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Impact of atmospheric pCO_2, seawater temperature, and calcification rate on the $\delta^{18}O$ and $\delta^{13}C$ composition of echinoid calcite (*Echinometra viridis*)

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ABSTRACT

The tropical echinoid *Echinometra viridis* was reared in controlled laboratory experiments at temperatures of approximately 20 °C and 30 °C to mimic winter and summer temperatures and at carbon dioxide (CO_2) partial pressures of approximately 487 ppm-v and 805 ppm-v to simulate current and predicted-end-of-century levels. Spine material produced during the experimental period and dissolved inorganic carbon (DIC) of the corresponding culture solutions were then analyzed for stable oxygen ($\delta^{18}O_e$, $\delta^{18}O_{DIC}$) and carbon ($\delta^{13}C_e$, $\delta^{13}C_{DIC}$) isotopic composition. Fractionation of oxygen stable isotopes between the echinoid spines and DIC of their corresponding culture solutions ($\Delta^{18}O = \delta^{18}O_e - \delta^{18}O_{DIC}$) was significantly inversely correlated with seawater temperature but not significantly correlated with atmospheric pCO_2. Fractionation of carbon stable isotopes between the echinoid spines and DIC of their corresponding culture solutions ($\Delta^{13}C = \delta^{13}C_e - \delta^{13}C_{DIC}$) was significantly positively correlated with pCO_2 and significantly inversely correlated with temperature, with pCO_2 functioning as the primary factor and temperature moderating the pCO_2–$\Delta^{13}C$ relationship. Echinoid calcification rate was significantly inversely correlated with both $\Delta^{18}O$ and $\Delta^{13}C$ across treatments, with effects of pCO_2 and temperature controlled for through ANOVA. Therefore, calcification rate and potentially the rate of co-occurring dissolution appear to be important drivers of the kinetic isotope effects observed in the echinoid spines. Study results suggest that echinoid $\Delta^{18}O$ monitors seawater temperature, but not atmospheric pCO_2, and that echinoid $\Delta^{13}C$ monitors atmospheric pCO_2, with temperature moderating this relationship. These findings, coupled with echinoids' long and generally high-quality fossil record, support prior assertions that fossil echinoid $\Delta^{18}O$ is a viable archive of paleo-seawater temperature throughout Phanerozoic time, and that $\Delta^{13}C$ merits further investigation as a potential proxy of paleo-atmospheric pCO_2. However, the apparent impact of calcification rate on echinoid $\Delta^{18}O$ and $\Delta^{13}C$ suggests that paleoceanographic reconstructions derived from these proxies in fossil echinoids could be improved by incorporating the effects of growth rate.

1. Introduction

The stable isotopic compositions of calcium carbonate minerals ($\delta^{13}C$, $\delta^{18}O$) are known to record changes in ocean temperature and atmospheric pCO_2 that have occurred throughout Earth history (e.g., Berner, 1990; Emiliani, 1955; Petit et al., 1999; Shackleton et al., 1983; Veizer et al., 2000; Weaver et al., 1997). Echinoids are globally distributed benthic calcifiers with a relatively long fossil record, dating back to the Lower Cambrian (e.g., Lebrato et al., 2010; Paul and Smith, 1984). They also tend to be well preserved in the fossil record owing to the hydrophobic organic matter that encapsulates their spines and plates (Dickson, 2002, 2004; O'Malley et al., 2013) and inhibits diagenetic resetting of their stable isotopic signatures, rendering echinoids a potentially valuable geochemical archive of ancient seawater conditions.

Numerous studies have investigated the impacts of seawater temperature on oxygen and carbon isotope fractionation within echinoderm Mg-calcite (e.g., Baumiller, 2001; Gorzelak et al., 2012; Richter and Bruckschen, 1998; Weber, 1968). Analysis of 116 modern ophiuroid (brittle star) skeletons showed a positive correlation between $\delta^{13}C$ and temperature, a negative correlation between $\delta^{18}O$ and temperature, and a weakly positive correlation between $\delta^{13}C$ and $\delta^{18}O$ (Weber, 1968). A negative correlation between $\delta^{18}O$ and temperature was also observed for modern crinoids with no significant correlation between $\delta^{13}C$ and temperature (Weber, 1968). In addition to observing a negative correlation between $\delta^{18}O$ and temperature, Gorzelak et al. (2012) also noted a weak positive correlation between $\delta^{13}C$ and $\delta^{18}O$ within the extant crinoid *Metacrinus rotundus*, which they asserted may have been confounded by metabolic factors such as respiration and/or diet. Richter and Bruckschen (1998) found the $\delta^{18}O$ of tests of the echinoid *Echinocyamus pusillus* to be positively correlated with salinity, negatively correlated with meteoric water input, and negatively correlated with temperature. Collectively, these results suggest that echinoderm $\delta^{18}O$

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may provide a useful proxy of paleoseawater temperature, while the potential impacts of seawater temperature on echinoderm $\delta^{13}C$ may be complicated by other environmental and/or metabolic factors that affect carbon isotope fractionation.

Equilibrium fractionation of oxygen and carbon isotopes occurs among species of dissolved inorganic carbon (DIC) as a function of seawater temperature once isotopic equilibrium is reached (e.g., McCrea, 1950). Abiotic precipitation experiments have confirmed that $\delta^{18}O$ (e.g., Beck et al., 2005; Wang et al., 2013; McCrea, 1950) and $\delta^{13}C$ (McCrea, 1950; Zhang et al., 1995) of seawater DIC species vary inversely with temperature in a manner consistent with equilibrium isotope fractionation. However, abiogenic calcite precipitation experiments performed by Romanek et al. (1992) revealed calcite to be approximately 1‰ enriched in ^{13}C relative to HCO_3^- with no significant correlations between $\delta^{13}C$ and temperature, indicating that kinetic factors can lead to disequilibrium fractionation of carbon and oxygen isotopes even in abiotically precipitated carbonates.

Carbon and oxygen isotopic disequilibrium has also been observed in numerous studies of biogenic carbonates, apparently due to the biological processes involved in calcification (Adkins et al., 2003; Bemis et al., 2000; Gorzelak et al., 2012; McConnaughey, 1989a; Weber, 1968; Weber and Raup, 1966; Zeebe, 1999). Adkins et al. (2003) proposed a novel vital effect for the deepwater corals *Desmophyllum cristagalli* and *Lophelia* sp., in which apparent isotopic disequilibrium of $\delta^{13}C$ is established by mixing of carbon reservoirs driven by a pH gradient across the cell membrane at the site of calcification, with $\delta^{18}O$ disequilibrium driven by pH induced DIC speciation. Bemis et al. (2000) observed the calcite of the foraminifera *Orbulina universa* to have $\delta^{13}C$ that is approximately 1‰ more positive than seawater DIC when grown in low light conditions and attributed this disequilibrium to kinetic isotope effects arising from selective uptake of lighter isotopes by organic matrices surrounding the site of calcification. Rates of calcification have also been shown to impart kinetic isotope effects, resulting in shell $\delta^{13}C$ that is up to 10–15‰ lighter than seawater DIC and shell $\delta^{18}O$ that is up to 4‰ lighter than seawater DIC (McConnaughey, 1989a). Negative correlations have also been observed between rates of respiration and $\delta^{13}C$ of seawater DIC (McConnaughey, 1989a).

Because echinoderms lack structurally complex respiratory systems, perivisceral coelomic fluids must transport respired CO_2 throughout the organism (Weber, 1968). Stumpp et al. (2012) also demonstrated that larval echinoids have a leaky integument, indicating that their intracellular fluid is exposed to changes in the pH of their extracellular fluid, which is directly impacted by pH changes in ambient seawater—although they also demonstrated that echinoids are able to control pH of their intracellular fluid. Collectively, these studies indicate that ambient seawater (heavier isotope signal) and respired seawater (lighter isotope signal) are mixed within the echinoderm tissue, suggesting that seawater pH, growth rate, and respiration are all important factors to consider when investigating the source of isotopic disequilibrium in biogenic carbonates such as echinoid spines.

Prior studies have also investigated phylogenetic and intraspecimen variability in the stable isotopic disequilibria ($\delta^{13}C$, $\delta^{18}O$) of echinoderm skeletons (Gorzelak et al., 2012; Weber and Raup, 1966; Weber and Raup, 1968). A study of 45 families of fossil echinoderms found that the $\delta^{13}C$ and $\delta^{18}O$ composition of their tests varied among families, as well as among different skeletal elements within individuals (Weber and Raup, 1968). That study concluded that the overall variation in the stable isotopic composition of echinoderms has increased throughout geologic time as the phylum diversified (Weber and Raup, 1968). Gorzelak et al. (2012) also identified approximately 10‰ variations in $\delta^{13}C$ among clades of crinoids and significant variability in the stable isotopic composition of extant crinoids—across species, across individuals within a given species, and across skeletal elements within a given individual. Likewise, Weber and Raup (1966) found that aboral spines of *Echinometra lucunter* are enriched in ^{13}C and ^{18}O relative to spines located closer to the mouth and that tests were generally depleted in ^{13}C and ^{18}O relative to spines. They also found no significant variation in stable isotopic composition across the length of the spine. These studies reveal variability in echinoderm $\delta^{18}O$ and $\delta^{13}C$ across species, individuals, and skeletal elements. This variability must be taken into account when employing these isotopes in paleoceanographic reconstructions.

Although Weber (1973) originally proposed that echinoids are prone to diagenesis and thus poorly suited for paleoceanographic reconstructions, Dickson (2002, 2004) found echinoderm stereom calcite to be unusually well preserved throughout the geologic record owing to its encasement in hydrophobic organic matter. Echinoderms' unique quality of preservation in the fossil record enabled Dickson to reconstruct the Phanerozoic history of seawater Mg/Ca from the Mg/Ca of fossil echinoderms. Although Hasiuk and Lohmann (2008) determined that early diagenetic alteration caused crinoid skeletal $\delta^{13}C$ and $\delta^{18}O$ to initially converge on isotopic compositions of their surrounding cement, they also concluded that this process of early alteration ultimately protected the crinoid skeletons from more severe, subsequent alteration. Well-preserved echinoderm-specific organic molecules found in Mississippian-age (340 Ma) crinoid fossils (O'Malley et al., 2013) further support Dickson's conclusions that echinoderm skeletal material may be geochemically preserved over geologic time scales. O'Malley et al. (2013) attributed the crinoids' high quality preservation to their deposition in fine-grained sediments that inhibited the flow of diagenetic fluids, and also to the absence of metamorphism at the crinoid collection site. These findings collectively suggest that well-preserved fossilized echinoderms are a potentially valuable and relatively underutilized archive of paleoceanographic conditions.

The objective of the present study is to investigate the impact of seawater temperature and atmospheric pCO_2 on the $\delta^{13}C$ and $\delta^{18}O$ composition of Mg-calcite produced by *Echinometra viridis*, a cryptic rock- and reef-dwelling echinoid found throughout the Caribbean Sea (McPherson, 1969). The results of the present study reveal the utility and limitations of echinoid $\delta^{13}C$ and $\delta^{18}O$ as a proxy of paleoseawater temperature and atmospheric pCO_2 and provide insight into the mechanisms of echinoid calcification.

2. Materials and methods

2.1. Echinoid culture experiment

Approximately 44 specimens of the tropical echinoid *E. viridis* were collected near Key Largo in southern Florida and reared for 60 days in a three-way replicated two-way factorial experiment in which low (circa 487 ppm-v) and high (circa 805 ppm-v) pCO_2 treatments were crossed with low (circa 20 °C) and high temperature treatments (circa 30 °C; see Courtney et al., 2013, for detailed methods). In brief, the urchins were reared in 34 L aquaria filled with seawater of salinity 32.06 (SE = 0.02), formulated from deionized water mixed with *Instant Ocean Sea Salt*—identified in a prior study as the commercial sea salt that best replicates the chemical composition of natural seawater (Atkinson and Bingham, 1998). The aquaria were filtered at 757 L/h with activated carbon in a floss-filter cartridge and illuminated for 10 h/day at 884 (SE = 38) Lux. Experimental aquaria were allowed to equilibrate with the bubbled gas mixture for 24-h prior to the beginning of the rearing experiment. The echinoids were fed to satiation every other day with approximately 60 mg of dehydrated marine green algae per tank. Net calcification rates were estimated from changes in the echinoids' buoyant weight between the beginning and end of the experiment. Details regarding application of the buoyant weight method to estimating net calcification rates of echinoids are available in the supplementary information of Ries et al. (2009).

The actual pCO_2 and temperature for the four treatments (±SE) were: (1) 20.3 ± 0.1 °C and 524 ± 33 ppm-v; (2) 20.6 ± 0.1 °C and