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## *Interactive comment on* "Biomineralization of dolomite and magnesite discovered in tropical coralline algae: a biological solution to the geological dolomite problem" *by* M. C. Nash et al.

## Anonymous Referee #1

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The authors attempt to provide a solution to the 'dolomite problem' by proposing that dolomite formation is the product biomineralization by coralline red algae. Samples from a single species of a tropical coralline alga were studied by X-ray diffraction and other analytical techniques to determine mineral composition and were imaged by scanning electron microscopy, using backscattered and secondary electrons. From these studies, the authors conclude that in living thalli, "cell spaces are typically filled with magnesite, rimmed by dolomite, or both."

Finding a correlation of dolomite deposition over geological time and the evolutionary history of the coralline algae would be most interesting. After giving a brief account of

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early red algae, the authors state: "They have a high magnesium calcite skeleton." A reader might concluded that 'They' refers to all the preceding red algae listed, but, in fact, it is known to be true of only members of the Corallinales, whose fossil record before the Cretaceous is sparse. Whether Paleozoic solenopores deposited magnesium-rich calcites is unknown, and there is no basis for extending this characterization to the cited Proterozoic red algae, because they are not believed to have been calcified. Even if one assumes corallinalean red algae have always deposited high magnesium carbonate, the comparison to the geological history of dolomite formation can only begin in the Cretaceous. Therefore, the ability of this study to solve the "dolomite problem" based only on a single species of extant algae is severely constrained.

The Methods section provides no information about the methods by which sections were prepared. Use of a resin is mentioned in a legend, but not in the Methods. The extent to which resin infiltrates the fabric of the thallus, especially the cell lumens and conceptacles, should be stated, because it could profoundly affect interpretations.

Given the authors' assertion of a novel type of intracellular biomineralization, it is important to demonstrate that the cells were, in fact, living, and that the filling of cell lumens by mineral was not the result of post-mortem precipitation. The possibility that the specimens overgrew other coralline thalli or other calcareous organisms also needs to be ruled out. (In discussing aragonite findings, the authors do mention the possibility of growth on a coral that could have affected their analytical results). Parallel histological study of the same specimens to show well preserved cell contents is the only way to establish that cells deep in the thallus were living; SEM of dried specimens alone is not sufficient.

An effective use of conventional secondary electron imaging and backscattered electron imaging would have provided correlated and complementary interpretations. None of the images shown demonstrate identifiable cell structures, such as starch grains or organelles. Fig. 6 attempts to use the difference in the amount of specimen charging as a basis for comparing different cells, concluding that the upper cells in the thallus have less content. Normally, cells near the upper surface of the thallus would be much richer in cellular organelles. High magnification SEM images should reveal the crystal structure of each of the different mineral phases.

The results from compositional analysis are intriguing. However, elemental localization is complicated by the presence of organic material and the porous texture and locally complex contours of the cell lumens. These features will affect beam penetration and X-ray emission.

The "protodolomite rims" are stated to be part of the cell wall surrounding living cells. Intercellular connections, the pit plugs, form organic bridges between living cells. The plugs may be sealed off after cell death, but otherwise there should be no wall or mineral between cells that share pit connections. The presumed extracellular "protodolomite rims" shown in Fig. 4 are present in places that would cover the ends of the pit plugs, and therefore would have to be present in an intercellular location. The homogeneous texture of this layer of apparently intercellular material and its radial cracking do not fit with the features of any native cell structures.

In the Discussion, the authors state, "we could find no previous record of magnesite in coralline algae. We propose that the standard method of bleaching prior to analysis ... may ... remove... the magnesite within the cell space." This speculation, which explains away a major point of contradiction with existing literature, should have been tested.

The authors' proposal that this alga has multiple methods of biomineralization, one that deposits minerals in the cell walls and another, never before seen, that deposits a different mineral within the cell, is not supported by convincing evidence. Until all the various aspects of this proposal are convincingly demonstrated, extrapolation to the geological history of dolomite formation is unwarranted.

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