volcanism commonly corresponds with mass extinctions (Clapham and Renne, 2019), questions remain about the link between Deccan volcanism and the K-Pg extinction, given the timing and magnitude of eruptions (Schoene et al., 2019; Sprain et al., 2019).

Deccan volcanism released large quantities of CO₂ (Nordt et al., 2003), which likely caused warming (Petersen et al., 2016; Barnet et al., 2018) and ocean acidification (OA; Henehan et al., 2016; Dameron et al., 2017). OA, which encompasses transient decreases in pH, [CO₂²⁻], and carbonate mineral saturation states resulting from the large and rapid injection of CO₂ into the atmosphere-ocean system, may have caused extinctions throughout Earth history (Hönisch et al., 2012). Sedimentological indicators, such as reduced carbonate weight percent and increased planktic foraminiferal fragmentation, suggest eruption of the Deccan Traps forced OA before the K-Pg boundary (Henehan et al., 2016; Dameron et al., 2017). The bolide impact may have caused lesser and transient OA (e.g., 1–10 yr; Tyrrell et al., 2015). During and following OA, dissolution of seafloor carbonate (Ridgwell and Zeebe, 2005) and biological compensation (Boudreau et al., 2018) restore balance by neutralizing acidity and elevating alkalinity. Over longer timescales, silicate weathering plays a similar role (Ridgwell and Zeebe, 2005; Blättler and Higgins, 2017).

The calcium isotope system offers a valuable proxy for detecting OA in deep time (Payne et al., 2010). The δ⁴⁴/⁴⁰Ca values of seawater (δ⁴⁴/⁴⁰Ca,sw) and carbonate sediment are sensitive to the balance between weathering inputs and carbonate output (Fanite, 2010), carbonate mineralogy (Blättler et al., 2012), and changes in isotopic fractionation during primary carbonate mineral production (Du Vivier et al., 2015). To determine if Deccan volcanism or the bolide impact perturbed ocean carbonate chemistry, we measured the δ⁴⁴/⁴⁰Ca of aragonitic mollusks from Seymour Island, Antarctica (Fig. 1), that span the late Maastrichtian to the earliest Danian interval.

MATERIALS AND METHODS
Geological Setting
The López de Bertodano Formation was deposited in the James Ross Basin, in an open-ocean–facing shelf environment with water depths near 150 m (Huber, 1988). The formation consists of siliciclastic clays and silts with interbedded sand beds and carbonate concretions. Sedimentation rates were high (10–30 cm/k.y.; Tobin et al., 2012; Witts et al., 2015). We applied a linear age model between magnetostratigraphic reversals (C30r-C30n-C29r-C29n [r—reverse, n—normal]) and the K-Pg boundary horizon using Ar-Ar ages from Sprain et al. (2018). An age model uncertainty of ~13–40 k.y. was estimated by comparing the stratigraphic thicknesses of molluscan units (defined by Macellari, 1988) in measured sections (Tobin et al., 2012) with
those derived from plane projection (Zinsmeister, 2001). Correlation to other sections and the Deccan eruption estimates relied on the magnetostratigraphic reversal horizons and the K-Pg horizon, with linear age scaling between these horizons. For more explanation of the age model, see the extended description of the geological setting in the GSA Data Repository1.

Materials
Analyses included samples from 23 horizons. Most shells were from bivalves (Fig. 1; Table DR1 in the Data Repository) of the genera Lahilla (n = 26) and Cucullaea (n = 9). Two Amberleya gastropods and four samples of carbonate cement from sediment attached to shells were also measured (Fig. 2). Sampling of shells combined multiple years of growth (Petersen et al., 2016) and averaged potential seasonal variation in δ44/40Ca (Hippler et al., 2013). Lahilla and Cucullaea were shallow infauna that recorded δ44/40O from seawater rather than pore water (Hall et al., 2018), so shell δ44/40Ca most likely reflects a seawater source. Amberleya was a slow motile epifaunal surface deposit–feeding gastropod with similar characteristics (Witts et al., 2016).

Analytical Methods
Elemental and isotopic analyses were performed at Northwestern University (Illinois, USA). Elemental analyses by inductively coupled plasma–optical emission spectrometry (ICP-OES) have an uncertainty of ±5%. Calcium isotope ratios (δ44/40Ca) were measured using a high-precision 44Ca–40Ca double-spike thermal ionization mass spectrometry (TIMS) technique (Lehn et al., 2013). Results are reported in delta notation (Δ44/40Ca) relative to the Ocean Scientific International Ltd. (OSIL) seawater (SW) standard. During the period of study, analyses of OSIL SW and U.S. National Institute of Standards and Technology (NIST) 915b (calcium carbonate) yielded mean δ44/40Ca values of 0.000 ± 0.009‰ (2 standard error of the mean; SEM) and −1.130‰ ± 0.016‰ (2 SEM, n = 10). These results correspond to a short-term, external reproducibility of ±0.05‰ (2 standard deviation [SD]), which is the uncertainty adopted here. Replicate analyses of the same shells produced an average range of 0.03‰, and replicates of different shells within horizons produced an average range of 0.04‰. Radiogenic strontium isotope ratios (87Sr/86Sr) were also analyzed by TIMS (Andrews et al., 2016). Analyses of U.S. National Bureau of Standards (NBS) 987 (strontium carbonate) yielded a 87Sr/86Sr ratio of 0.710252 ± 0.000008 (2 SD, n = 5). See the extended analytical methods in the Data Repository for more details, as well as Tables DR4 and DR5 for TIMS and ICP-OES data.

RESULTS AND DISCUSSION
Sample δ44/40Ca values ranged between −2.25‰ and −0.82‰, with carbonate cement having much higher values than shells (Fig. 2A). Changes through stratigraphy also exist (Fig. 3A). Temperatures calculated from δ44/40Ca for 13 shells with paired analyses (Fig. 2B). Different mollusks from the same or closely spaced horizons yielded similar δ44/40Ca values (Fig. 3A), suggesting no species-specific “vital effects.” Variations in δ44/40Ca coincide with excursions in sedimentological indicators of carbonate saturation from globally distributed locations (Fig. 3C), which presumably reflect fluctuations in seawater pH and [CO32−] forced by volcanic CO2 emissions (Fig. 3E).

Diagenesis of δ44/40Ca in Mollusks
Diagenetic alteration of aragonitic mollusk shells can increase Sr/Ca and change O and Sr isotope ratios, even when original mineralogy is mostly preserved (Cochran et al., 2010). Three shells showing the highest Sr/Ca have lower δ44/40Ca than shells with low Sr/Ca from the same horizons (Fig. 2A; Fig. DR1). Diagenesis of aragonitic mollusk shells appears to affect δ44/40Ca differently compared to bulk carbonate sediments and microfossils, where progressive alteration decreases Sr/Ca and increases δ44/40Ca (Higgins et al., 2018). We excluded these shells with anomalously high Sr/Ca from further interpretation, similar to previous studies (Tobin et al., 2012; Petersen et al., 2016).

Controls on δ44/40Ca Variation Through Time
Secular Evolution of δ44/40Ca
One hypothesis to explain the observed record is that the mollusk fractionation factor...
(Δ44/40Ca_{shell-sw}) remained constant while Δ44/40Ca_{sw} changed (Fig. 4). Imbalances between calcium input and output fluxes, as well as changes in the isotope fractionation factor between seawater and globally integrated carbonate sediment, offer the most plausible mechanisms for shifting Δ44/40Ca_{sw} (Fantle, 2010). Seawater [Ca] values, and residence time by extension, determine the shape, magnitude, and duration of Δ44/40Ca_{sw} excursions (Fig. 4). Nearly uniform 87Sr/86Sr ratios through the study interval suggest stable weathering inputs (Fig. 3B), whereas variable carbonate weight percent (w%_carb) data from deep-sea cores indicate fluctuating carbonate output (Fig. 3C).

A simple flux-balance model forced by scaling the carbonate burial flux according to Ocean Drilling Program (ODP) Site 690 (southwestern flank of Maud Rise) w%_carb values produces maximum estimates of Δ44/40Ca_{sw} variation (Fig. 4; see the Data Repository for details). To establish an initial steady state, the weathering flux (F_w) was set equal to the carbonate burial flux, which was modeled as the total ocean Ca mass in moles (N_{Ca}) divided by residence time (τ_{Ca}). Ocean Ca values were set at the limits of estimated ranges for Late Cretaceous seawater (~10–50 mmol/kg; Lasaga et al., 1985; Wallmann, 2001), and residence time was scaled to maintain initial steady state with a fixed weathering flux. The carbonate output flux was then scaled by the carbonate weight percent (w%_carb) based on change from initial conditions (i) using smoothed data from ODP Site 690 (O’Connell, 1990; Ehrendorfer, 1993). The model equations are:

\[ \frac{dN_{Ca}}{dt} = F_w \cdot \frac{w_{Ca_{sh}} \cdot N_{Ca}}{\tau_{Ca}} \]  
\[ \frac{d(N_{Ca} \cdot \delta_{sw})}{dt} = F_w \cdot \delta_{sw} - (\delta_{sw} + \Delta_c) \]  

Figure 3. Stratigraphic distribution of δ44/40Ca values through the section at Seymour Island, Antarctica, compared to other local and global data sets. Horizontal dashed and dotted lines correspond to the initiation of Deccan Traps volcanism, a minor putative local extinction (Tobin, 2017), and the Cretaceous-Paleogene (K-Pg) boundary. (A) Mollusk δ44/40Ca values from samples in this study showing variation through time; same symbols as used in Figure 2: SW—seawater. (B) Minimal change in δ7Sr/δ8Sr suggests uniform weathering rates (this study; mollusk data from McArthur et al., 1998; Petersen et al., 2016). (C) Sedimentological indicators (carbonate wt%, coarse fraction, and foraminiferal fragmentation percent) of ocean acidification (OA) from Ocean Drilling Program (ODP) Site 690 (Maud Rise near Antarctica; data from Ehrendorfer, 1993; O’Connell, 1990) and Site 1209 (Shatsky Rise, equatorial Pacific; data from Westerhold et al., 2011; Henehan et al., 2016). (D) Seymour Island mollusk Δ_{w}-based temperatures (Petersen et al., 2016) and deep-sea foraminifera δ^{18}O-based temperatures (gray line) from ODP Site 1262 (Angola Basin; Barnet et al., 2018). (E) Flow volumes and timing from Sprain et al. (2019). Eruption rate and timing estimates are from Schoene et al. (2019).

Mollusk δ44/40Ca Fractionation Factor

If δ44/40Ca_{sw} did not significantly vary though this interval, then Δ44/40Ca_{sh-sw} must have changed (Fig. 4). Research examining carbonate precipitation predicts less fractionation, and hence positive Δ44/40Ca excursions, during decreased saturation and vice versa during increased saturation (Tang et al., 2008; Kiskürek et al., 2011; Nielsen et al., 2012; Mejía et al., 2018). The mollusk δ44/40Ca record illustrates such a pattern when evaluated against sedimentological proxies for saturation state (Figs. 3A and 3C). In mollusks, fractionation likely occurs during Ca transport into the extrapallial fluid (EPF) from which the shell precipitates, as some buffering of the EPF occurs across a range of seawater pH and pCO2 conditions (Heinemann et al., 2012). Ion-selective intracellular channels transport most of the Ca into the EPF, where biomimeralization rates regulate concentration gradients with surrounding seawater, which in turn control the magnitude of diffusive fluxes across membranes (Carré et al., 2006). Passive, nonselective intercellular pathway diffusion and active enzymatic (Ca\(^2+\)-ATPase and carbonic anhydrase) pumping may also elicit isotope fractionation (Carré et al., 2006). Carbonate chemistry could affect Δ44/40Ca_{sh-sw} by altering one pathway or changing the relative balance among the three, although the exact fractionation mechanisms remain unknown (Gussone et al., 2012).

Figure 4. Forward modeling of δ44/40Ca_{sw} (sw—seawater) variation across a range of [Ca] driven by flux imbalance. Seawater Ca concentrations for the Cretaceous-Paleogene (K-Pg) ranged from 9 to 50 mmol/kg (Lasaga et al., 1985; Wallmann, 2001). (A) Flux estimates based on scaled burial flux of carbonate (F_{Ca}) using carbonate content (w%_carb) at Ocean Drilling Program (ODP) Site 690 (Maud Rise near Antarctica) assuming constant weathering flux (F_w). (B) Modeled δ44/40Ca_{sh} compared to measured δ44/40Ca (gray line) showing that variation before the K-Pg was much larger than predicted from flux imbalances alone, and the excursion across the boundary is only partially predicted when low [Ca] values are assumed.
and Heuser, 2016; see the Data Repository for an extended discussion of biomineralization).

Implications for the Mass Extinction

Our high-precision $\delta^{44/40}$Ca record through the K-Pg mass extinction displays considerable complexity (Fig. 3A) driven by the response of biocalcifiers to volcanic CO$_2$ outgassing. In particular, the short time scales of carbonate saturation state variation point to biotic compensation rather than chemical compensation as the dampening mechanism to OA (Boudreau et al., 2018). The first positive excursion corresponds to deep-sea warming and may indicate reduced saturation from CO$_2$ outgassing that was independent of the size of Deccan flows (Fig. 3). The first negative excursion lags increased flow size (Fig. 3E) but coincides with increased carbonate export (Fig. 3C) and a local extinction identified by statistical analysis of fossil occurrences (Tobin, 2017).

The minor extinction may relate to water depth change (Witts et al., 2016). The second positive excursion indicates a return to lower saturation due to either biocalcification recovery or renewed OA. Volcanic CO$_2$ inputs may have prolonged this excursion and stressed biocalcifiers, eventually causing increased carbonate saturation and thereby the negative excursion that begins below the K-Pg boundary (Fig. 3A). If the foraminiferal “dissolution facies” of Huber (1988) is due to OA, then an additional positive $\delta^{44/40}$Ca excursion may be found in mollusks recovered from low in this interval. In total, our data suggest that Deccan volcanism perturbed ocean carbonate chemistry before and across the K-Pg boundary. We contend that Deccan volcanism and the Chicxulub impact may have coincided before and across the K-Pg boundary. We argue that the bolide impact coincided with preexisting carbon cycle instability resulting from Deccan volcanism and may have occurred during a phase of carbonate saturation increase due to biocalcification stress.

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CONCLUSIONS

Mollusk shells from Seymour Island, Antarctica, show analytically resolvable $\delta^{44/40}$Ca variations before and across the K-Pg boundary. We found that diagenetic alteration drives mollusk aragonite $\delta^{44/40}$Ca lower—rather than converging on cement calcite values. Neither temperature nor species-specific vital effects explain the changes in the $\delta^{44/40}$Ca of well-preserved shells. Similarly, neither input/ output flux imbalances nor changes in the global fractionation factor ascribed to bulk carbonate sediment can reproduce shifts in the mollusk record, given high Late Cretaceous seawater Sr concentrations, as well as the geologically instantaneous time scale over which the shifts occurred. We propose that mollusk $\Delta^{44/40}$Cd(tot,vs) is dynamic. Negative $\Delta^{44/40}$Cd shifts coincide with globally distributed sedimentological indicators of increased carbonate mineral saturation and vice versa for positive shifts. Calcium isotope variability before and crossing the K-Pg boundary suggests that the bolide impact coincided

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