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Anoxygenic phototrophs and the forgotten art of making dolomite

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Dolomite [$CaMg(CO_3)_2$] is abundant in ancient rocks and rare in younger ones; why is unclear. Evidence is now emerging (Daye et al., 2019, p. 509 in this issue of *Geology*) that primitive microbes can mediate the formation of dolomite, and they apparently do it better than their younger and more-evolved descendants (DiLoreto et al., 2019). If this is only a coincidence, it is an intriguing one!

Among the many minerals that occur in the geological record, dolomite is surely among those whose formation mechanism has been most studied, discussed and energetically debated (e.g., McKenzie, 1991; Arvidson and Mackenzie, 1999; Warren, 2000; Petrash et al., 2017). Such debate, often referred to as "the Dolomite Problem," stems from the difficulty of precipitating dolomite in laboratory experiments conducted at low temperatures (Land, 1998) although, in some modern environments, dolomite is evidently forming at temperatures lower than 50 °C (e.g., Illing and Taylor, 1993). Moreover, dolomite is abundant in Precambrian sedimentary rocks, while its presence becomes progressively rarer in younger sediments (McKenzie, 1991). This observation suggests the existence of a link between global environmental change and dolomite formation, but the nature of this change remains elusive (Burns et al., 2000).

In 1995, Vasconcelos et al. proposed that dolomite formation at low temperature might be the result of microbial activity, adding a new "multidisciplinary dimension" to this field of research. Besides being a possible solution to the long-standing Dolomite Problem, this idea also gave a new exciting significance to dolomite: some dolomites that form at low temperature may represent a biosignature, evidence for past microbial activity. This hypothesis is particularly captivating for the study of early life. Indeed, many Precambrian stromatolites (laminated accretionary sedimentary structures that are interpreted as fossils of microbial mats) have laminae consisting of dolomite (Wright and Tucker, 1990; Wright, 2000; Allwood et al., 2009). It would, therefore, be remarkable to conclude that not only the morphology, but also the mineralogy of these structures points to past microbial activity.

The reasons for being excited about the microbial dolomite hypothesis are clear. However, despite the more than 20 years that have passed since the inception of the "microbial model," many aspects of this mineralization process remain too ambiguous to allow for establishing a solid link between microbes and some ancient dolomites. Indeed, it is yet unclear which microbes (which phyla of the various domains) can mediate dolomite formation, and whether such process is favored—or occurs exclusively—within a defined window of environmental conditions (i.e., specific water chemistry, Mg/Ca ratio, salinity, temperature, pH, alkalinity; McCormack et al., 2018). To interpret dolomite as a biosignature, it is also essential to find a way of differentiating microbial dolomite from abiotic dolomite that forms at high temperatures, precipitating from hydrothermal fluids or by metamorphic replacement of other primary carbonate minerals. Unfortunately, at least for now, there is no distinctive geochemical or morphological signature that can be uniquely attributed to microbial dolomite (Petrash et al., 2017).

In addition to all these uncertainties, the validity of the microbial model was recently attacked at its foundations by reviewing and questioning the interpretation of previously published data on the subject. Gregg et al. (2015) concluded that all Mg-rich carbonates produced by microbes in laboratory experiments lack evidence for cation ordering. Even though Ca^{2+} and Mg^{2+} are present, in (or close to) the right proportion, they are not arranged in alternating layers within the crystal lattice, which is the key crystallographic characteristic differentiating dolomite from calcite. Many researchers feel comfortable with the hypothesis that, once the chemistry of dolomite is achieved, crystal ordering will happen spontaneously in time. This explains the widespread use of the term "protodolomite" to refer to a mineral with the chemistry of dolomite but lacking X-ray diffraction–detectable ordering peaks. However, Gregg et al. (2015) points out that there is no demonstration that such microbially mediated mineral phases will actually evolve into the ordered dolomite found in the geological record.

The study by Daye et al. (2019) provides important new momentum to the field of microbial dolomite, by possibly solving the abovementioned "lack of ordering" issue and by providing new insight on which microbes, and under which environmental conditions, may have produced the petrographic textures observed in some Archean and Proterozoic stromatolites. The article reports results of laboratory experiments in which dolomite was precipitated within biofilms of anoxygenic phototrophic microbes, grown in the presence of Mn^{2+}.

The fact that dolomite that was formed in the experiments of Daye et al. shows some signs of cation ordering already after two weeks is important, not only in view of the concerns expressed by Gregg et al. (2015), but also because it demonstrates that some dolomites present in ancient rocks may be primary minerals. Some dolomites not excessively compromised by late-stage metamorphic processes might, therefore, record geochemical signals inherited directly from seawater/porewaters. This is essential for paleoenvironmental reconstructions, and contrasts with the view that all ancient dolomites are bad targets for geochemical proxies, as they record, at best, the composition of diagenetic fluids.

Active anoxygenic photosynthetic microbial cells, exopolymeric substances (EPS), and the presence of Mn^{2+} are identified by Daye et al. as the key factors for the mineralization process. While EPS has been proposed as important in several previous studies on dolomite formation (e.g., Bontognali et al., 2010, 2014; Zhang et al., 2012; Roberts, et al., 2013), the addition of Mn^{2+} to the bacterial growth media represents a more

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Figure 1. The intertidal zone of the Khor Al-Adaid sabkha in Qatar (A) is colonized by microbial mats that mediate the formation of various carbonate minerals. However, ordered dolomite has been identified exclusively in mats with a community composition in the uppermost layer dominated by anoxygenic phototrophs (orange layer visible in B), whereas only very high-Mg calcite (also referred to as protodolomite) has been detected in mats dominated by cyanobacteria.

rare and innovative approach. The mechanistic role of this transition metal for the mineralization process remains unexplained, but the results pointing to a catalytic role are consistent with observations made in natural environments, where dolomite occurs within buried microbial mats in chemofacies associated with Mn-S redox cycling (Petrash et al., 2015).

Anoxygenic phototrophs are organisms that use electron donors other than water, and that do not produce molecular oxygen. Their metabolism is considered to be much older than oxygenic photosynthesis, and may have prevailed during the early history of our planet, maybe even for longer than previously thought (i.e., until the time slightly predating the Paleoproterozoic rise of oxygen) (Fischer et al., 2016). Accordingly, Daye et al. suggest that a microbially mediated process orchestrated by anoxygenic phototrophs may explain the preservation of microbial textures before the oxygenation of the oceanic photic zone.

The work of Daye et al. does not provide a direct comparison of oxygenic versus anoxygenic phototrophs in respect to their ability to form dolomite under the same experimental conditions. However, such a comparison was made in a recent study on dolomite formation within natural microbial mats colonizing some hypersaline ponds in the sabkhas of Qatar (Fig. 1) (DiLoreto et al., 2019). Consistent with what is observed in the experiments of Daye et al., that study has revealed the presence of ordered dolomite in mats whose uppermost layer was dominated by anoxygenic phototrophs (Fig. 1B), while only very high-Mg calcite was detected within mats dominated by oxygenic cyanobacteria that occur in the same area of the sabkha.

Redox conditions within microbial mats do not represent global ocean chemistry, and the diversity of a single microbial mat is far from being a representative snapshot of the evolution of life at a given time of our planet's history. That said, in the light of these new findings linking dolomite to anoxygenic phototrophs, it is difficult to refrain from formulating the following hypothesis: were early microorganisms better at making dolomite than their younger descendants? Does this explain the generally declining abundance of dolomite throughout the geological record?

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