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Evidence for end-Permian ocean acidification from calcium isotopes in biogenic apatite

Jessica L. Hinojosa^{1*}, Shaun T. Brown², Jun Chen³, Donald J. DePaolo^{2,4}, Adina Paytan⁵, Shu-zhong Shen⁶, and Jonathan L. Payne¹

¹Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA

²Center for Isotope Geochemistry, Earth Science Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Guangzhou 510640, China

⁴Department of Earth and Planetary Science, University of California, Berkeley, California 94720, USA

⁵Institute of Marine Sciences, University of California, Santa Cruz, California 95064, USA

⁶State Key Laboratory of Palaeontology and Stratigraphy, Nanjing Institute of Geology and Palaeontology, Nanjing 210008, China

ABSTRACT

End-Permian (ca. 252 Ma) carbon isotope, paleobiological, and sedimentary data suggest that changes in ocean carbonate chemistry were directly linked to the mass extinction of marine organisms. Calcium isotopes provide a geochemical means to constrain the nature of these changes. The $\delta^{44/40}\text{Ca}$ of carbonate rocks from southern China exhibits a negative excursion across the end-Permian extinction horizon, consistent with either a negative shift in the $\delta^{44/40}\text{Ca}$ of seawater or a change in the calcite/aragonite ratio of carbonate sediments at the time of deposition. To test between these possibilities, we measured the $\delta^{44/40}\text{Ca}$ of hydroxyapatite conodont microfossils from the global stratotype section and point (GSSP) for the Permian-Triassic boundary at Meishan, China. The conodont $\delta^{44/40}\text{Ca}$ record shows a negative excursion similar in stratigraphic position and magnitude to that previously observed in carbonate rocks. Parallel negative excursions in the $\delta^{44/40}\text{Ca}$ of carbonate rocks and conodont microfossils cannot be accounted for by a change in carbonate mineralogy, but are consistent with a negative shift in the $\delta^{44/40}\text{Ca}$ of seawater. Such a shift is best accounted for by an episode of ocean acidification, pointing toward strong similarities between the greatest catastrophe in the history of animal life and anticipated global change during the twenty-first century.

INTRODUCTION

Paleobiological, geochemical, and sedimentary records from strata spanning the end-Permian mass extinction indicate a link between the biotic crisis and perturbation of seawater carbonate chemistry. Evidence includes preferential extinction of heavily calcified marine organisms (Knoll et al., 1996, 2007; Kiessling and Simpson, 2011; Clapham and Payne, 2011), negative excursions in the $\delta^{13}\text{C}$ of carbonate rocks and organic carbon across the boundary (reviewed in Korte and Kozur, 2010), and an abrupt transition on carbonate platforms from skeletal to microbial and abiotic carbonate factories (reviewed in Kershaw et al., 2011).

Several scenarios have been proposed to account for these observations, including upwelling of anoxic and sulfidic waters in a physically or chemically stratified ocean (Knoll et al., 1996; Kump et al., 2005), carbon release from sediments resulting in accelerated weathering and ocean acidification (Payne et al., 2007; Erwin, 2006), or a drastic reduction in marine primary productivity following the mass extinction (Rampino and Caldeira, 2005). Because each of the above hypotheses can account for the abrupt negative excursion in the $\delta^{13}\text{C}$ record of carbonate rocks ($\delta^{13}\text{C}_{\text{carb}}$), for the selective extinction of heavily calcified marine animals,

and for the abrupt transition in carbonate facies across the extinction horizon, an additional proxy is necessary to distinguish among these options.

Calcium isotopes hold promise for differentiating between suggested scenarios for change in seawater carbonate chemistry linked with the end-Permian extinction. The calcium cycle is linked to the carbon cycle through the weathering of limestone and the deposition of calcium carbonate sediments. Calcium isotopes fractionate by $\sim 0.6\text{‰}$ and $\sim 1.3\text{‰}$ in calcite and aragonite, respectively, during the precipitation of modern carbonate minerals, meaning carbonate sediments are enriched in the lighter isotope relative to the seawater from which they precipitated (Skulan et al., 1997; Tang et al., 2008). Imbalances between calcium delivery and burial fluxes and changes in the magnitude of fractionation during carbonate deposition will result in changes in the $\delta^{44/40}\text{Ca}$ of seawater and will be recorded in marine sediments (DePaolo, 2004; Farkaš et al., 2007). Therefore, variation in the $\delta^{44/40}\text{Ca}$ of seawater can provide an additional constraint on temporal variation in seawater carbonate chemistry.

Changes in the oceanic $\delta^{44/40}\text{Ca}$ resulting from the various proposed scenarios for end-Permian global change are expected to differ: collapse of the biological pump would cause a very minor negative $\delta^{44/40}\text{Ca}$ excursion; an

ocean overturn scenario associated with an increased carbonate depositional flux (Knoll et al., 1996) would cause a positive $\delta^{44/40}\text{Ca}$ excursion; and ocean acidification would cause a potentially large negative $\delta^{44/40}\text{Ca}$ excursion by reducing the carbonate depositional flux and increasing the calcium weathering flux (Fig. 1) (Payne et al., 2010). Calcium has a residence time in the ocean of ~ 1 m.y., which is long enough for it to be isotopically homogeneous, both globally and with depth (Farkaš et al., 2007), and there is no measurable spatial variation in $\delta^{44/40}\text{Ca}$ in the modern ocean (De La Rocha and DePaolo, 2000). Fluid inclusion data indicate that [Ca] during the Late Permian to Early Triassic was similar to modern [Ca] (~ 10 mM) (Horita et al., 2002).

Existing calcium isotope data from marine carbonates spanning the Phanerozoic have low temporal resolution (Farkaš et al., 2007), but a higher-resolution record exists for the Permian-Triassic (P-Tr) boundary from a stratigraphic section at Dajiang in southern China. The high-resolution $\delta^{44/40}\text{Ca}$ of carbonate rocks ($\delta^{44/40}\text{Ca}_{\text{carb}}$) exhibits a negative excursion of $\sim 0.3\text{‰}$ across the end-Permian extinction horizon, consistent with the ocean acidification hypothesis (Payne et al., 2010). However, a change in the dominant carbonate mineralogy at the time of deposition could also explain this observation because aragonite and calcite differ in calcium isotope fractionation relative to seawater by up to 0.6‰ (Gussone et al., 2005).

The three scenarios compatible with the $\delta^{44/40}\text{Ca}_{\text{carb}}$ record make differing predictions for stratigraphic variation in $\delta^{44/40}\text{Ca}$ of seawater ($\delta^{44/40}\text{Ca}_{\text{sw}}$), which would be recorded in biogenic apatite ($\delta^{44/40}\text{Ca}_{\text{conodont}}$) (Fig. 1). If the $\delta^{44/40}\text{Ca}_{\text{carb}}$ reflects a change in the isotope composition of seawater, then the $\delta^{44/40}\text{Ca}_{\text{conodont}}$ should also exhibit a negative shift of similar magnitude at the same stratigraphic position. If the $\delta^{44/40}\text{Ca}_{\text{carb}}$ excursion results from a local shift in carbonate mineralogy, there would be no change in $\delta^{44/40}\text{Ca}_{\text{sw}}$ and, therefore, no change in the $\delta^{44/40}\text{Ca}$ of conodonts. If the $\delta^{44/40}\text{Ca}_{\text{carb}}$ shift were the result of a global change in the calcite/aragonite ratio (also expressed locally) and

*E-mail: jess.l.hinojosa@gmail.com.

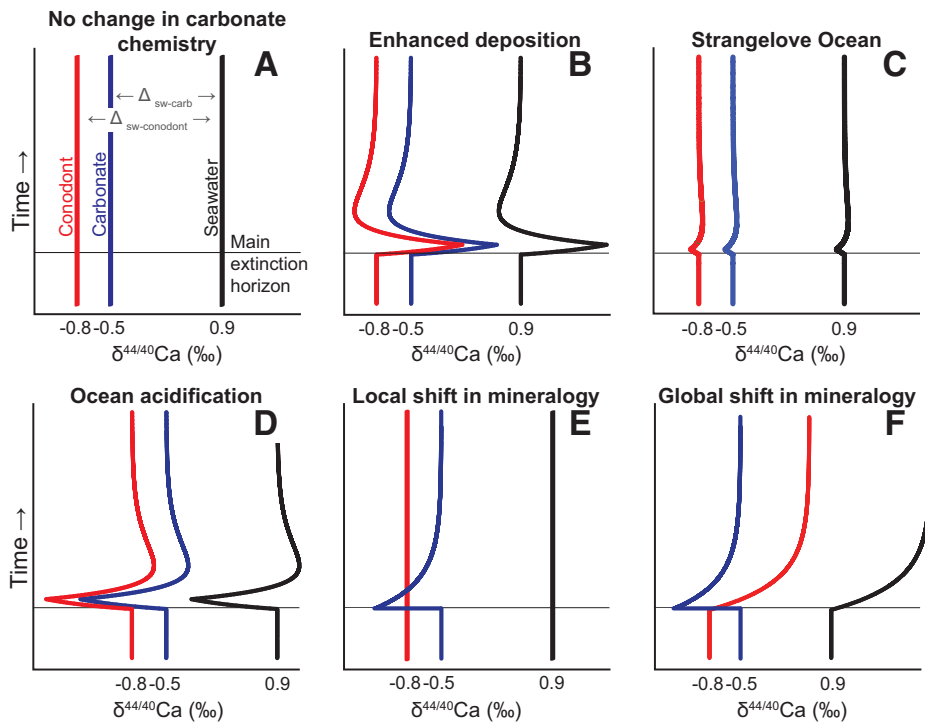


Figure 1. Predicted variation in the $\delta^{44/40}\text{Ca}$ of seawater, bulk carbonate sediments, and conodont microfossils under six potential scenarios for the end-Permian mass extinction. **A:** No perturbation. The $\delta^{44/40}\text{Ca}$ records would remain unchanged across the main extinction horizon. Δ values indicate relative fractionations between seawater and conodonts and carbonates. **B:** Ocean overturn. A shoaling of alkaline deep waters associated with increased carbonate precipitation would cause positive excursions in all three $\delta^{44/40}\text{Ca}$ records. **C:** Collapse of the biological pump. Changes in the vertical distribution of dissolved inorganic carbon would lead to a brief initial decrease in carbonate precipitation observed in all three $\delta^{44/40}\text{Ca}$ records. **D:** Ocean acidification. Rapid addition of CO_2 to the atmosphere would result in decreased carbonate saturation, causing a large decrease in carbonate deposition accompanied by increased weathering resulting in negative excursions for all three $\delta^{44/40}\text{Ca}$ records. **E:** Local shift in carbonate mineralogy. If local carbonate precipitation switched between carbonate polymorphs, the $\delta^{44/40}\text{Ca}_{\text{carb}}$ record could show a negative excursion, but the $\delta^{44/40}\text{Ca}$ of seawater and conodonts would remain unchanged because the global isotopic value of seawater would not be altered by the local shift. **F:** Global shift in carbonate mineralogy. If the mineralogical shift were a global event, the oceanic reservoir of calcium would become depleted in ^{40}Ca , causing seawater and conodonts to incorporate heavier calcium, resulting in a shift to a more positive $\delta^{44/40}\text{Ca}$ steady state, and $\delta^{44/40}\text{Ca}_{\text{carb}}$ would exhibit a negative excursion. For information on model construction, see the Data Repository (see footnote 1).

^{40}Ca were preferentially precipitated out of the ocean, then $\delta^{44/40}\text{Ca}_{\text{sw}}$ and $\delta^{44/40}\text{Ca}_{\text{conodont}}$ would trend toward heavier values, eventually reaching a new steady state.

MATERIALS AND METHODS

To assess whether the $\delta^{44/40}\text{Ca}_{\text{carb}}$ record reflects global ocean acidification versus a local or global mineralogical shift, we measured the $\delta^{44/40}\text{Ca}$ of hydroxyapatite conodont microfossils from the Meishan section in southeastern China across the P-Tr boundary interval. The strata from Beds 22–30, spanning ~3.5 m, were deposited in a shallow carbonate ramp located within the Lower Yangtze block in the northern part of the eastern Tethys at a paleolatitude of 20°N (Yin et al., 2005). Because biogenic apatite is not a major sink for calcium, it can serve as a passive tracer of seawater composition, assuming that the conodont-associated fraction-

ation does not change significantly over time. Moreover, these phosphatic microfossils are less likely than calcite to be affected by dissolution during ocean acidification events, making them robust recorders of $\delta^{44/40}\text{Ca}$ variations in paleoseawater.

$\delta^{44/40}\text{Ca}$ was determined by thermal ionization mass spectrometry using a double-spiked solution. All values are reported in $\delta^{44/40}\text{Ca}$ (‰) relative to bulk Earth, which yields a $\delta^{44/40}\text{Ca}$ of approximately -1.0‰ relative to reference material NIST915A and a $\delta^{44/40}\text{Ca}$ value of $+0.9\text{‰}$ for standard mean ocean water (SMOW) (Simon and DePaolo, 2010).

RESULTS AND DISCUSSION

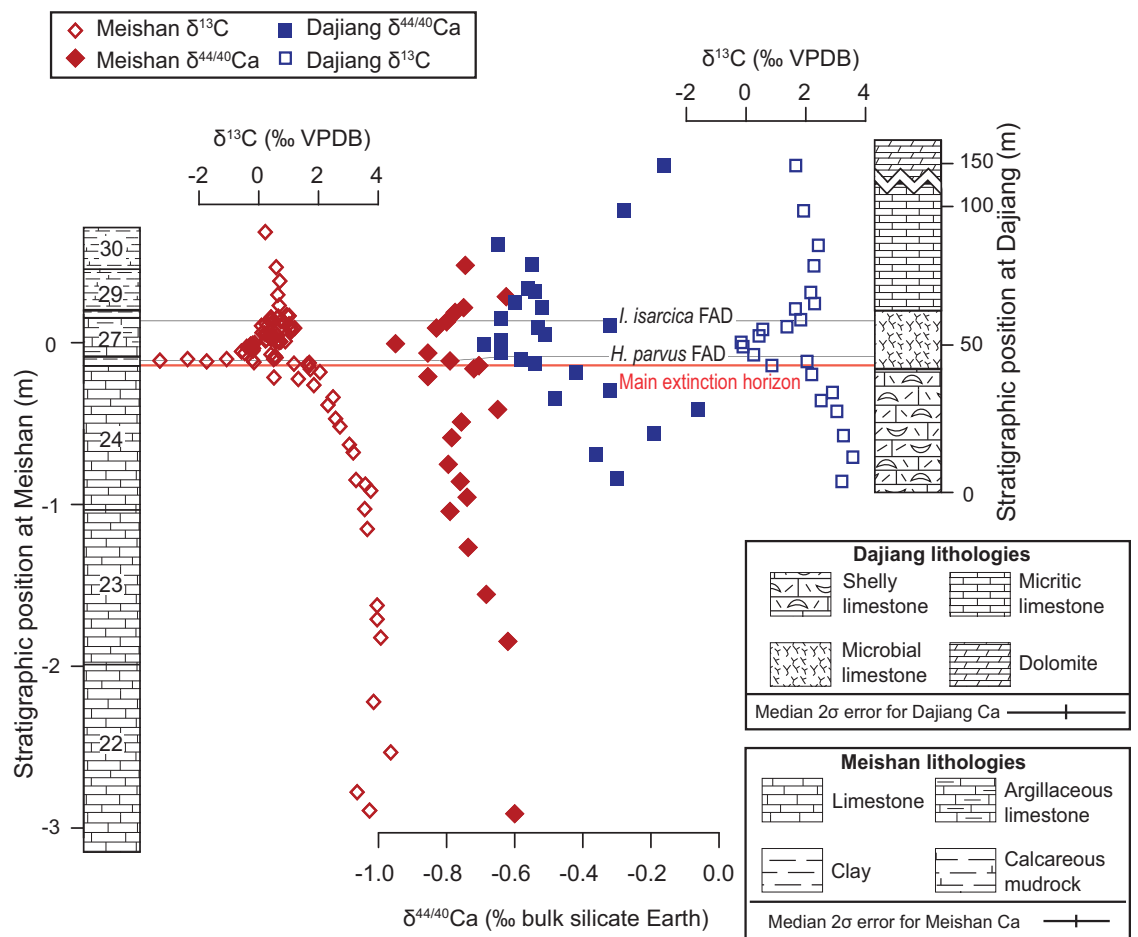
Biostratigraphic correlation between Meishan and Dajiang shows strong congruence of the $\delta^{13}\text{C}$ and $\delta^{44/40}\text{Ca}$ records. Figure 2 illustrates the conodont $\delta^{44/40}\text{Ca}$ record from Meishan

alongside previous results for the same interval from bulk carbonate rock at Dajiang. The most prominent feature of the conodont record is a negative excursion of 0.2‰ – 0.3‰ that occurs directly above the main extinction horizon at Bed 25. The Early Triassic samples trend toward heavier $\delta^{44/40}\text{Ca}$ values. The negative shifts in the $\delta^{44/40}\text{Ca}$ records are broadly coincident with similar shifts in the $\delta^{13}\text{C}$ records from bulk carbonate rock. $\delta^{44/40}\text{Ca}_{\text{conodont}}$ values from Meishan are $\sim 0.3\text{‰}$ – 0.6‰ lighter than $\delta^{44/40}\text{Ca}_{\text{carb}}$ from Dajiang, which we interpret to reflect differences in fractionation factors between seawater and carbonate versus biogenic phosphate minerals (Skulan et al., 1997). The carbon and calcium isotope data show excursions and recoveries over similar stratigraphic intervals in both study sections. This similarity in response times despite differences in residence times may result from the complex coupling of the carbon and calcium cycles through shared weathering and burial fluxes and other feedbacks, or from limitations in the data to resolve response times beyond a factor of two or three.

Both $\delta^{44/40}\text{Ca}$ records exhibit minima above the extinction horizon in the *Hindeodus parvius* zone, which is indicative of a negative shift in $\delta^{44/40}\text{Ca}_{\text{sw}}$ in the same zone. Mineralogical shifts or diagenetic effects may contribute to small-scale fluctuations in the $\delta^{44/40}\text{Ca}_{\text{carb}}$ record, but the lack of a correlated positive shift in $\delta^{44/40}\text{Ca}_{\text{conodont}}$ indicates no major effect of a change in the relative ratio of calcite versus aragonite precipitation on $\delta^{44/40}\text{Ca}_{\text{sw}}$. To be explained by carbonate mineralogy, our data would require a temporary global shift toward calcite deposition across the P-Tr boundary that was not expressed at Dajiang. Given (1) the petrographic similarity of the strata at Dajiang to localities across the globe (Payne et al., 2007; Kershaw et al., 2011), (2) the fact that this was a time of aragonite seas, and (3) the observed increase in the proportional abundance of aragonitic skeletal animals across the P-Tr boundary (Kiessling et al., 2008), such a scenario appears highly unlikely. The Late Permian baseline values for the $\delta^{44/40}\text{Ca}_{\text{carb}}$ record show more scatter than the $\delta^{44/40}\text{Ca}_{\text{conodont}}$ record, which may be due to diagenetic alteration or contributions from multiple carbonate phases that were variably fractionated.

Although it is conceivable that other factors could influence the $\delta^{44/40}\text{Ca}_{\text{conodont}}$ record, it appears unlikely that any actually do account for the observed trends throughout the entire record. Processes that may impact $\delta^{44/40}\text{Ca}_{\text{conodont}}$ include (1) postdepositional exchange of Ca, (2) vital effects, and (3) impurities included in samples. Diagenetic alteration appears unlikely to have differentially affected samples immediately above the extinction horizon. Due to the highly condensed nature of the Meishan section, particularly the beds sampled in this study,

Figure 2. Calcium and carbon isotope data from Meishan and Dajiang (China). Jin et al. (2000) place the main extinction horizon at Meishan in Bed 25. The Permian-Triassic boundary, defined by the first appearance of the conodont *Hindeodus parvus*, falls in Bed 27c. These points, along with the first appearance datum (FAD) of *Isarcicella isarcica*, were used to correlate the Meishan section with previously reported $\delta^{44/40}\text{Ca}_{\text{carb}}$ data from Dajiang (Payne et al., 2010). Both sections exhibit a negative excursion above the main extinction horizon. Conodont zones and lithologies are based on Yin et al. (2001) for Meishan, and on Lehrmann et al. (2003), Chen et al. (2009), and Payne et al. (2010) for Dajiang. Meishan $\delta^{13}\text{C}$ data from Cao et al. (2009). Both sections exhibit positive correlations between the $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$ records. For Meishan, Pearson's $r = 0.4$, $p = 0.09$; for Dajiang, Pearson's $r = 0.6$, $p = 0.005$. Because multiple carbon isotope measurements were performed on each bed, a mean carbon isotope value was determined for each and compared to the corresponding calcium isotope value in the regression analysis. Dajiang $\delta^{44/40}\text{Ca}$ data from Payne et al. (2010) have been rescaled upward by 0.2% based upon a revised estimate of the $\delta^{44/40}\text{Ca}$ value for the bulk silicate Earth (Simon and DePaolo, 2010).



influence of meteoric water would likely affect all samples similarly.

Strontium isotope data indicate that the calcium isotope composition of the conodonts and carbonate samples have not been substantially altered during diagenesis. Five conodont samples from Meishan were tested for $^{87}\text{Sr}/^{86}\text{Sr}$, and all fell between 0.7071 and 0.7072, matching published values from other sites for the same time period (Korte et al., 2003, 2004, 2006; Martin and MacDougall, 1995), and most carbonate samples from Dajiang also appear to retain near-primary Sr isotope compositions (see the GSA Data Repository¹ for values). The preservation of a primary strontium isotope composition is a good indication that a primary calcium isotope composition is also likely to be preserved, because strontium is a divalent

¹GSA Data Repository item 2012204, Meishan and Dajiang $\delta^{44/40}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values; calcium-cycle box model parameter values and model construction; and expanded information on sample preparation, is available online at www.geosociety.org/pubs/ft2012.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

cation that substitutes into Ca sites in apatite, and its sources and sinks have greater isotopic variation. Moreover, because strontium is preferentially lost from carbonate sediments during diagenesis (Banner and Hanson, 1990), calcium should be more robust against diagenetic alteration than strontium.

Another potential source of error is inclusion of other sources of Ca in the analysis. Because carbonates exhibit heavier values than conodonts at all stratigraphic levels, the negative shift in $\delta^{44/40}\text{Ca}_{\text{conodont}}$ across the extinction horizon would require a substantial reduction in the input of Ca from adhered calcite or dolomite. However, specimens encrusted with dolomite crystals, which could introduce calcium to the measurement, were excluded from analysis. Additionally, samples were washed in acid prior to analysis to remove any carbonate minerals external to the elements (see the Data Repository).

Changes in the calcium weathering rate can drive excursions in oceanic calcium isotopes (De La Rocha and DePaolo, 2000; Griffith et al., 2011; Blättler et al., 2011). Rapid addition of CO_2 to the atmosphere could increase weath-

ering input to the ocean and decrease carbonate saturation, leading to the flux imbalances observed in the $\delta^{44/40}\text{Ca}$ records. Eruption of the Siberian Traps provides a mechanism for inducing the rapid release of CO_2 and other acid volatiles to the atmosphere and oceans (Svensen et al., 2009; Sobolev et al., 2011). This geological trigger can explain the combined observations of negative excursions in $\delta^{13}\text{C}$ and $\delta^{44/40}\text{Ca}$, shifts in carbonate sedimentation, and preferential extinction of massively calcifying marine organisms.

CONCLUSIONS

The $\delta^{44/40}\text{Ca}$ trends seen in the combined carbonate rocks and conodont microfossils at the P-Tr boundary are best explained by an excursion in the $\delta^{44/40}\text{Ca}$ of seawater. Paleontological evidence for selective extinction of heavily calcified marine animals (e.g., Knoll et al., 1996; Clapham and Payne, 2011) and a negative excursion in $\delta^{13}\text{C}$ likely to reflect the rapid input of ^{13}C -depleted carbon (Korte and Kozur, 2010) together suggest that the calcium isotope record is best interpreted to reflect an imbalance between calcium weathering and burial fluxes triggered by ocean acidification.

These findings suggest that the end-Permian mass extinction can serve as a useful case study for the long-term response of marine ecosystems to severe ocean acidification.

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