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Subannual stable isotope records reveal climate warming and seasonal anoxia associated with two extinction intervals across the Cretaceous-Paleogene boundary on Seymour Island, Antarctica

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ABSTRACT

High-resolution stable isotope ($\delta^{18}O$ and $\delta^{13}C$) sclerochronology of accretionary carbonate bivalve shells can provide subannual environmental records useful for understanding intervals of extinction, which are commonly periods of rapid change and instability. Here, we present results from high-resolution serial sampling of *Lahillia larseni* bivalve shells across the Cretaceous-Paleogene boundary (KPB) on Seymour Island, Antarctica. These data highlight two intervals of anomalous $\delta^{18}O$ and $\delta^{13}C$ values that coincide with condensed fossil last occurrences: one at the KPB and one at an apparent extinction event 150 k.y. earlier. We interpret these two intervals to represent periods of both climate warming, as indicated by lower $\delta^{18}O$, and seasonal anoxia or euxinia, as evidenced by anomalously low (–21.6% to –3.0% VPDB [Vienna Peedee belemnite]) $\delta^{13}C$ values with high (2% to 19% in magnitude) seasonal variation. Low-oxygen conditions may have acted as a kill mechanism at the earlier extinction interval and possibly prolonged recovery from the KPB extinction.

INTRODUCTION

The Cretaceous-Paleogene (K-Pg) boundary (KPB) is defined by the presence of asteroid ejecta (Molina et al., 2006) resulting from the Chicxulub bolide impact (offshore Yucatán, Mexico), which was a major contributor to the K-Pg mass extinction (Schulte et al., 2010). The environmental effects of this collision may have been exacerbated by the ongoing eruption of the Deccan Traps large igneous province (India) across the KPB (Archibald et al., 2010), though the relative timing of these two events remains in dispute (Schoene et al., 2019; Sprain et al., 2019). Both phenomena could have significantly perturbed global atmospheric and oceanic conditions across this time interval, albeit at different magnitudes and time scales. Subannual environmental records can detail the seasonal variation inherent in climatic changes during this period of instability.

Seymour Island, Antarctica, is an important high-paleolatitude site for studying both secular

temperature change and seasonal environmental variations. The polar response to global climate change in the Late Cretaceous is poorly understood (Tabor et al., 2016), and the magnitude of seasonal temperature and productivity variations were likely large (Winder and Cloern, 2010). Recent studies on Seymour Island have found evidence for distinctive seasonal processes in this environment, including intermittent euxinia (Schoepfer et al., 2017) and seasonal fluxes of biogenic methane (Hall et al., 2018). The relatively high sedimentation rate (10–20 cm/k.y.) at Seymour Island also allows the K-Pg interval to be studied at a high temporal resolution (Macellari, 1988; Tobin et al., 2012).

The accretionary carbonate shells of bivalve mollusks precipitate in equilibrium with their environment, preserving subannual records of climate and other environmental conditions during their life spans, which can be accessed via high-resolution serial sampling and stable isotope ($\delta^{18}O$ and $\delta^{13}C$) analysis (e.g., Ivany, 2012). In this study, we use this approach on aragonitic shells of *Lahillia larseni*, an infaunal bivalve

from Seymour Island. We incorporate additional data (Petersen et al., 2016; Hall et al., 2018) to produce a high-resolution single-species record of subannual environmental signals across the KPB that contains evidence for intervals of seasonal shelf anoxia associated with faunal turnover.

GEOLOGIC SETTING

The López de Bertodano Formation on Seymour Island (Fig. 1) comprises an expanded, highly fossiliferous succession of shallow marine sediments (Macellari, 1988; Olivero, 2012) that are Maastrichtian to Danian in age (Tobin et al., 2012). The paleoenvironment was a shallow marine shelf with water depths <200 m (Macellari, 1988) located at a latitude of 62°S during the Late Cretaceous (Tobin et al., 2012). Though traditionally interpreted as an oxygenated and open-marine shelf due to the presence of a fully marine fauna (e.g., Macellari, 1988; Crame et al., 2004), analyses of pyrite framboids and trace element enrichments provide evidence for conditions that fluctuated between oxic and euxinic at the sediment-water interface throughout this interval (Schoepfer et al., 2017). The molluscan fossils of the López de Bertodano Formation are known to be well preserved and have successfully been used in a variety of isotopic studies aimed at reconstructing paleoenvironmental conditions during this interval (e.g., Tobin et al., 2012: Petersen et al., 2016: Witts et al., 2018; Hall et al., 2018).

METHODS

We collected 20 specimens of *L. larseni* from a measured stratigraphic section of units 8–10 of the López de Bertodano Formation on

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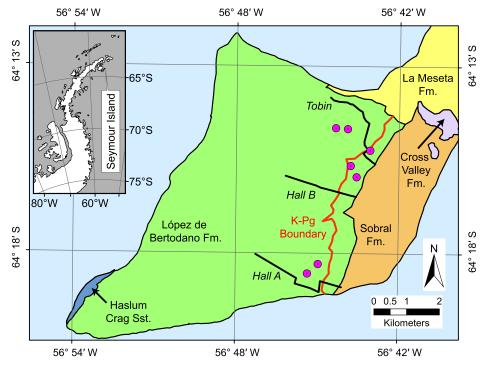


Figure 1. Simplified geological map of Seymour Island, Antarctica, after Schoepfer et al. (2017) and Montes et al. (2019), with black lines indicating stratigraphic sections. Shells sampled for this study were collected either along the stratigraphic section of Tobin et al. (2012), labeled "Tobin" (those analyzed at University of Alabama, USA), or from localities represented by purple dots (those analyzed at University of Michigan, USA). Shells sampled by Hall et al. (2018) are from stratigraphic sections labeled "Hall A" and "Hall B." Fm.—Formation; Sst.—Sandstone.

Seymour Island during field seasons from 2009 to 2016 (Fig. 1) and analyzed them at the University of Alabama (UA; Tuscaloosa, Alabama, USA). Two smaller sets of specimens were collected by William Zinsmeister and analyzed at the University of Michigan (UM; Ann Arbor, Michigan, USA): five specimens from a doctoral thesis (Dutton, 2003) and five newly analyzed (see the Supplemental Material¹). All of the samples were placed in their stratigraphic context with respect to the well-defined KPB, which also allowed us to correlate our data with previous data collected from L. larseni shells (Petersen et al., 2016; Hall et al., 2018), an approach that is robust within 100 m of this boundary (Schoepfer et al., 2017). The combined data span a stratigraphic interval of 298 m, representing a period of ~2.3 m.y., and present a record of environmental conditions and (minimum) seasonal variability across the KPB (Figs. 2-3).

Diagenesis was assessed by evaluating shell microstructure with scanning electron microscopy (Knoll et al., 2016; Figs. S1–S4) and analyzing shell mineralogy and trace element concentration (see the Supplemental Material).

High-resolution (subannual) serial sampling (>28 samples/cm; in total spanning 1–3 yr of growth) was conducted on 16 shells using a computerized micromill (Fig. 4; Figs. S5–S6), usually targeting toward the middle of each valve (see Table S1 in the Supplemental Material). Low-resolution sampling (~1–2 samples/ cm; in total spanning 5–15+ yr of growth) was conducted on 14 shells. Sample powders and isotopic standards were analyzed using standard methods at both UA and UM (see the Supplemental Material). Paleotemperatures were calculated from δ^{18} O values (Kim et al., 2007), assuming a -1.2% oVSMOW (Vienna standard mean ocean water) seawater value for an icefree world (Shackleton and Kennett, 1975), with an applied correction for latitude (Zachos et al., 1994).

RESULTS

The subannual ontogenetic $\delta^{13}C$ profiles from our analyzed shells exhibited clear episodic patterns, with nearly all shells recording $\delta^{13}C$ minima near the dark growth band separating each growth increment (Fig. 4). The shell $\delta^{13}C$ patterns fell in two general types: most (10 of 16) of the shells had $\delta^{13}C$ variations <2.0% in magnitude and average values between -1.3% and 2.4% VPDB, but some ontogenetic profiles exhibited anomalously low $\delta^{13}C$ values (as low as -21.6% VPDB) and large seasonal variations of as much as 7.7% in magnitude (profile

UWBM-107343-A had a 19.1% seasonal range, but excluding a single measurement yielded a 7.6% range). The cuspate nature of the δ^{13} C records implies that the growth bands mark seasonal growth terminations, as assumed previously (Moss et al., 2017). The subannual ontogenetic δ^{18} O profiles of *L. larseni* shells (Fig. S6) show little to no seasonal variation (maximum range, 2.3%; median range, 0.9‰).

Our $\delta^{\scriptscriptstyle 13}C$ and $\delta^{\scriptscriptstyle 18}O$ data correlate well with previously published work (Petersen et al., 2016; Hall et al., 2018) where the data sets overlap (Fig. 2). A LOESS (locally estimated scatterplot smoothing) regression through the composite stratigraphic record (Fig. 2) reveals two intervals (intervals I and II) where δ^{13} C values are lower than expected in a well-mixed ocean (Kroopnick, 1985). These intervals also contain low δ^{18} O values when compared to "background" values outside of these intervals. While comparative statistics are artificially controlled by the selection of interval bounds, Tukey-Kramer post hoc pairwise tests (on Kruskal-Wallis test results) for all analyses do show that the intervals are clearly distinct from each other and from the background for both δ^{13} C and δ^{18} O, with one exception (p = 0.21 for δ^{18} O between interval I and background; $p < 10^{-6}$ for δ^{18} O between intervals I and II; $p < 10^{-9}$ for all other comparisons). The two intervals correspond with previously identified horizons of condensed fossil last occurrences (LOs), which may represent periods of increased extinction (Tobin, 2017). The first interval (interval I) occurs ~67–48 m below the KPB (ca. 66.3–66.2 Ma) and is concurrent with the initiation of major Deccan Traps eruptions (Schoene et al., 2019; Sprain et al., 2019), while the second (interval II) is concurrent with the KPB (ca. 66.1-65.9 Ma).

DISCUSSION

Subannual δ¹⁸O and δ¹³C Records

Assuming a consistent seawater $\delta^{18}O$ ($\delta^{18}O_w$) value, the best explanation for the minimal seasonal $\delta^{18}O$ variation in *L. larseni* shells at a high-paleolatitude location is that the habitat is at water depths where the seasonal temperature variation is muted or absent (e.g., Ivany, 2012), likely the middle to outer shelf.

The low-variation (<2.0%) δ^{13} C profiles are consistent with the magnitude of δ^{13} C variation in the dissolved inorganic carbon (DIC) pool expected as a result of seasonal productivity in a high-latitude environment (Barrera et al., 1994). The seasonal pattern in the ontogenetic δ^{13} C profiles suggests that these shells grew for a significant portion of the year despite largely invariant δ^{18} O profiles.

The ontogenetic $\delta^{13}C$ profiles with high-magnitude variation and anomalously low $\delta^{13}C$ values were similar to those previously reported from subannual sampling of a few *L. larseni* shells by Hall et al. (2018). They interpreted these profiles

^{&#}x27;Supplemental Material. Supplemental Figures S1–S9, Table S1, Tables S2–S4 as raw data in Excel file, and additional methodological text. Please visit https://doi.org/10.1130/GEOL.S.12620630 to access the supplemental material, and contact editing@geosociety.org with any questions.

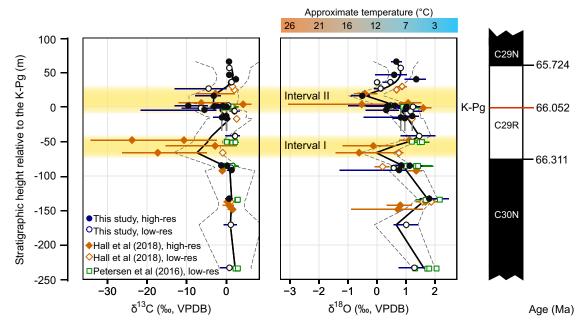


Figure 2. Stratigraphic plots of mean carbon or oxygen isotope values for each specimen of Lahillia larseni. Magnetostratigraphy is from Tobin et al. (2012), and age model is from Sprain et al. (2018). Blue circles represent data from L. larseni shells sampled in this study. Orange diamonds (Hall et al., 2018) and green squares (Petersen et al., 2016) represent previously published data from L. larseni shells. Solid symbols indicate shells sampled at high (subannual) ontogenetic resolution, and open symbols indicate shells sampled at low resolution. Horizontal range bars indicate total range of isotopic values recorded in each shell. Vertical error

bars indicate stratigraphic uncertainty for each shell and are in most cases smaller than the symbol representing each data point. Pale yellow rectangles represent the durations of intervals I and II. LOESS (locally estimated scatterplot smoothing) curve (black line, span = 0.25) is fitted through the average values for each shell, with dashed lines indicating the window of error. K-Pg—Cretaceous-Paleogene boundary; VPDB—Vienna Peedee belemnite; res—resolution.

to record a seasonal contribution of 13C-depleted carbon to the bottom-water DIC pool via oxidation products of biogenic methane, which we agree is the most likely explanation for anomalously low $\delta^{13}C$ values in both data sets. The production of significantly 13C-depleted biogenic methane (-50% to -110%; Whiticar, 1999), known as methanogenesis, can occur in highly anoxic or euxinic environments, commonly as a response to a large influx of organic carbon (e.g., Zhang et al., 2008). The subsequent oxidation of the methane in less-reducing conditions releases ¹³C-depleted carbon into the bottom-water DIC pool, where it is incorporated into bivalve shells. The large variation in $\delta^{13}C$ values within a single growing season of L. larseni therefore suggests the presence of seasonally fluctuating redox conditions and seasonal fluxes of organic carbon, which may have been driven by the annual bloom of primary producers or supply of terrestrial carbon from spring meltwater runoff.

Stratigraphic δ¹⁸O and δ¹³C Trends

The co-occurrence of lower $\delta^{18}O$ and $\delta^{13}C$ values in intervals I and II can be attributed to climate warming, which would have decreased $\delta^{18}O$ values by directly increasing water temperatures. Warming can drive water-column stratification and reduce oxygen solubility, leading to anoxic or euxinic bottom-water conditions and subsequent methanogenesis (Keeling et al., 2010), resulting in decreased $\delta^{13}C$ values as described above. Alternatively, abrupt shallowing could increase the flux of low- $\delta^{18}O_{\rm w}$ continental water containing significant organic material, directly decreasing both $\delta^{18}O$ and $\delta^{13}C$ values,

but there is no sedimentological support for facies variation in this section (Crame et al., 2004).

It is possible for fossil LOs to be condensed by facies changes or sedimentary hiatuses (e.g., Holland and Patzkowsky, 2015) instead of by increased extinction rates. Abrupt shallowing at either interval I or II could have provided both the facies change and possibly the sedimentary hiatus (erosional) necessary to condense LOs. A regression coincident with interval I was proposed previously, but its recognition was largely based on a faunal shift (Macellari, 1988) and was notably not recognized in later work (Crame et al., 2004). Tobin (2017) argued that a biological event was more likely, as no sedimentological changes indicative of

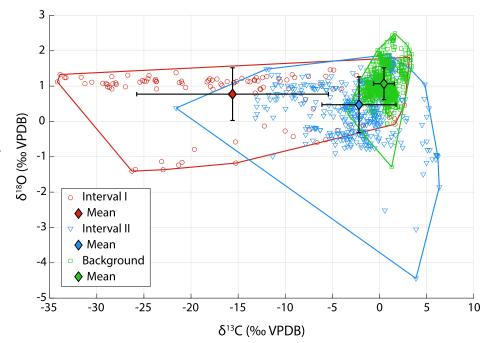


Figure 3. Isotope crossplot for all analyses, differentiated between intervals I (red circles) and II (blue triangles) and background (green squares). Means (diamonds) and 1₀ error bars for each group are outlined in black; convex hulls for each group are plotted as solid lines. VPDB—Vienna Peedee belemnite.

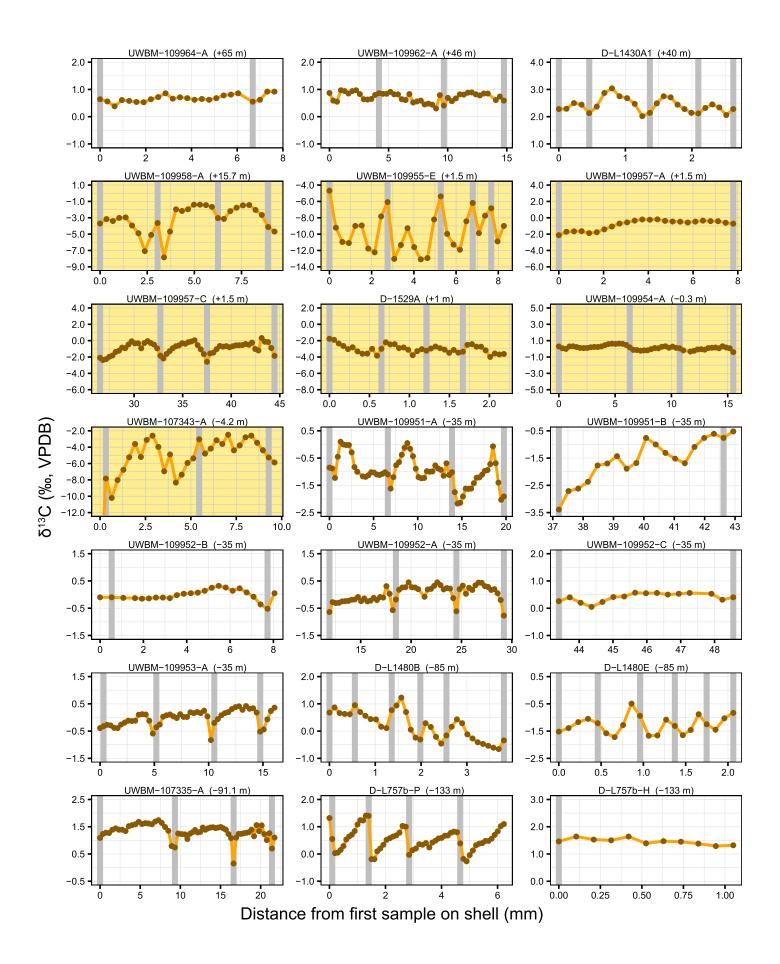


Figure 4. Ontogenetic carbon isotope profiles of Lahillia larseni shells sampled at high (subannual) resolution, labeled with the profile identifier and stratigraphic height of the sample in meters relative to the Cretaceous-Paleogene boundary. Vertical gray bars indicate locations of visually distinct dark growth bands separating annual growth increments. Direction of growth is from left to right in all plots. Samples occurring within interval Il are highlighted with a yellow background and have y-axes with a range of 10 ... All other samples have y-axis ranges of 3‰. Note that the first data point on profile UWBM-107343-A (-21.6%) falls outside the visible plotted area. VPDB—Vienna Peedee belemnite.

a facies change or hiatus were observed over the interval I duration. Given the lack of sedimentological evidence for an abrupt facies change, we believe a period of increased extinction driven by euxinia and coincident with warming is the most likely explanation for the condensed LOs at interval I. Interestingly, the case for LOs to be condensed by a sedimentary hiatus is much stronger at the KPB, which is located in the middle of a glauconitic sand layer. Considering the global context and presence of impact ejecta in this layer (Elliot et al., 1994), a geologically abrupt extinction is still the best explanation for condensed fossil LOs at interval II.

The correlation of interval I with the onset of Deccan Traps volcanism (Schoene et al., 2019; Sprain et al., 2019) suggests that this isotopic anomaly records a local environmental response (methane release and oxidation in seasonally euxinic bottom waters) to global atmospheric changes (including warming) resulting from volcanic degassing. Euxinic bottomwater conditions can be toxic to many fauna, particularly benthic mollusks, and have been implicated as a kill mechanism in other extinction events (e.g., Wignall and Twitchett, 1996; Zou et al., 2018). Almost all the fauna with LOs in interval I are restricted to the sedimentwater interface, consistent with euxinia as a kill mechanism, implicating the Deccan Traps as the cause of extinction at interval I on Seymour Island. However, during interval II (i.e., the KPB), the LOs are dominated by mobile demersal organisms (mostly ammonites; Tobin, 2017), indicating that despite the return of euxinic bottom waters, a different kill mechanism related to the Chicxulub impact is required here, though a low-oxygen environment may have affected post-extinction recovery. Notably, δ^{13} C values recorded during interval II are not as low as those during interval I (Fig. 3), implying that methanogenesis was present but weaker around the KPB. Warming in interval II was similar to post-impact warming following the KPB observed in the Northern Hemisphere (MacLeod et al., 2018), suggesting that this signal is global.

CONCLUSION

The periods of warming and seasonal euxinia we observe in intervals I and II may have been phenomena limited to Seymour Island, but it is possible that they are the local expression of global events that are only recorded at this location due to the high stratigraphic resolution. Interval I in particular may be a unique polar response to Deccan Traps eruptions that is not present at lower latitudes. Our isotopic evidence suggests it is likely that both the Deccan Traps and the Chicxulub impact contributed to the overall faunal turnover associated with the KPB on Seymour Island.

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