

# Calcite-aragonite seas as a driver of echinoderm evolution? Experimental insight and deep-time decoupling

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## ABSTRACT

Seawater magnesium (Mg) and calcium (Ca) have undergone secular fluctuations throughout the Phanerozoic, controlling whether the dominant calcium carbonate precipitant is calcite or aragonite + high-Mg calcite. Although these oscillations in seawater Mg/Ca ratios have been implicated as an important control on Phanerozoic diversification of calcifying marine organisms, determining the degree to which Mg/Ca ratios affected different clades requires integration of experimental data with historical patterns of biodiversity from the fossil record. We explore short-term and long-term responses of echinoderms to shifting calcite-aragonite seas by combining experimental and deep-time biodiversity investigations. While experimental results support a strong relationship between Mg/Ca ratios and short-term echinoderm regeneration rates, patterns of Phanerozoic echinoderm diversification dynamics show no correspondence with Mg/Ca ratios or calcite-aragonite sea transitions. This decoupling between short- and long-term responses of echinoderms to seawater Mg/Ca ratios suggests echinoderms were relatively unaffected by seawater chemistry throughout their evolutionary history, possibly due to their ability to alter skeletal Mg fractionation and/or adapt to gradual shifts in seawater chemistry. Notably, our results indicate a strict uniformitarian extrapolation of experimental results over geological time scales may not be appropriate for many calcifying marine invertebrates. Instead, the effect of seawater Mg/Ca ratios should be evaluated for individual clades using both experimental and deep-time biodiversity data in a time series.


## INTRODUCTION

Ratios of seawater magnesium (Mg) and calcium (Ca) have fluctuated throughout the Phanerozoic due to differential rates of seafloor spreading (Spencer and Hardie, 1990; Hardie, 1996; for alternative mechanisms, see Zhuravlev and Wood, 2009), controlling whether the dominant calcium carbonate precipitant is calcite, resulting in “calcite seas,” or aragonite + high-Mg calcite, resulting in “aragonite seas” (Sandberg, 1983; Stanley and Hardie 1998, 1999). Because Mg/Ca ratios can impact biomineralization in carbonate skeletonized taxa, they are frequently implicated as a major driver of Phanerozoic biodiversity (Ries, 2010). Experimental

work has established that many organisms react negatively when their skeletal mineralogy is out of phase with the ambient seawater carbonate precipitant, resulting in depressed growth rates (Ries, 2005; Kołbuk et al., 2020, 2021), slower population growth (Stanley et al., 2005), and/or suboptimal Mg fractionation during biomineralization (Stanley et al., 2002; Ries, 2004; Ries et al., 2006). These effects on biomineralizing organisms are predicted to scale over millions of years and profoundly affect the evolutionary success of carbonate skeletonized taxa (Stanley and Hardie, 1998, 1999; Ries, 2005; Ries et al., 2006; Stanley, 2006). Indeed, an extensive body of research indicates seawater Mg/Ca ratios have impacted many aspects of past biodiversity, including organismal abundance or dominance (Stanley and Hardie, 1998; Stanley et al. 2005), *de novo* acquisition of skeletal

chemistry (Porter, 2007; Quattrini et al., 2020), and broad trends in skeletal mineralogy (Stanley and Hardie, 1999; for an alternate view, see Kiessling et al., 2008). To date, however, most paleontological evidence comes from identifying intervals when clades with in-phase skeletal mineralogy were dominant or those with out-of-phase mineralogy declined (e.g., Stanley et al., 2005; Ries et al., 2006; Stanley, 2006; Ries, 2009). While informative, this approach fails to capture how diversification dynamics of calcifiers have responded to repeated changes in seawater Mg/Ca during their evolutionary history. Instead, this goal can only be achieved by quantitatively comparing patterns of shifting Mg/Ca ratios and biodiversity data within a time series (e.g., Kiessling et al., 2008; Key et al., 2021) supported by data from experimental studies to establish physiological responses of organisms to seawater Mg/Ca ratios.

To better understand how varying Mg/Ca ratios have affected the Phanerozoic history of life, we used echinoderms as a model system to evaluate short-term and long-term responses to changing seawater Mg/Ca ratios. Specifically, we experimentally tested the influence of high, low, and intermediate Mg/Ca ratios on rates of regenerative growth in living ophiuroid echinoderms and compiled data on Phanerozoic echinoderm diversity to assess whether deep-time patterns of diversification and/or extinction can be explained by fluctuations in Mg/Ca ratios or calcite-aragonite sea transitions. Echinoderms are an ideal group for this investigation because (1) their skeletons are made of high-Mg calcite, so Mg/Ca ratios are expected to have greatly influenced their evolutionary history; (2) they have a diverse Cambrian–Recent fossil record, which is ideal for evaluating whether their past biodiversity was affected by shifts in calcite-aragonite

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seas; and (3) living representatives can be readily cultured in saltwater aquaria, permitting experimental study of physiological responses to varying Mg/Ca ratios.

## ECHINODERMS AND CALCITE-ARAGONITE SEAS

Echinoderms can regenerate their high-Mg calcite skeletons following damage from sublethal predation, a significant evolutionary strategy for increasing survival likelihood under predation pressure (Vermeij, 1982; Lawrence and Vasquez, 1996; Bely and Nyberg, 2010). The interplay between predation and regeneration has been established as a significant driver of deep-time macroevolutionary dynamics in echinoderms (e.g., Baumiller and Gahn, 2004; Sallan et al., 2011; Syverson and Baumiller, 2014; Thompson and Ausich, 2015), so understanding the response of echinoderm regeneration to different Mg/Ca regimes is essential for determining how seawater chemistry impacted the evolutionary history of the clade. Because echinoderms possess high-Mg calcite skeletons, they most effectively biomineralize under aragonite sea regimes ( $>2.5$  mol Mg/Ca) (Ries, 2010). Thus, calcite seas with low Mg/Ca ratios are

expected to slow echinoderm regeneration rates and impact the likelihood of recovery following sublethal predation, thus potentially playing a major role in the diversification history and evolutionary success of echinoderms. If short-term physiological responses of echinoderms to seawater Mg/Ca ratios scale over geological time scales, we would expect greater net diversification and/or standing diversity of echinoderms during aragonite seas and elevated extinction during calcite seas. However, this hypothesis has not been previously tested.

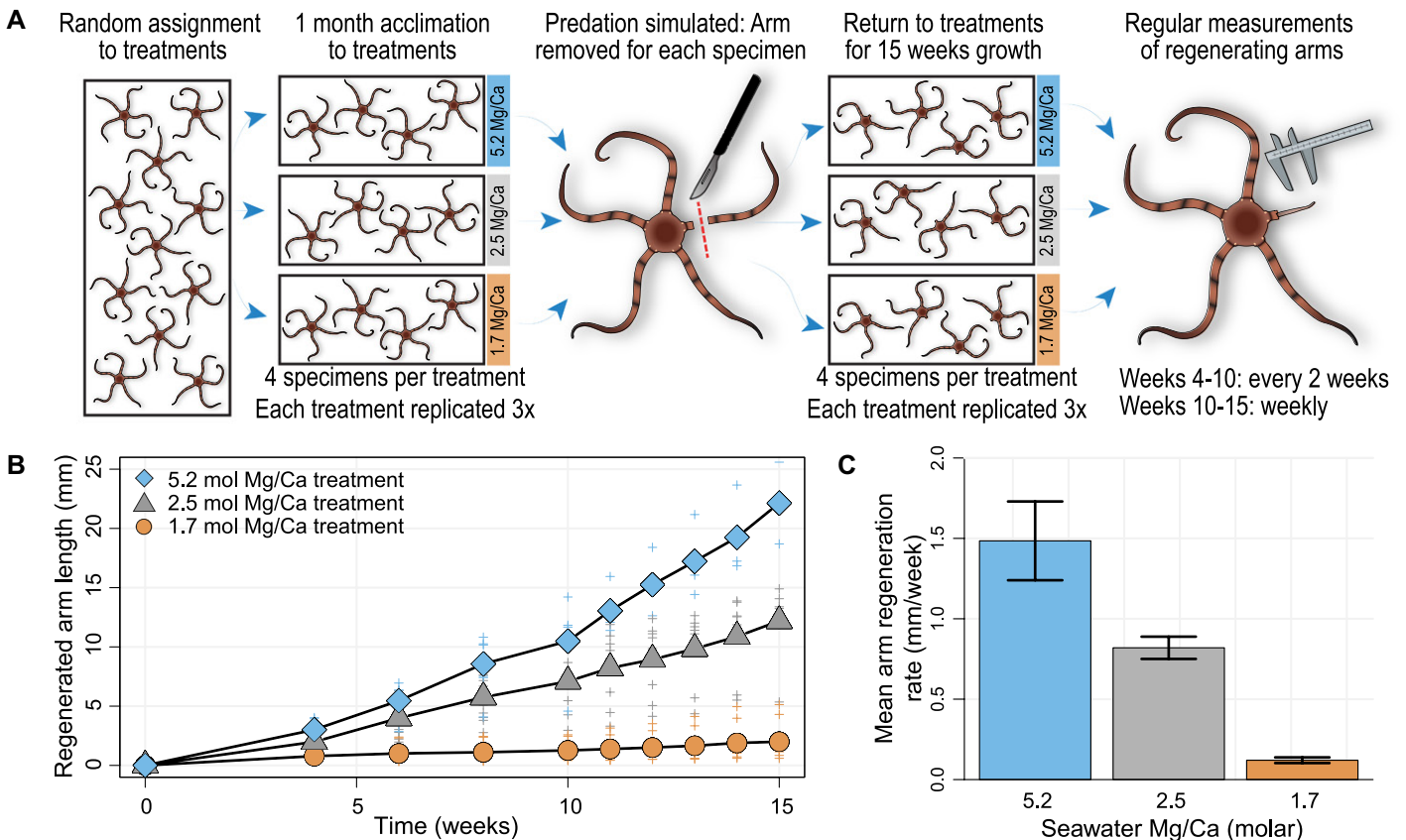
## Mg/Ca RATIOS AFFECT REGENERATION RATES IN LIVING ECHINODERMS

We experimentally tested the effect of seawater Mg/Ca ratios on echinoderm regeneration rates using the brittle star *Ophioderma cinerum* (Class Ophiuroidea). Following the experimental setup of Ries (2005), three seawater Mg/Ca treatments were selected: (1) a low (1.7) Mg/Ca treatment from the calcite nucleation field; (2) an intermediate (2.5) Mg/Ca treatment slightly above the nucleation boundary between calcite and aragonite; and (3) a high (5.2) Mg/Ca treatment from the aragonite + high-Mg calcite

field that is representative of modern seawater chemistry (Morse et al., 1997; Balthasar and Cusack, 2015). For each treatment, artificial seawater was created from reagent grade chemicals and distilled, deionized water (Table S1 in the Supplemental Material<sup>1</sup>). All other conditions were held constant for all treatments and replicates during the experiment.

Individual *O. cinerum* were randomly assigned to one of the three seawater Mg/Ca treatments, each of which was replicated three times and run concurrently, with four individuals per replicate and a total of 12 specimens per seawater treatment (Fig. 1A). After an acclimation period, sublethal predation was simulated by removing an arm from each ophiuroid. Specimens were left to regenerate in their respective seawater treatments for a period of 15 weeks. Measurements of regenerated arms were taken at 4 weeks (when measurable growth was first reached), every two weeks during weeks 4–10, and weekly during weeks 10–15.

<sup>1</sup>Supplemental Material. Supplemental methods, Figures S1–S3, Tables S1–S3, and data files. Please visit <https://doi.org/10.1130/GEOL.S.24052854> to access the supplemental material, and contact editing@geosociety.org with any questions.



**Figure 1. Experimental design and results of ophiuroid (*Ophioderma cinerum*) regeneration experiments. (A) Schematic of the experimental setup, timeline, and data collection. (B) Regenerated arm growth as a function of time for each seawater Mg/Ca treatment; solid points represent mean regenerated arm length for treatments, crosses are measurements for all specimens. (C) Bar plot of estimated  $\beta$  coefficients from a linear regression analysis of arm growth through time, revealing that all treatments have statistically different growth rates; error bars represent 95% confidence intervals.**

and weekly during weeks 10–15 as growth accelerated (Fig. 1A). See the Supplemental Material for additional experimental methods.

Experimental results show that regeneration rates in echinoderms are significantly positively correlated with seawater Mg/Ca ratios, with elevated arm regeneration observed in higher Mg/Ca seawater treatments. An ANOVA test performed on the first differences of arm-length measurements recovered statistically significant differences in ophiuroid growth between all three treatments ( $p \ll 0.001$ ). Length of regenerated arms in the 5.2 Mg/Ca treatment (maximum = 25.59 mm, mean = 22.14 mm) exceeded that of both the 2.5 Mg/Ca treatment (maximum = 14.07 mm, mean = 12.19 mm) and the 1.7 Mg/Ca treatment (maximum = 5.13 mm, mean = 2.00 mm) (Figs. 1B and 2). Comparison of arm regeneration rates confirmed significant differences in growth between all three treatments, where

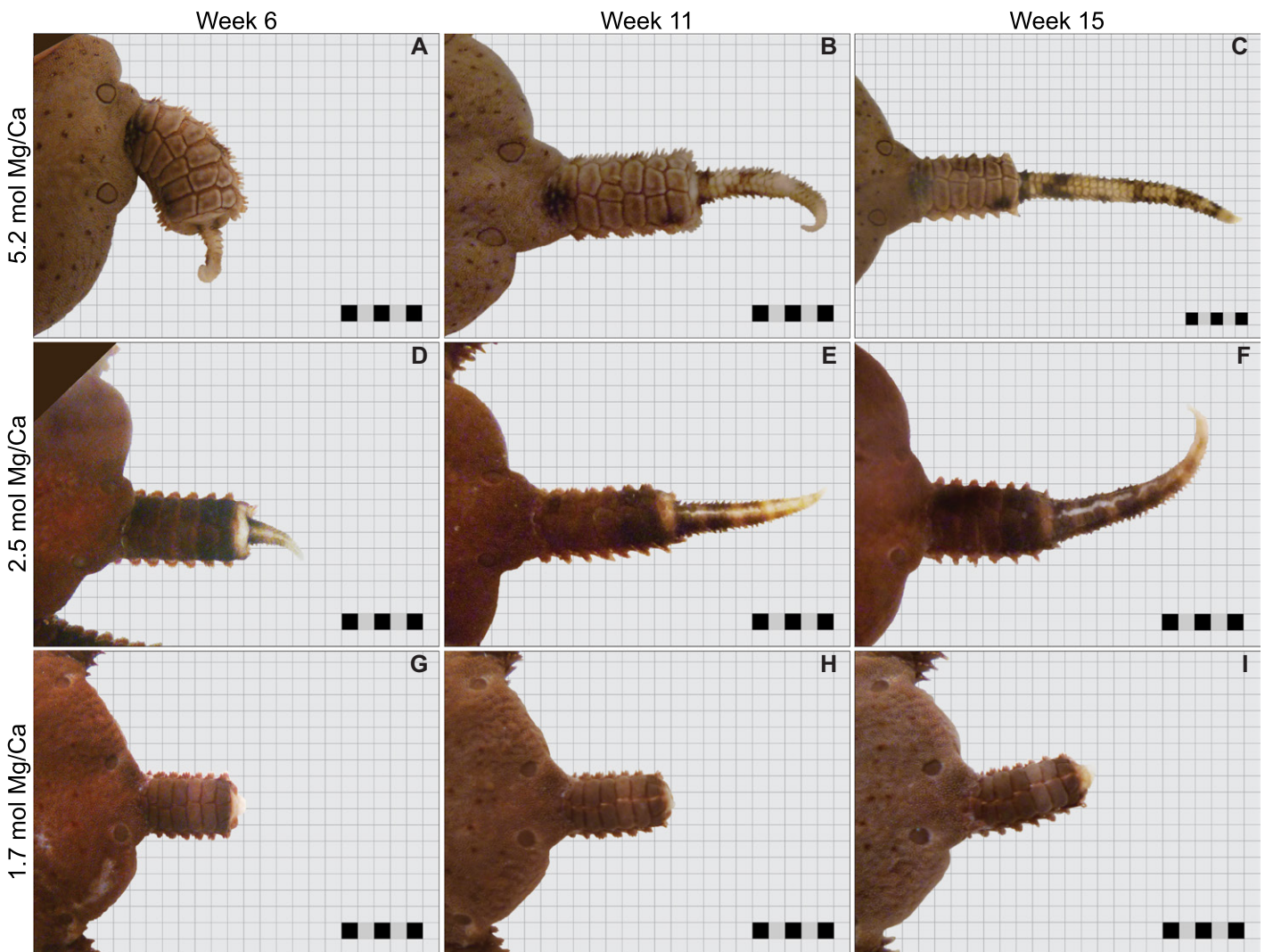
specimens in the 5.2 Mg/Ca treatment grew eight times faster than the 2.5 Mg/Ca treatment and 12 times faster than the 1.7 Mg/Ca treatment (Fig. 1C). To explore how increases in Mg/Ca ratios above the calcite-aragonite nucleation boundary ( $\sim 2.0$  mol Mg/Ca [Balthasar and Cusack, 2015]) affect growth rate, we compared the 5.2 and 2.5 Mg/Ca treatments with a Bonferroni correction and recovered significant differences between them ( $p \ll 0.001$ ). Results indicate that, even above the calcite-aragonite stability field boundary, higher Mg/Ca ratios result in faster regeneration rates.

Overall, our experimental results establish that echinoderm regeneration rates decrease significantly when echinoderms are out of phase with seawater chemistry (i.e., Mg/Ca < 2), which is consistent with previous growth experiments (echinoids, Ries, 2004; asterozoans, Kolbuk et al., 2020, 2021). Scaled over geological time, the physiological response

of echinoderms to Mg/Ca ratios in short-term experiments suggests echinoderm survivorship and diversification may have been suppressed during calcite sea intervals, and elevated during aragonite sea intervals, due to differential success in recovering from sublethal predation or skeletal damage. We directly tested this hypothesis using time series data from the Phanerozoic fossil record of echinoderms.

### Mg/Ca RATIOS AND PHANEROZOIC ECHINODERM DIVERSITY ARE DECOUPLED

To assess whether Mg/Ca ratios affected deep-time echinoderm diversity dynamics, we evaluated the relationship between fossil echinoderm occurrences and calcite-aragonite seas throughout the Phanerozoic. A total of 21,852, globally distributed Cambrian–present echinoderm occurrences were downloaded from the Paleobiology Database (paleobiodb.org)



**Figure 2.** Arm regeneration of representative *Ophioderma cinerum* specimens from Mg/Ca treatments over a 15-week period. (A–C) Arm regeneration of a specimen from the 5.2 mol Mg/Ca treatment at 6 weeks (5.18 mm), 11 weeks (11.39 mm), and 15 weeks (18.69 mm). (D–F) Arm regeneration of a specimen from the 2.5 mol Mg/Ca treatment at 6 weeks (4.14 mm), 11 weeks (9.70 mm), and 15 weeks (13.39 mm). (G–I) Arm regeneration of a specimen from the 1.7 mol Mg/Ca treatment at 6 weeks (0.63), 11 weeks (0.89 mm), and 15 weeks (1.15 mm). All scale bars 5 mm.

and used to calculate two measures of standing genus diversity (sampled-in-bin diversity [Miller and Foote, 1996] and shareholder quorum subsampling [SQS; Alroy, 2010]), net diversification (origination minus extinction), and extinction rate per lineage million years (see the Supplemental Material). Because mass extinctions can significantly affect diversification dynamics and influence skeletal mineralogy of calcifiers (KieSSLing et al., 2008; Quattrini et al., 2020), we also analyzed the relationship between diversification and Mg/Ca ratios both with and without mass extinction intervals included (i.e., excluding time bins during and immediately following the five major mass extinctions). Three Phanerozoic Mg/Ca curves were evaluated to avoid conditioning results on a single model (Wilkinson and Algeo, 1989; Stanley and Hardie, 1998; Horita et al., 2002). See the Supplemental Material for further analytical details.

If seawater Mg/Ca ratios affected Phanerozoic echinoderm diversification and extinction dynamics, aragonite sea intervals are expected to

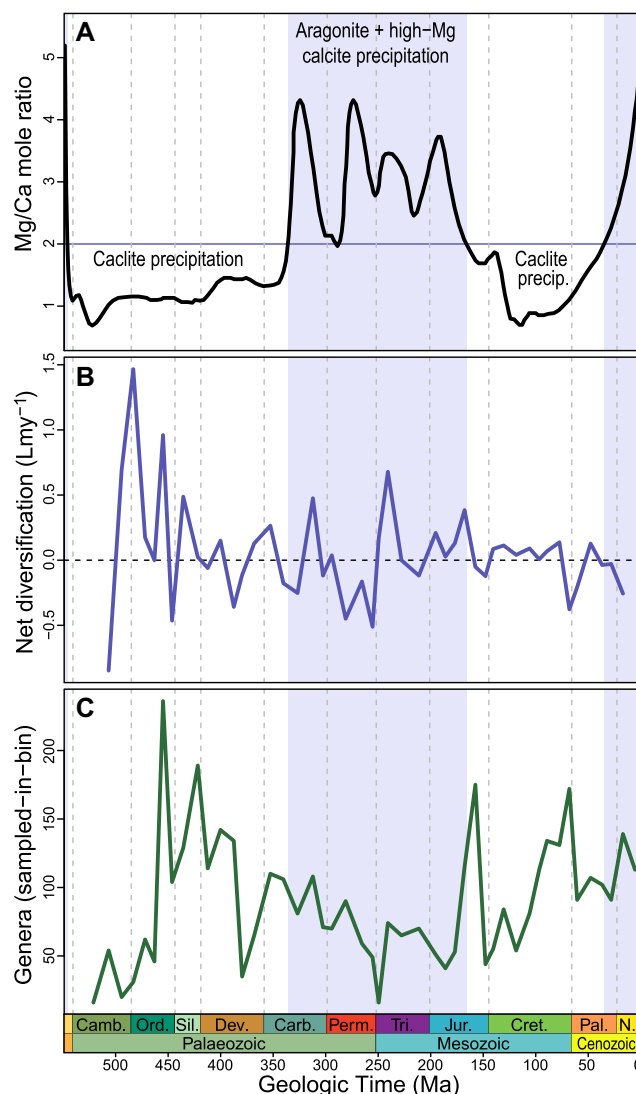
have higher standing diversity, increased diversification, and/or lower extinction rates compared to calcite sea intervals. Instead, no statistically significant relationships were identified between fluctuating calcite-aragonite seas and diversification dynamics regardless of the Mg/Ca model used (Tables S2 and S3). First differences of time series data show no significant correlations between changes in Mg/Ca ratios and changes in standing diversity (both sampled-in-bin and SQS), net diversification, or extinction rate (Fig. 3; Fig. S2). Likewise, Mann-Whitney U tests comparing diversity and extinction measures during all calcite sea intervals versus all aragonite sea intervals (i.e., without data in a continuous time series) show no evidence that standing diversity, net diversification, or extinction differ between calcite and aragonite sea regimes regardless of whether or not mass extinction intervals were included (Fig. S3, Tables S2 and S3).

## DISCUSSION

Our experimental work confirms seawater Mg/Ca ratios have a profound effect on short-

term regeneration rates in extant echinoderms, yet patterns of echinoderm biodiversity over the past ~500 m.y. show no correspondence with shifting calcite-aragonite seas. This mismatch between echinoderms' short- and long-term responses to changing seawater Mg/Ca indicates the mechanisms responsible for differences in echinoderm regeneration rates do not scale over geological time to affect diversification dynamics. There are several potential causes of this decoupling. First, transitions between calcite-aragonite seas are typically gradual, occurring over tens of millions of years, and echinoderms may be able to adapt to calcite seas if the transition to lower Mg/Ca ratios is slow. For example, some echinoderms alter their skeletal composition in low Mg/Ca seawater (Dickson 2002; Ries, 2004), which appears to depress growth rates in ophiuroids and echinoids (Kolbuk et al., 2020) but not asteroids (Kolbuk et al., 2021), and some groups like crinoids appear to have strong control over their biomineralization (GorzelaK et al., 2023). Thus, some echinoderm clades, including the >20 extinct classes that cannot be studied experimentally, may have been less severely impacted by changing Mg/Ca ratios than ophiuroids and/or were able to adapt to these conditions. A similar argument has been made for trepostome bryozoans, which appear to be capable of controlling their skeletal mineralogy via active calcification, thus minimizing the effects of seawater Mg/Ca ratios on their diversification dynamics (Key et al., 2021). Another possible explanation, which is not mutually exclusive of adaptation or changes in Mg/Ca fractionation, is that any negative effects echinoderms may have experienced in calcite seas, such as decreased growth rates, less robust calcification, higher metabolic cost, or lower likelihood of recovery following sublethal predation, were not substantial enough to produce a noticeable effect on diversification dynamics.

While our experimental results support a strong relationship between Mg/Ca ratios and echinoderm regeneration rates over short time scales, patterns of deep-time echinoderm diversity conflict with the predicted effects of Mg/Ca on hypercalcifying organisms (Stanley and Hardie 1998, 1999; Stanley 2006). Although calcite-aragonite seas have unquestionably played a role in the evolutionary history of many skeletonized marine organisms throughout the Phanerozoic, numerous predictions surrounding the effect of Mg/Ca ratios on hypercalcifiers remain untested or have been assumed without quantitative investigation of the fossil record. Our results demonstrate that experimental results should not be extrapolated using a strict uniformitarian approach, since short-term physiological responses of organisms to seawater conditions may not necessarily scale to macroevolutionary outcomes over geological timescales. Future work should focus on merging experimental



**Figure 3.** (A) Seawater Mg/Ca ratios throughout the Phanerozoic with shaded intervals representing aragonite seas and unshaded intervals representing calcite seas; the horizontal line denotes the boundary between calcite and aragonite + high-Mg calcite precipitation (data from Stanley and Hardie, 1998). (B) Phanerozoic net diversification rates for echinoderms. (C) Sampled-in-bin generic richness of Phanerozoic echinoderms. Camb.—Cambrian; Ord.—Ordovician; Sil.—Silurian; Dev.—Devonian; Carb.—Carboniferous; Perm.—Permian; Tri.—Triassic; Jur.—Jurassic; Cret.—Cretaceous; Pal.—Paleogene; N.—Neogene.

results with fossil time series data to more fully evaluate the impact of Mg/Ca ratios on the Phanerozoic diversity of calcifying clades.

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#### REFERENCES CITED

- Alroy, J., 2010, Geographical, environmental and intrinsic biotic controls on Phanerozoic marine diversification: *Palaeontology*, v. 53, p. 1211–1235, <https://doi.org/10.1111/j.1475-4983.2010.01011.x>.
- Balthasar, U., and Cusack, M., 2015, Aragonite-calcite seas—Quantifying the gray area: *Geology*, v. 43, p. 99–102, <https://doi.org/10.1130/G36293.1>.
- Baumiller, T.K., and Gahn, F.J., 2004, Testing predator-driven evolution with Paleozoic crinoid arm regeneration: *Science*, v. 305, p. 1453–1455, <https://doi.org/10.1126/science.1101009>.
- Bely, A.E., and Nyberg, K.G., 2010, Evolution of animal regeneration: Re-emergence of a field: *Trends in Ecology & Evolution*, v. 25, p. 161–170, <https://doi.org/10.1016/j.tree.2009.08.005>.
- Dickson, J.A.D., 2002, Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans: *Science*, v. 298, p. 1222–1224, <https://doi.org/10.1126/science.1075882>.
- Gorzelak, P., Kołbuk, D., Stolarski, J., Baçal, P., Januszewicz, B., Duda, P., Środek, D., Brachaniec, T., and Salamon, M.A., 2023, A Devonian crinoid with a diamond microlattice: *Proceedings of the Royal Society B*, v. 290, <https://doi.org/10.1098/rspb.2023.0092>.
- Hardie, L.A., 1996, Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y.: *Geology*, v. 24, p. 279–283, [https://doi.org/10.1130/0091-7613\(1996\)024<0279:SVISCA>2.3.CO;2](https://doi.org/10.1130/0091-7613(1996)024<0279:SVISCA>2.3.CO;2).
- Horita, J., Zimmermann, H., and Holland, H.D., 2002, Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites: *Geochimica et Cosmochimica Acta*, v. 66, p. 3733–3756, [https://doi.org/10.1016/S0016-7037\(01\)00884-5](https://doi.org/10.1016/S0016-7037(01)00884-5).
- Key, M.M., Jr., Wyse Jackson, P.N., and Reid, C.M., 2021, Trepostome bryozoans buck the trend and ignore calcite-aragonite seas: *Palaeobiodiversity and Palaeoenvironments*, v. 102, p. 253–263, <https://doi.org/10.1007/s12549-021-00507-x>.
- Kiessling, W., Aberhan, M., and Viller, L., 2008, Phanerozoic trends in skeletal mineralogy driven by mass extinctions: *Nature Geoscience*, v. 1, p. 527–530, <https://doi.org/10.1038/ngeo251>.
- Kołbuk, D., Di Giglio, S., M'Zouidi, S., Dubois, P., Stolarski, J., and Gorzelak, P., 2020, Effects of seawater Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio and diet on the biomineralization and growth of sea urchins and the relevance of fossil echinoderms to paleoenvironmental reconstructions: *Geobiology*, v. 18, p. 710–724, <https://doi.org/10.1111/gbi.12409>.
- Kołbuk, D., Dubois, P., Stolarski, J., and Gorzelak, P., 2021, Impact of seawater Mg<sup>2+</sup>/Ca<sup>2+</sup> on Mg/Ca of asterozoan skeleton—Evidence from culturing and the fossil record: *Chemical Geology*, v. 584, <https://doi.org/10.1016/j.chemgeo.2021.120557>.
- Lawrence, J.M., and Vasquez, J., 1996, The effect of sublethal predation on the biology of echinoderms: *Oceanologica Acta*, v. 19, p. 431–440.
- Miller, A.I., and Foote, M., 1996, Calibrating the Ordovician radiation of marine life: Implications for Phanerozoic diversity trends: *Paleobiology*, v. 22, p. 304–309, <https://doi.org/10.1017/S0094837300016237>.
- Morse, J.W., Wang, Q., and Tsio, M.Y., 1997, Influences of temperature and Mg:Ca ratio on CaCO<sub>3</sub> precipitates from seawater: *Geology*, v. 25, p. 85–87, [https://doi.org/10.1130/0091-7613\(1997\)025<0085:IOTAMC>2.3.CO;2](https://doi.org/10.1130/0091-7613(1997)025<0085:IOTAMC>2.3.CO;2).
- Porter, S.M., 2007, Seawater chemistry and early carbonate biomineralization: *Science*, v. 316, 1302, <https://doi.org/10.1126/science.1137284>.
- Quattrini, A.M., et al., 2020, Palaeoclimate ocean conditions shaped the evolution of corals and their skeletons through deep time: *Nature Ecology & Evolution*, v. 4, p. 1531–1538, <https://doi.org/10.1038/s41559-020-01291-1>.
- Ries, J.B., 2004, Effect of ambient Mg/Ca ratio on Mg fractionation in calcareous marine invertebrates: A record of the oceanic Mg/Ca ratio over the Phanerozoic: *Geology*, v. 32, p. 981–984, <https://doi.org/10.1130/G20851.1>.
- Ries, J.B., 2005, Aragonite production in calcite seas: Effect of seawater Mg/Ca ratio on the calcification and growth of the calcareous alga *Penicillus capitatus*: *Paleobiology*, v. 31, p. 445–458, [https://doi.org/10.1666/0094-8373\(2005\)031\[0445:APICSE\]2.0.CO;2](https://doi.org/10.1666/0094-8373(2005)031[0445:APICSE]2.0.CO;2).
- Ries, J.B., 2009, Effects of secular variation in seawater Mg/Ca ratio (calcite–aragonite seas) on CaCO<sub>3</sub> sediment production by the calcareous algae *Halimeda*, *Penicillus* and *Udotea*—Evidence from recent experiments and the geological record: *Terra Nova*, v. 21, p. 323–339, <https://doi.org/10.1111/j.1365-3121.2009.00899.x>.
- Ries, J.B., 2010, Review: Geological and experimental evidence for secular variation in seawater Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification: *Biogeosciences*, v. 7, p. 2795–2849, <https://doi.org/10.5194/bg-7-2795-2010>.
- Ries, J.B., Stanley, S.M., and Hardie, L.A., 2006, Scleractinian corals produce calcite, and grow more slowly, in artificial Cretaceous seawater: *Geology*, v. 34, p. 525–528, <https://doi.org/10.1130/G22600.1>.
- Sallan, L.C., Kammer, T.W., Ausich, W.I., and Cook, L.A., 2011, Persistent predator-prey dynamics revealed by mass extinction: *Proceedings of the National Academy of Sciences of the United States of America*, v. 108, p. 8335–8338, <https://doi.org/10.1073/pnas.1100631108>.
- Sandberg, P.A., 1983, An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy: *Nature*, v. 305, p. 19–22, <https://doi.org/10.1038/305019a0>.
- Spencer, R.J., and Hardie, L.A., 1990, Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines, in Spencer, R.J., and Chou, I.-M., eds., *Fluid-Mineral Interactions: A Tribute to H.P. Eugster*: *Geochemical Society Special Publication 2*, p. 409–419.
- Stanley, S.M., 2006, Influence of seawater chemistry on biomineralization throughout Phanerozoic time: Paleontological and experimental evidence: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 232, p. 214–236, <https://doi.org/10.1016/j.palaeo.2005.12.010>.
- Stanley, S.M., and Hardie, L.A., 1998, Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 144, p. 3–19, [https://doi.org/10.1016/S0031-0182\(98\)00109-6](https://doi.org/10.1016/S0031-0182(98)00109-6).
- Stanley, S.M., and Hardie, L.A., 1999, Hypercalcification: Paleontology links plate tectonics and geochemistry to sedimentology: *GSA Today*, v. 9, no. 2, p. 1–7.
- Stanley, S.M., Ries, J.B., and Hardie, L.A., 2002, Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition: *Proceedings of the National Academy of Sciences of the United States of America*, v. 99, p. 15323–15326, <https://doi.org/10.1073/pnas.232569499>.
- Stanley, S.M., Ries, J.B., and Hardie, L.A., 2005, Seawater chemistry, coccolithophore population growth, and the origin of Cretaceous chalk: *Geology*, v. 33, p. 593–596, <https://doi.org/10.1130/G21405.1>.
- Syverson, V.J., and Baumiller, T.K., 2014, Temporal trends of predation resistance in Paleozoic crinoid arm branching morphologies: *Paleobiology*, v. 40, p. 417–427, <https://doi.org/10.1666/13063>.
- Thompson, J.R., and Ausich, W.I., 2015, Testing for escalation in Lower Mississippian camerate crinoids: *Paleobiology*, v. 41, p. 89–107, <https://doi.org/10.1017/pab.2014.6>.
- Vermeij, G.J., 1982, Unsuccessful predation and evolution: *American Naturalist*, v. 120, p. 701–720, <https://doi.org/10.1086/284025>.
- Wilkinson, B.H., and Algeo, T.J., 1989, Sedimentary carbonate record of calcium-magnesium cycling: *American Journal of Science*, v. 289, p. 1158–1194, <https://doi.org/10.2475/ajs.289.10.1158>.
- Zhuravlev, A.Y., and Wood, R.A., 2009, Controls on carbonate skeletal mineralogy: Global CO<sub>2</sub> evolution and mass extinctions: *Geology*, v. 37, p. 1123–1126, <https://doi.org/10.1130/G30204A.1>.

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