Phanerozoic variation in dolomite abundance linked to oceanic anoxia

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We commend Li et al. (2021) for their recent effort to explain dolomite abundance through time. The data sets presented are impressive. This discussion centers on two claims put forth in the paper. Firstly they state “there has been a long-running debate on whether Phanerozoic dolomites are predominantly syngentic (defined as primary nucleation [Petrasch et al., 2017]) or the product of secondary dolomitization of other carbonates,” the latter resulting from “deep burial.” Based on numerous petrographic studies, massive platform dolomites of the Phanerozoic are not the result of primary precipitation, but largely a replacement product of marine calcium carbonate, and therefore secondary (e.g., review by Land, 1985). Additionally, many ancient aerially extensive continental platform dolomites are understood to have never been greatly buried or to have only suffered uplift, with examples including the Miocene Dam Formation and Eocene Rus and Umm er Radhuma Formations of the southern Arabian Gulf (Van Buchem et al., 2014). Furthermore, petrographic relationships indicate that more deeply buried examples regularly suffered early dolomite replacement prior to burial (e.g., Morrow, 1990).

Secondly, Li et al. state that dolomite abundance negatively correlates with marine invertebrate genus richness, and peaks during anoxia events due to sulfate-reducing microbes capable of “efficient” dolomite formation. However, Li et al. utilized a method for calculating dolomite abundance that allows thin units to skew abundances. If normalized for total carbonate thickness, spikes in dolomite abundances would also be observed for Epochs that do not correlate to anoxia events such as the Furongian, Middle Jurassic, and Miocene. Also, given the low R²-value they report for the dolomite abundance versus genus richness correlation (0.20) and the observation that only 5 out of 12 documented anoxic events appear to correlate with local peaks in their abundance curve (Li et al.’s figure 1), the “link” specified by their article title is tenuous. The coincidence between dolomite abundance peaks and extinction events is more convincing, yet this may correspond to other changes in ocean chemistry, for instance ocean acidification (e.g., Tyrrell et al., 2015).

Recent investigations (e.g., Manche and Kaczmarek, 2019) have shown that platform-scale dolomite formation can occur on a cycle-by-cycle basis within the depositional setting. Such replacive synsedimentary dolomite forming in response to low carbonate saturation states in marine pore systems leads to lithification of the sediment (Rivers et al., 2021). The production of this process was likely akin to modern beachrock (i.e., lithified deposits near the sediment surface), but more widespread. The early dolostones forming in these systems frequently captured high-diversity trace fossil assemblages (e.g., Ryan et al., 2020), indicating oxygenated pore water conditions. Conversely, marine hydrocarbon source rocks (by definition anoxic organic-rich deposits) more commonly bear calcite than dolomite (Lazar et al., 2015). Additionally, in restricted settings, such as coastal Qatar where oxygen levels are significantly depressed (Rivers et al., 2019) and microbial mats form prolifically, evidence of ongoing replacive dolomite formation during the Holocene and Pleistocene is scant (Rivers et al., 2021). This is in spite of the presence of dolomite-forming sulfate-reducing microbes (e.g., DiLoreto et al., 2019), and dolomite saturation states higher than 10,000X!

In summary, the presence of anoxic pore waters and associated sulfate reducing microbes does not necessarily cause efficient replacive dolomite formation, whereas the absence of sulfate-reducing microbes does not prevent dolomite formation. Abiotic precipitation of dolomite is achievable at low temperature in association with calcite dissolution by pulsed CO₂ flood in concentrated seawater (e.g., Liebermann, 1967).

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REFERENCES CITED
DiLoreto, Z.A., et al., 2019, Microbial community composition and dolomite formation in the hypersaline microbial mats of the Khor Al-Adaid sabkhas, Qatar: Extremophiles, v. 23, p. 201–218, https://doi.org/10.1007/s00792-018-01074-4.
Land, L.S., 1985, The origin of massive dolomite: Journal of Geological Education, v. 33, p. 112–125, https://doi.org/10.5408/0022-1368-33.2.112.
Lazar, O. R., Bohacs, K., Schieber, J., Macquaker, J., and Demko, T., 2015, Mudstone primer: Lithofacies variations, diagnostic criteria, and sedimentological/stratigraphical implications at Lamina to Bedset Scale: Society for Sedimentary Geology (SEPM), Concepts in Sedimentology and Paleontology 12, 198 p., https://doi.org/10.2110/sepm.conf/12.
Li, M., Wignall, P.B., Dai, X., Hu, M., and Song, H., 2021, Phanerozoic variation in dolomite abundance linked to oceanic anoxia: Geology, v. 49, p. 698–702, https://doi.org/10.1130/G48502.1.
Liebermann, O., 1967, Synthesis of dolomite: Nature, v. 213, p. 241–245, https://doi.org/10.1038/213241a0.
Manche, C.J., and Kaczmarek, S.E., 2019, Evaluating reflux dolomitization using a novel high-resolution record of dolomite stoichiometry: A case study from the Cretaceous of central Texas, USA: Geology, v. 47, p. 586–590, https://doi.org/10.1130/G46218.1.
Morrow, D.W., 1990, Synsedimentary dolospars cementation: a possible Devonian example in the Camshill Formation, Northwest Territories, Canada: Sedimentology, v. 37, p. 763–773, https://doi.org/10.1111/j.1365-3091.1990.tb00633.x.
Petrasch, D.A., Bialik, O.M., Bottongrai, T.R.R., Vasconcelos, C., Roberts, J.A., McKenzie, J.A., and Konhauer, K.O., 2017, Microbially catalyzed dolomite formation: From near-surface to burial: Earth-Science Reviews, v. 171, p. 558–582, https://doi.org/10.1016/j.earscirev.2017.06.015.
Rivers, J.M., Varghese, L., Youis, R., Whitaker, F.F., Skat, S.L., and Al-Shaikh, I., 2019, The geochemistry of Qatar coastal waters and its Impact on carbonate sediment chemistry and early marine diagenesis: Journal of Sedimentary Research, v. 89, p. 293–309, https://doi.org/10.2110/jsr.2019.17.
Rivers, J.M., Yousif, R., Kaczmarek, S.E., and Al-Shaikh, I., 2021, Cenozoic coastal carbonate deposits of Qatar: Evidence for dolomite preservation bias in highly-arid systems: Sedimentology, v. 68, p. 771–787, https://doi.org/10.1111/sed.12805.
Ryan, B.H., Kaczmarek, S.E., and Rivers, J.M., 2020, Early and pervasive dolomitization by near-normal marine fluids: New lessons from an Eocene evaporative setting in Qatar: Sedimentology, v. 67, p. 2917–2944, https://doi.org/10.1111/sed.12726.
Tyrrell, T., Merchó, A., and McKay, D.I.A., 2015, Severity of ocean acidification following the end-Cretaceous asteroid impact: Proceedings of the National Academy of Sciences of the United States of America, v. 112, p. 6556–6561, https://doi.org/10.1073/pnas.1418604112.
Van Buchem, F.S.P., Svendsen, N., Hoch, E., Pedersen-Tatalovic, R., and Habib, K., 2014, Depositional history and petroleum habitat of Qatar, in Marlow, L., et al., eds., Petroleum Systems of the Tethyan Region: American Association of Petroleum Geologists Memoir 106, p. 641–677, https://doi.org/10.1306/13431868M106361.