GEOLOGY | THE GEOLOGICAL SOCIETY OF AMERICA®

https://doi.org/10.1130/G49984.1

Manuscript received 9 December 2021
Revised manuscript received 14 January 2022
Manuscript accepted 24 January 2022

Published online 14 April 2022

Apparent preservation of primary foraminiferal Mg/Ca ratios and Mg-banding in recrystallized foraminifera

Philip T. Staudigel[1,2]*, Eleanor H. John[2], Ben Buse[3], Paul N. Pearson[2] and Caroline H. Lear[2]
[1]Goethe-Universität, Institute for Geosciences, 60438 Frankfurt, Germany
[2]Cardiff University, School of Earth and Environmental Sciences, Cardiff CF10 3AT, UK
[3]University of Bristol, School of Earth Sciences, Bristol BS8 1RL, UK

ABSTRACT

Trace element and $\delta^{18}O$ values of foraminifera are widely used to reconstruct oceanic temperatures throughout the Cenozoic and beyond. Previous work evaluating the geochemistry of foraminifera with differing degrees of physical preservation have shown that Mg/Ca and $\delta^{18}O$ paleothermometers give discrepant values in recrystallized tests, with planktonic oxygen isotopes often yielding significantly lower temperatures than Mg/Ca ratios. To study the mobility of elements during diagenesis, we performed microspatial trace element analyses in Eocene *Morozovella*. Element maps show that trace element banding is readily identifiable and preserved, to an extent, in texturally recrystallized tests. A reaction-diffusion model was used to test whether the preservation of Mg-banding and the decoupling of $\delta^{18}O$ and Mg/Ca values could be the result of diffusively limited "closed-system" recrystallization. Results show that, in a closed system, internal features (such as Mg-banding) will dissipate prior to changes in bulk Mg/Ca composition, while the bulk $\delta^{18}O$ value will typically change faster than Mg/Ca. This is observed regardless of what partitioning coefficient is used for Mg and demonstrates that the planktonic Mg/Ca proxy is more diagenetically robust than the $\delta^{18}O$ proxy. Thus, this model can explain the observed decoupling of these two proxies. Furthermore, the preservation of intra-test Mg-banding shows potential for use in evaluating the preservation of primary Mg/Ca values and hence the accuracy of paleotemperature reconstructions.

INTRODUCTION

Paleoclimatic data from many open ocean sediment cores have been discredited because the foraminifera tests have been microstructurally altered, and their $\delta^{18}O$ values give significantly colder sea-surface temperatures than contemporaneous, texturally pristine foraminifera preserved in hemipelagic clays with no microstructural alteration (Pearson et al., 2001). The corresponding impact of recrystallization on the Mg/Ca paleothermometer is less certain. Sexton et al. (2006) demonstrated that Mg/Ca and $\delta^{18}O$ values yield different paleotemperatures, which could be attributed to uncertainty in Mg partitioning coefficients or to burial diagenesis in a closed system. We present an early diagenetic mechanism by which primary Mg/Ca values could be preserved even as $\delta^{18}O$ values are overprinted.

Diagenetic alteration of foraminifera during burial is typically categorized into one of three categories: partial dissolution, authigenic overgrowth, and recrystallization (Edgar et al., 2015). Microspatial *in situ* analysis of foraminiferal geochemistry has been applied to study the effects of partial dissolution and authigenic overgrowth (Kozdon et al., 2011; Fehrenbacher and Martin, 2014; Stainbank et al., 2020). These methods can differentiate among these three processes, as well as analyze unaltered regions (Kozdon et al., 2013). Researchers have shown that diagenetic exchange can result in heterogenous alteration and that Mg/Ca and $\delta^{18}O$, as measured by microspatial sampling techniques, retain a primary signal in certain domains of recrystallized foraminifera, possibly due to recrystallization in a closed system (Kozdon et al., 2011, 2013). This result is important, as it hints at the possibility of reconstructing paleotemperatures from previously discredited core sites using micro-analytical techniques. However, such applications are currently limited by our understanding of the diagenetic alteration of foraminifera.

In our study, one mechanism was investigated, where foraminiferal test recrystallization is facilitated by inter-crystalline water films (Wardlaw et al., 1978). Experiments with benthic foraminifera show that exchange between the test and surrounding water occurs along microstructural fractures between "cogwheel structures" and along organic layers in the test wall (Cisneros-Lazaro et al., 2022). Diffusion along these films enables solute transport into the test from surrounding fluid and between adjacent layers of calcite. ^{45}Ca tracer experiments demonstrate element mobility from external fluid into the foraminiferal test, which resembles a diffusive gradient (Chanda et al., 2019). The amount of transport determines the extent to which the diagenesis is dominated by the chemistry of the external fluids (i.e., an "open system") or the chemistry of the original foraminiferal calcite ("closed system"). Elements within the test would change at a rate proportional to their relative abundance in the fluid and carbonate phases (Ahm et al., 2018); this provides a mechanism by which whole-test Mg/Ca, $\delta^{18}O$, and other values could feasibly change at different rates. We also tested an alternative hypothesis, wherein high- and low-magnesium calcite layers have different reactivities, following Chanda et al. (2019). If recrystallization slows or stops before reaching equilibrium, then the effects of this early process would be preserved, potentially explaining observed offsets in temperature reconstructions from $\delta^{18}O$ and Mg/Ca proxies. The implications of these hypotheses are explored here by comparing numerical models with new and published geochemical analyses, and with new electron probe microanalyzer (EPMA) maps of Eocene glassy and frosty foraminifera. Our results imply that the preservation of foraminiferal Mg-banding could be used as a tool for assessing the impact of foraminiferal

*E-mail: staudigel@em.uni-frankfurt.de

CITATION: Staudigel, P.T., et al., 2022, Apparent preservation of primary foraminiferal Mg/Ca ratios and Mg-banding in recrystallized foraminifera: Geology, v. 50, p. 760–764, https://doi.org/10.1130/G49984.1

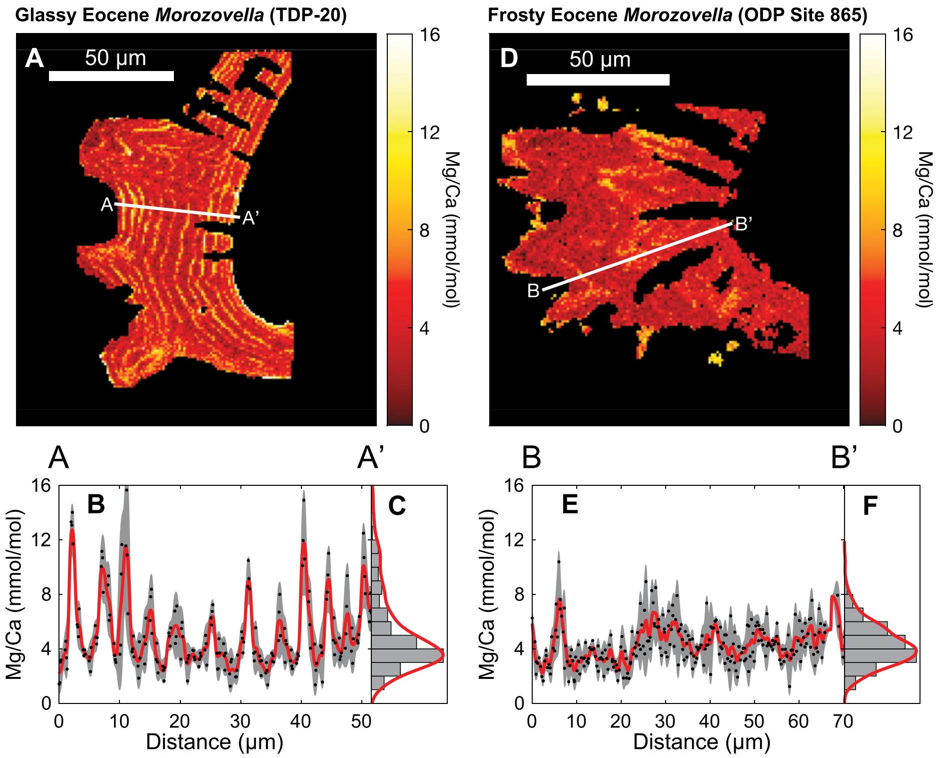

Figure 1. Analysis of early to middle Eocene *Morozovella aragonensis*. (A) Electron probe microanalyzer Mg/Ca map of a glassy test from Tanzanian Drilling Project (TDP) Core 20. (B) Transect A–A′ Mg/Ca values. Red line and gray region represent moving weighted mean ±95% confidence interval. (C) Histogram (gray) and Kernel density function (KDF; red) of Mg/Ca values across transect A–A′. (D) EPMA Mg/Ca map of a frosty test from Ocean Drilling Program Site 865. (E) Transect B–B′ Mg/Ca values. (F) Histogram and KDF of Mg/Ca values across transect B–B′.

recrystallization on geochemical climate proxies on a site-specific basis.

METHODS AND RESULTS

Sample Sites

Our study focuses on fossil tests of *Morozovella*, a common Paleogene genus of planktonic foraminifera, from sediments in two low-latitude sites: (1) clay-rich sediments from core TDP20 of the Kilwa Group, Tanzania (extracted during the Tanzanian Drilling Project, [TDP]), which contain middle Eocene well-preserved (glassy) foraminifera (Pearson et al., 2001), and (2) carbonate-rich sediments from Ocean Drilling Program (ODP) Site 865 in the central Pacific Ocean, which host early Eocene recrystallized (frosty) foraminifera. Paired Mg/Ca and $\delta^{18}O$ analyses of different species of planktonic foraminifera were presented for both sites by Sexton et al. (2006). We supplement these whole-test analyses with EPMA microanalyses, as well as whole-test $\delta^{18}O$ and Mg/Ca measurements for *M. aragonensis*. A more detailed description of the analyses is provided in the Supplemental Material[1].

[1]Supplemental Material. Supplemental methods, discussion, tables, and figures. Please visit https://doi.org/10.1130/GEOL.S.19386218 to access the supplemental material, and contact editing@geosociety.org with any questions.

Electron Probe Microanalyzer

Tests of *M. aragonensis* were picked from the 300–425 µm sediment fraction and cleaned at Cardiff University and then analyzed at the Electron Microbeam Suite of the University of Bristol, UK. Results show evident Mg/Ca banding in the TDP test, and less pronounced banding in the frosty ODP test (Figs. 1A and 1D).

Model

We constructed three models that simulated diffusively limited reactive exchange between a foraminifer test and the surrounding fluids. Two 0-D "bulk" models simulated the whole test: one as a single component, and one divided into 25% high-magnesium and 75% low-magnesium calcite components with different reactivities (following Chanda et al., 2019). A 1-D model investigates the preservation of internal heterogeneity (e.g., Mg-banding). These models simulate the behavior of Mg, Sr, Ca, $\delta^{18}O$, and $\delta^{13}C$ in fluid and carbonate. The outer boundary condition simulates expected Eocene benthic seawater: $\delta^{18}O = -0.89‰$ (Cramer et al., 2011), $[Ca^{2+}] = 16$ mmol (Horita et al., 2002), Mg/Ca = 2.2 mol/mol (Evans et al., 2018), Sr/Ca = 8 mmol/mol (Lear et al., 2003), and temperature = 12 °C (Lear et al., 2000). In the 1-D model, the inner boundary condition is a zero-flux boundary. The glassy TDP foraminifera are assumed to represent the primary geochemical composition (Pearson et al., 2001), and thus the initial state of both models was either the bulk chemistry or internal variability measured by EPMA (Fig. 1B) of the TDP *Morozovella*.

Exchange between fluid and solid phases is assumed to be at equilibrium for the given temperature and fluid composition and governed by a partition coefficient (e.g., $K_{Sr} = [Sr/Ca_{carbonate}]/[Sr^{2+}/Ca^{2+}{}_{water}]$) ($K_{Sr} = 0.05$; Banner and Hanson, 1990; Banner, 1995) and $\delta^{18}O$ and $\delta^{13}C$ fractionation factor (Romanek et al., 1992; Kim and O'Neil, 1997). Due to the many published values for Mg partitioning, K_{Mg}, two are used that represent two extremes: 0.00081 (Baker et al., 1982) and 0.012 (Mucci, 1987). The models were run with different reaction rates, resulting in varying degrees of "closed-system" diagenesis. Because many of the parameters of these models were chosen somewhat arbitrarily, it is helpful to quantify the relative contribution of different fluxes (Fantle et al., 2020). The relative contribution of diffusion relative to the reactive flux is described by normalizing the diffusive lengthscale of oxygen to the width of the model unit, which gives the normalized diffusive flux (NDF).

$$NDF = \frac{\sqrt{\frac{D_O}{RMK}}}{\Delta z}, \quad (1)$$

where D_o, R, M, and K are the diffusion coefficient, reaction rate, mass ratio, and absolute partitioning coefficient (respectively) for the element in question (here, the value for oxygen is used). Three model settings are used, representing "open" (NDF = 126), "semi-closed" (NDF = 4.0), and "closed" (NDF = 0.4). The models wherein high- and low-magnesium calcite have different reactivities are exclusively run using the "open" model settings. Details regarding model implementation and specific equations, as well as example Matlab scripts, are provided in the Supplemental Material.

All model outputs are illustrated (Figs. S7–S24 in the Supplemental Material). Bulk Mg/Ca and Sr/Ca changed at a similar rate regardless of reaction rate as the Ca–Mg–Sr behavior is governed by the K_{Mg} and K_{Sr} values, although some minor difference can be observed due to different ionic diffusivities. This has been discussed by previous workers as a possible screening tool for this form of exchange (Kozdon et al., 2013; Tripati et al., 2003). The "open," "semi-closed," and "closed" models showed varying degrees of decoupling between $\delta^{18}O$ and Mg/Ca (Figs. 2A and 2B) regardless of which K_{Mg} value was used. This closed-system behavior is also evident in the 1-D models, which also show a dissipation of banding (expressed as the range of Mg/Ca values in Fig. 3) alongside changes in $\delta^{18}O$, but the bulk Mg/Ca changes more slowly in these

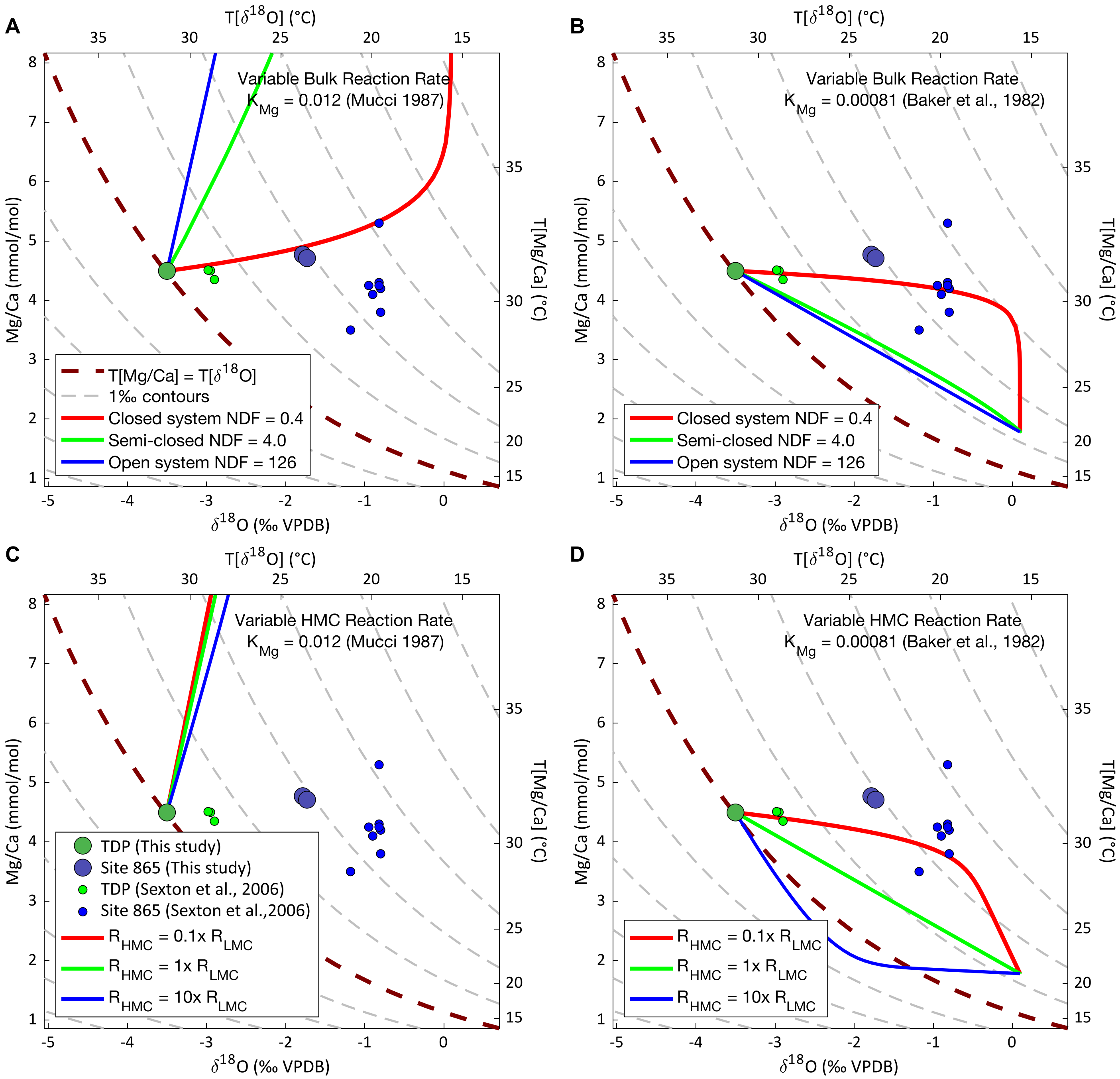

Figure 2. Whole-test Mg/Ca and $\delta^{18}O$ values for planktonic foraminifera (51 Ma samples, this study; 45 Ma samples, Sexton et al., 2006) compared with model-simulated evolution of test composition. (A,B) Whole test models where high-magnesium calcite (HMC) and low-magnesium calcite (LMC) have equal reactivity but are otherwise identical to the "open-system model." K_{Mg}—Mg partitioning; NDF—normalized diffusive flux; VPDB—Vienna Peedee belemnite. (C,D) Whole test models where high- and low-magnesium calcite have different reactivities. A and C show models using the Mucci (1987) K_{Mg}. B and D show models using the Baker et al. (1982) K_{Mg}.

closed-system models. In the 1-D model, $\delta^{18}O$ values are spatially homogenous, and little rock buffering is evident in the results.

Carbon isotopes are the most internally buffered component of these models due to their abundance in carbonate (10 mol/kg) and relative scarcity in seawater (2 mmol/kg); thus, the $\delta^{13}C$ value changes more slowly than Mg/Ca ratios in these diffusively limited faster models. This would make $\delta^{13}C$ a tempting tool for identifying open-system recrystallization or authigenic overgrowths; however, the primary $\delta^{13}C$ of foraminifera is itself highly variable by up to several ‰ due to the effects of photosymbionts (Gaskell and Hull, 2019).

DISCUSSION

Two hypotheses are investigated using numerical modeling alongside isotopic and chemical analyses. The first investigates the behavior of increasingly closed-system diagenesis as a means of explaining decoupled Mg/Ca and $\delta^{18}O$-derived paleo-temperatures. The second investigates the effect of variable high- and low-magnesium calcite reaction rates. Both mechanisms vary with K_{Mg} value; the higher K_{Mg} value (Mucci, 1987) is shown in Figures 2A and 2C, and the lower from Baker et al. (1982) is shown in Figures 2B and 2D. Our models show that with increasingly closed-system recrystallization, Mg/Ca and $\delta^{18}O$ values become decoupled, where Mg/Ca initially remains unchanged, irrespective of which K_{Mg} value was used (Fig. 2).

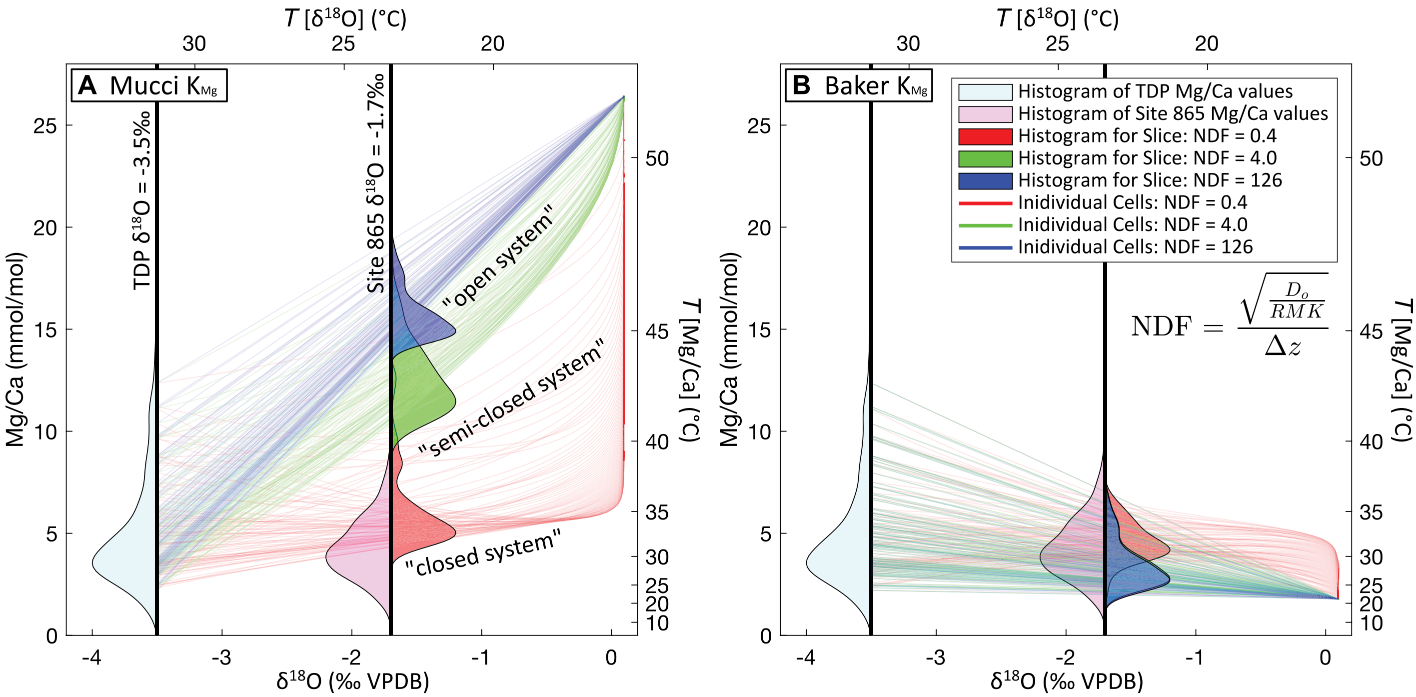

Figure 3. One-dimensional, 100 element model Mg/Ca and δ18O values compared to measured gas-source mass spectrometry whole-test δ18O and electron probe microanalyzer (EPMA) Mg/Ca values. Panels show results of models using different Mg partitioning, K_{Mg}, values: Mucci—Mucci (1987); Baker—Baker et al. (1982). Left-side kernel density functions (KDFs) in each panel show the distribution of Mg/Ca values measured using EPMA from Figures 1C and 1F; right-side KDFs show the Mg/Ca values of model elements where the elements' δ18O value is equal to the measured bulk δ18O value of glassy and frosty early Eocene *Morozovella aragonensis* (shown as a black line). TDP—Tanzanian Drilling Project; Site 865—Ocean Drilling Program Site 865; NDF—normalized diffusive flux; VPDB—Vienna Peedee belemnite. See equation 1 in the text for the NDF variables.

The "closed-system" model can account for much of the observed difference in measured values for glassy and frosty foraminifera, with the remaining difference well within the expected natural variance of sea-surface temperatures. When the "open-system" model is applied, and high- and low-magnesium calcite components are given different reactivities, it is only possible to account for the observed differences between glassy and frosty foraminifera if the lower K_{Mg} is used and high-magnesium calcite is less reactive than low-magnesium calcite (Figs. 2C and 2D). This seems to contradict observations from EPMA, which show that the Mg-enriched regions appear to have changed more in the recrystallized test (Fig. 1D). When assessed using whole-test analyses, the "open model" appears similar to the effect of adding authigenic calcite, although these would be differentiable using petrography, scanning electron microscopy, or microspatial analysis (Kozdon et al., 2013; Stainbank et al., 2020). This highlights the importance of these techniques for resolving potentially ambiguous geochemical signatures.

We observe prominent banding in glassy Eocene *M. aragonensis*, a feature previously observed in some modern taxa, which is attributed to day/night cycles and chamber formation (Jonkers et al., 2016; Fehrenbacher et al., 2017). The effects of variably closed-system diagenesis on Mg-banding were investigated using the 1-D model. Results show that, in open-system models, the degree of "bandedness" (expressed as the range of Mg/Ca values in Figure 3, compared with the distribution of values from transects A–A′ and B–B′) diminishes as the model approaches equilibrium, and it changes at the same rate as Mg/Ca and δ18O values. However, in the more closed-system models, the bandedness is lost prior to the bulk change in Mg/Ca values but occurs alongside the change in bulk δ18O value. Thus, the loss of Mg-banding could only occur at the same rate, or faster, than changes in bulk Mg/Ca, but it cannot be used as an indicator of pristine δ18O value. This is to be expected, because the bands would only need to diffuse the 5–10 μm scale of banding, as opposed to bulk Mg/Ca, which would need to diffuse through the entire width of the test. Because Mg-bands are often associated with organic layers, it is possible that they are more directly connected with outside fluid and thus would change more rapidly, as shown by reaction-transport experiments (Cisneros-Lazaro et al., 2022). Thus, the observed preservation of Mg-banding is a prerequisite, albeit not wholly unambiguous, indication of well-preserved Mg/Ca values.

The K_{Mg} value is shown to be important; when the Mucci (1987) value is used, only the most closed-system model approximates the observed range of Mg/Ca values from EPMA (Fig. 3A), although the bulk value is slightly offset but within the expected range of values (see previous paragraph). When the lower value for K_{Mg} is used, most models predict largely overlapping ranges of Mg/Ca, which compare more favorably with EPMA observations. These models and observations are not meant to argue for one K_{Mg} or the other; we reason that the difference matters less when diagenesis occurs in a closed system. If this restricted diagenesis of biogenic particles in the sediment is common, analyses of bulk sediments and pore fluids would yield a lower apparent value for K_{Mg}, which could plausibly explain the lower apparent K_{Mg} values described for bulk sediment diagenesis by Baker et al. (1982).

CONCLUSIONS

Early recrystallization of foraminifera in a diffusively limited system provides a plausible mechanism for the observed robustness of Mg/Ca-derived paleo-temperatures when compared to δ18O values. The preservation of compositional heterogeneity such as Mg-banding could be used as an indicator for the extent of Mg uptake or loss, as Mg-banding requires less time to change than the bulk Mg/Ca ratio. This assumes that diffusive transport occurs through a distributed, interconnected network of inter-crystalline water, which makes up a small fraction of the foraminiferal test. Our model provides testable predictions, which agree with those of published data sets, and gives a plausible explanation for the apparently decoupled paleo-thermometers and a possible means of identifying this process. Microspatial techniques, such as EPMA, can be used to screen for a variety of diagenetic effects in addition to this. In circumstances where fractional dissolution or authigenic mineral formation can be ruled out using EPMA, and EPMA reveals decent preservation of Mg-banding, Mg/Ca-derived paleotemperatures would be expected to better represent the primary temperature than those derived from oxygen isotopes in texturally recrystallized foraminifera. Optimistically, our results show that in some cases, Mg/Ca paleothermometry may still be applicable even in texturally recrystallized foraminifera with compromised $\delta^{18}O$ values.

ACKNOWLEDGMENTS

This work was funded by Natural Environment Research Council grant NE/P019102/1 to C.H. Lear. This work benefitted from feedback from Matthew Fantle and Phil Sexton, two anonymous reviewers, and the editor of *Geology*. We thank Sandra Arndt for her advice on numerical model construction.

REFERENCES CITED

Ahm, A.S.C., Bjerrum, C.J., Blättler, C.L., Swart, P.K., and Higgins, J.A., 2018, Quantifying early marine diagenesis in shallow-water carbonate sediments: Geochimica et Cosmochimica Acta, v. 236, p. 140–159, https://doi.org/10.1016/j.gca.2018.02.042.

Baker, P.A., Gieskes, J.M., and Elderfield, H., 1982, Diagenesis of carbonates in deep-sea sediments: Evidence from Sr/Ca ratios and interstitial dissolved Sr^{2+} data: Journal of Sedimentary Petrology, v. 52, p. 71–82

Banner, J.L., 1995, Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis: Sedimentology, v. 42, p. 805–824, https://doi.org/10.1111/j.1365-3091.1995.tb00410.x.

Banner, J.L., and Hanson, G.N., 1990, Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis: Geochimica et Cosmochimica Acta, v. 54, p. 3123–3137, https://doi.org/10.1016/0016-7037(90)90128-8.

Chanda, P., Gorski, C.A., Oakes, R.L., and Fantle, M.S., 2019, Low temperature stable mineral recrystallization of foraminiferal tests and implications for the fidelity of geochemical proxies: Earth and Planetary Science Letters, v. 506, p. 428–440, https://doi.org/10.1016/j.epsl.2018.11.011.

Cisneros-Lazaro, D., et al., 2022, Fast and pervasive diagenetic isotope exchange in foraminifera tests is species-dependent: Nature Communications, v. 13, p. 113, https://doi.org/10.1038/s41467-021-27782-8.

Cramer, B.S., Miller, K.G., Barrett, P.J., and Wright, J.D., 2011, Late Cretaceous–Neogene trends in deep ocean temperature and continental ice volume: Reconciling records of benthic foraminiferal geochemistry ($\delta^{18}O$ and Mg/Ca) with sea level history: Journal of Geophysical Research: Oceans, v. 116, C12023, https://doi.org/10.1029/2011JC007255.

Edgar, K.M., Anagnostou, E., Pearson, P.N., and Foster, G.L., 2015, Assessing the impact of diagenesis on $\delta^{11}B$, $\delta^{13}C$, $\delta^{18}O$, Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite: Geochimica et Cosmochimica Acta, v. 166, p. 189–209, https://doi.org/10.1016/j.gca.2015.06.018.

Evans, D., et al., 2018, Eocene greenhouse climate revealed by coupled clumped isotope-Mg/Ca thermometry: Proceedings of the National Academy of Sciences of the United States of America, v. 115, p. 1174–1179, https://doi.org/10.1073/pnas.1714744115.

Fantle, M.S., Barnes, B.D., and Lau, K.V., 2020, The role of diagenesis in shaping the geochemistry of the marine carbonate record: Annual Review of Earth and Planetary Sciences, v. 48, p. 549–583, https://doi.org/10.1146/annurev-earth-073019-060021.

Fehrenbacher, J.S., and Martin, P.A., 2014, Exploring the dissolution effect on the intrashell Mg/Ca variability of the planktic foraminifer *Globigerinoides ruber*: Paleoceanography, v. 29, p. 854–868, https://doi.org/10.1002/2013PA002571.

Fehrenbacher, J.S., Russell, A.D., Davis, C.V., Gagnon, A.C., Spero, H.J., Cliff, J.B., Zhu, Z., and Martin, P., 2017, Link between light-triggered Mg-banding and chamber formation in the planktic foraminifera *Neogloboquadrina dutertrei*: Nature Communications, v. 8, 15441, https://doi.org/10.1038/ncomms15441.

Gaskell, D.E., and Hull, P.M., 2019, Symbiont arrangement and metabolism can explain high $\delta^{13}C$ in Eocene planktonic foraminifera: Geology, v. 47, p. 1156–1160, https://doi.org/10.1130/G46304.1.

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.

Jonkers, L., Buse, B., Brummer, G.-J.A., and Hall, I.R., 2016, Chamber formation leads to Mg/Ca banding in the planktonic foraminifer *Neogloboquadrina pachyderma*: Earth and Planetary Science Letters, v. 451, p. 177–184, https://doi.org/10.1016/j.epsl.2016.07.030.

Kim, S.T., and O'Neil, J.R., 1997, Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonate: Geochimica et Cosmochimica Acta, v. 61, p. 3461–3475, https://doi.org/10.1016/S0016-7037(97)00169-5.

Kozdon, R., Kelly, D.C., Kita, N.T., Fournelle, J.H., and Valley, J.W., 2011, Planktonic foraminiferal oxygen isotope analysis by ion microprobe technique suggests warm tropical sea surface temperatures during the early Paleogene: Paleoceanography, v. 26, PA3206, https://doi.org/10.1029/2010PA002056.

Kozdon, R., Kelly, D.C., Kitajima, K., Strickland, A., Fournelle, J.H., and Valley, J.W., 2013, In situ $\delta^{18}O$ and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene–Eocene thermal maximum: Paleoceanography, v. 28, p. 517–528, https://doi.org/10.1002/palo.20048.

Lear, C.H., Elderfield, H., and Wilson, P.A., 2000, Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite: Science, v. 287, p. 269–272, https://doi.org/10.1126/science.287.5451.269.

Lear, C.H., Elderfield, H., and Wilson, P.A., 2003, A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes: Earth and Planetary Science Letters, v. 208, p. 69–84, https://doi.org/10.1016/S0012-821X(02)01156-1.

Mucci, A., 1987, Influence of temperature on the composition of magnesian calcite overgrowths precipitated from seawater: Geochimica et Cosmochimica Acta, v. 51, p. 1977–1984, https://doi.org/10.1016/0016-7037(87)90186-4.

Pearson, P.N., Ditchfield, P.W., Singano, J., Harcourt-Brown, K.G., Nicholas, C.J., Olsson, R.K., Shackleton, N.J., and Hall, M.A., 2001, Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs: Nature, v. 413, p. 481–487, https://doi.org/10.1038/35097000.

Romanek, C.S., Grossman, E.L., and Morse, J.W., 1992, Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate: Geochimica et Cosmochimica Acta, v. 56, p. 419–430, https://doi.org/10.1016/0016-7037(92)90142-6.

Sexton, P.F., Wilson, P.A., and Pearson, P.N., 2006, Microstructural and geochemical perspectives on planktic foraminiferal preservation: "Glassy" versus "Frosty": Geochemistry Geophysics Geosystems, v. 7, Q12P19, https://doi.org/10.1029/2006GC001291.

Stainbank, S., et al., 2020, Assessing the impact of diagenesis on foraminiferal geochemistry from a low latitude, shallow-water drift deposit: Earth and Planetary Science Letters, v. 545, 116390, https://doi.org/10.1016/j.epsl.2020.116390.

Tripati, A.K., Delaney, M.L., Zachos, J.C., Anderson, L.D., Kelly, D.C., and Elderfield, H., 2003, Tropical sea-surface temperature reconstruction for the early Paleogene using Mg/Ca ratios of planktonic foraminifera: Paleoceanography, v. 18, 1101, https://doi.org/10.1029/2003PA000937.

Wardlaw, N., Oldershaw, A., and Stout, M., 1978, Transformation of aragonite to calcite in a marine gasteropod: Canadian Journal of Earth Sciences, v. 15, p. 1861–1866, https://doi.org/10.1139/e78-193.

Printed in USA