https://doi.org/10.1130/G4xxxxY.1

A dolomitization event at the oceanic chemocline during the Permian-Triassic transition

Mingtao Li[1], Haijun Song[1], Thomas J. Algeo[1,2,3], Paul B. Wignall[4], Xu Dai[1], and Adam D. Woods[5]
[1]State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China
[2]State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Science, China University of Geosciences, Wuhan 430074, China
[3]Department of Geology, University of Cincinnati, Cincinnati, Ohio 45221-0013, USA
[4]School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[5]Department of Geological Sciences, California State University, Fullerton, California 92834-6850, USA

In the Li et al. (2018) paper, we presented evidence of a dolomitization event at the Permian-Triassic boundary (PTB) and linked it to microbial blooms under anoxic conditions. We welcome this opportunity to clarify some important points in our paper in response to the comment of Gregg et al. (2019).

Gregg et al. (2019) argue that we did not provide data to confirm the presence of dolomite, and that the proxy mol Mg/(Mg+Ca) of carbonate rocks may be affected by the content of Mg-rich clay. In order to minimize the influence of clays in marly samples, we used the element Al for preliminary screening. All samples with Al >4% were excluded from the analysis (since pure shales typically contain 8-12% Al, this threshold excluded samples containing >33-50% non-carbonate material). Furthermore, samples with Al <4% were checked by cross-plotting Mg/Ca versus Al to determine whether a regression existed (Fig. DR5). Moreover, XRD data were available for some (but not all) of our studied sections, and we checked these records against our dolomite values based on Mg-Ca concentrations. Among the sections that we checked were Yangou (Li et al., 2017), Meishan (Liang, 2002), and Nhi Tao (Algeo et al., 2007). At Yangou, for example, both the XRD data and our geochemical data show a shift from pure calcium carbonate (> 90%) below the PTB to dolomite (> 80%) above it. In all cases tested, the XRD and geochemical data yielded consistent interpretations of changes in carbonate mineralogy.

Gregg et al. (2019) propose that recrystallization of primary Mg carbonates during late diagenesis may be an explanation for PTB dolomitization. Late diagenetic dolomitization is common in the geological record (Holland and Zimmerman, 2000), but this hypothesis cannot account for dolomitization of our study units for the following reasons: (I) Late diagenetic dolomitization preferentially occurs in supratidal facies, in which high Mg concentrations promote dolomite precipitation (Alsharhan and Kendall, 2003), and in deep-water facies, in which clays provide a Mg source. However, PTB dolomites are concentrated in intermediate-depth facies and are rare in shallow- and deep-water facies. (II) The PTB dolomitization event was temporally constrained to the earliest Triassic Griesbachian substage, an interval characterized by significant seawater sulfate drawdown (Song et al., 2014), which would have facilitated dolomite formation at that time. (III) Dolomite precipitated during late burial diagenesis commonly consists of coarse rhombs with multizoned cements in CL images (Choquette et al., 2008). Photomicrographs and CL images of dolomite samples from the PTB sections show that the homogenous dolomitic matrix consists of fine subhedral to euhedral dolomite crystals (Fig. DR7), showing weak signs of late diagenetic dolomitization. (IV) Enclosed in the PTB dolomite crystals are abundant fossilized bacteria and organic matter with honeycomb structures (interpreted as extracellular polymeric substances, EPS), suggesting microbial influences on dolomite precipitation.

Gregg et al. (2019) also argue that the experiments we cited provide no convincing evidence of laboratory dolomite synthesis via microbial mediation. Although the XRD patterns of microbially induced minerals grown in experiments did not confirm the presence of a stoichiometric dolomite phase (Gregg et al., 2015), these Mg-rich carbonate or Ca-dolomite precipitates overcame the hydration energy barriers of Mg^{2+} cations and are interpreted as precursors of stoichiometric dolomite (Petrash et al., 2017). Some uncertainty exists regarding how Ca-rich, disordered precursor phases stabilize to ordered stoichiometric dolomite in the natural environment, but this transformation must occur as the latter has been widely documented in organic-rich marine sediments of Neogene age (Burns and Baker, 1987; Bontognali et al., 2010).

REFERENCES CITED

Algeo, T.J., Ellwood, B., Nguyen, T.K.T., Rowe, H., and Maynard, J.B., 2007, The Permian–Triassic boundary at Nhi Tao, Vietnam: Evidence for recurrent influx of sulfidic watermasses to a shallow-marine carbonate platform: Palaeogeography Palaeoclimatology Palaeoecology, v. 252, p. 304–327, https://doi.org/10.1016/j.palaeo.2006.11.055.

Alsharhan, A.S., and Kendall, C.G.St.C., 2003, Holocene coastal carbonates and evaporites of the southern Arabian Gulf and their ancient analogues: Earth Science Reviews, v. 61, p. 191–243, https://doi.org/10.1016/s0012-8252(02)00110-1.

Bontognali, T.R.R., Vasconcelos, C., Warthmann, R.J., Bernasconi, S.M., Dupraz, C., Strohmengers, C.J., and Mckenzie, J.A., 2010, Dolomite formation within microbial mats in the coastal sabkha of Abu Dhabi (United Arab Emirates): Sedimentology, v. 57, p. 824–844, https://doi.org/10.1111/j.1365-3091.2009.01121.x.

Burns, S.J., and Baker, P.A., 1987, A geochemical study of dolomite in the Monterey Formation, California: Journal of Sedimentary Research, v. 57, p. 128–139, https://doi.org/10.1306/212f8ac6-2b24-11d7-8648000102c1865d.

Choquette, P.W., and Hiatt, E.E., 2008, Shallow−burial dolomite cement: a major component of many ancient sucrosic dolomites: Sedimentology, v. 55, p. 423–460, https://doi.org/10.1111/j.1365-3091.2007.00908.x.

Gregg, J.M., Bish, D.L., Kaczmarek, S.E., and Machel, H.G., 2015, Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: a review: Sedimentology, v. 62, p. 1749–1769, https://doi.org/10.1111/sed.12202.

Gregg, J.M., Kaczmarek, S.E., Bish, D.L., Machel, H.G., and Fouke, B.W., 2019, A dolomitization event at the oceanic chemocline during the Permian-Triassic transition: Comment: Geology, v. xx, p. xxx, https://doi.org/10.1130/G46203C.1

Holland D. Heinrich, and Zimmermann Heide, 2000, The dolomite problem revisited1: International Geology Review, v. 42, p. 481–490, https://doi.org/10.1080/00206810009465093.

Li, R., 2017, Petrography and geochemistry of the Permian-Triassic boundary interval, Yangou section, South China: Implications for early Griesbachian seawater $\delta^{13}C_{DIC}$ gradient with depth: Sedimentary Geology, v. 351, p. 36-47, https://doi.org/10.1016/j.sedgeo.2017.02.008.

Li, M.T., Song, H.J., Algeo, T.J., Wignall, P.B., Dai, X., and Woods, A.D., 2018, A dolomitization event at the oceanic chemocline during the Permian-Triassic transition: Geology, v. 46, p. 1043–1046, https://doi.org/10.1130/g45479.1.

https://doi.org/10.1130/G4xxxxY.1

Liang, H., 2002, End-Permian catastrophic event of marine acidification by hydrated sulfuric acid: Mineralogical evidence from Meishan Section of South China: Science Bulletin, v. 47, p. 1393–1397, https://doi.org/10.1360/02tb9307.

Petrash, D.A., Bialik, O.M., Bontognali, T.R.R., Vasconcelos, C., Roberts, J.A., McKenzie, J.A., and Konhauser, 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.

Song, H.Y., Tong, J.N., Algeo, T.J., Song, H.J., Qiu, H.O., Zhu, Y.Y., Tian, L., Bates, S., Lyons, T.W., Luo, G.M., and Kump, L.R., 2014, Early Triassic seawater sulfate drawdown: Geochimica et Cosmochimica Acta, v. 128, p. 95–113, https://doi.org/10.1016/j.gca.2013.12.009.