

## Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas: Comment and Reply

### COMMENT

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Hardie (2003) identified intervals of “aragonite” and “calcite seas” by modeling Mg/Ca ratios in Neoproterozoic to Neoproterozoic seawater using estimates of hydrothermal and weathering fluxes of key ions. His results agree with most published reports of aragonite pseudomorphs with the exception of the time period between 2.5 and 2.6 Ga. During this interval, his model predicts calcite seas, but aragonite pseudomorphs have been reported (Hardie, 2003). Hardie’s preferred interpretation for the difference between model results and the presence of aragonite pseudomorphs is that the described pseudomorphs were not originally aragonite. I disagree with this interpretation.

**Evidence for Neoproterozoic Aragonite Precipitation.** Sumner and Grotzinger (2000) documented evidence for aragonite precipitation in four geographically diverse carbonate units spanning 2.9–2.5 Ga. The 2.6–2.5 Ga Campbellrand-Malmani carbonate platform, South Africa, contains abundant pseudomorphs that Hardie (2003) argues probably were gypsum. In this 2-km-thick platform, aragonite pseudomorphs are abundant and consist of fibrous marine cements in addition to radiating bundles of decimeter-long crystals. The fibrous cements contain most of the features typical of calcite replacing aragonite (Loucks and Folk, 1976; Assereto and Folk, 1980; Mazzullo, 1980; Sandberg, 1985; Peryt et al., 1990), including: (1) relict crystal morphology defined by inclusions and [Mn] that demonstrates the crystals were fibrous and had blunt to feathery fiber bundle terminations; (2) replacement by optically unoriented, equant to elongate calcite crystals with unit extinction; and (3) strontium concentrations of up to 3700 ppm.

The fibrous cements show no morphological similarity to any reported gypsum textures; they are entirely analogous to Phanerozoic aragonitic cements using the same identification criteria used in carbonate platforms of any age with the exception that relict aragonite inclusions have not been identified (see Sumner and Grotzinger, 2000).

Some large botryoidal and prismatic crystal pseudomorphs interpreted by Sumner and Grotzinger (2000) show similarities to gypsum pseudomorphs with respect to the size and geometrical arrangement of crystals. However, crystal morphology, petrographic characteristics, and geochemical compositions are similar to the fibrous cement pseudomorphs rather than gypsum pseudomorphs. The only similarity in crystal properties to gypsum are pseudo-hexagonal cross sections in some prismatic pseudomorphs, which is also consistent with an aragonite precursor. Measurements of interfacial angles are consistent with either an aragonite or gypsum precursor due to the sensitivity of results to small errors in cross section orientation, the absence of micrite drapes on pseudomorphs, and the originally fibrous character of macroscopically prismatic pseudomorphs. Errors were estimated to be 5–10°, which are too high to aid in primary mineral identification. However, the petrographic and geochemical characteristics provide very strong evidence for an aragonite precursor mineralogy for most decimeter-scale pseudomorphs (Sumner and Grotzinger, 2000).

**Gypsum Pseudomorphs.** Rare gypsum pseudomorphs are present in Neoproterozoic carbonates (e.g., Simonson et al., 1993) and have been distinguished from aragonite pseudomorphs based on crystal morphology and replacement petrographic characteristics (see Sumner and Grotzinger, 2000, for discussion). The presence of some gypsum pseudomorphs does not require reinterpreting all aragonite pseudomorphs as gypsum pseudo-

morphs, as suggested by Hardie (2003). The identification of both precursor minerals adds confidence that the decades of high-quality research on methods to distinguish primary mineralogy in ancient sediments is consistent and reliable when suites of properties are considered together.

**Alternative Interpretation of Model Results.** The presence of aragonite pseudomorphs is well documented in 2.5–2.6 Ga carbonates deposited in storm- and tidally influenced facies (Sumner and Grotzinger, 2000; Sumner, 2001). The presence of Mg-calcite cements in the same platforms (Simonson et al., 1993; Sumner and Grotzinger, 2000) also supports a seawater chemistry typical of “aragonite seas” during late Neoproterozoic time. Thus, alternative interpretations of the disagreement between Hardie’s (2003) model results for aragonite-calcite seas and observational data should be considered. Three possible origins for this disagreement include: (1) the ionic composition of average river water was different when the atmosphere contained little or no O<sub>2</sub> and more CO<sub>2</sub>; (2) the flux of river water was different when continental mass, freeboard, and climate may have been significantly different; (3) plutonic rock generation in North America may be an inaccurate representation of Neoproterozoic seafloor spreading rates.

Overall, evidence for aragonite precipitation from 2.6 to 2.5 Ga seawater should be used to constrain models of Neoproterozoic ocean chemistry rather than being discarded as unlikely on the basis of early attempts to model chemical fluxes.

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### REPLY

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In her comment on my paper on secular variations in Precambrian seawater chemistry, Dr. Sumner has argued that aragonite pseudomorphs are abundant in the 2.5–2.6 Ga Campbellrand-Malmani carbonates of the Transvaal Basin, South Africa, occurring mainly as fibrous cements replaced by calcite crystals.

My focus was not on the intragranular cements but on the very large crystal fans described by Sumner and Grotzinger (2000) in the Precambrian Campbellrand-Malmani carbonates of the Transvaal Basin, South Africa, and the “aragonite domes” described by Simonson et al. (1993) in the equivalent age carbonates of the Carawine Dolomite of the Hamersley Basin, Australia, once joined with the Transvaal Basin. I drew particular attention to the astonishingly similar morphologies and sizes of the large domes and the large radiating crystals that make up the internal fabric of these domes to those in the primary gypsum of the Miocene Solfifera Series of Sicily (Hardie, 2003, p. 787). The Solfifera Series contains beds of radiating prismatic gypsum crystals that form domes 0.5–4 m in diameter and 0.5–1 m in height. In shape and scale they closely match the domes described and illustrated by Simonson et al. (1993). These Precambrian domal features in the Carawine Dolomite are 4.4 m wide and 1.2 m high with cores made up of concentric layers of prismatic crystals 3–20 cm long, now composed of quartz, chert, or dolomite. Simonson et al. (1993) interpreted the crystals as originally having been aragonite but found it “worrisome” that the crystal morphologies lacked the “distinctive square-tipped terminations” of radiating aragonite crystals. Simonson is an outstanding petrographer and if it worries him, it worries me. The large crystal fans described and illustrated by Sumner and Grotzinger (2000) are also very similar in scale and morphology to the Solfifera radiating prismatic gypsum. The interested reader should compare 3A of Sumner and Grotzinger (2000) with Figure 23 in Hardie and Eugster (1971) and Sumner and Grotzinger’s (2000) Figure 8A with Figures 4, 5, and 6 in Hardie and Eugster (1971). Furthermore, Sumner and Grotzinger (2000, p. 134) pointed out that in the 2.7 Ga Steeprock Group of Ontario, Canada, Hofmann (1971) noted the presence of large radiating pseudomorphs that he suggested were originally either gypsum or aragonite. Sumner and Grotzinger (2000, p. 134) pointed out that later authors such as Walter (1983) and Wilks (1986) “favored only the gypsum interpretation, on the basis of the large size of the crystals, which extend for up to 25 cm.”

There are other features that support an evaporitic environment for both the Campbellrand-Malmani carbonates and the Carawine Dolomite. Both Sumner and Grotzinger (2000) and Simonson et al. (1993) report “halite pseudomorphs,” clear evidence for highly evaporative conditions. Indeed, Simonson et al. (1993) have identified dolomite pseudomorphs after gypsum associated with halite molds. It must be pointed out that whether we are considering periods of “calcite seas” or “aragonite seas,” gypsum will precipitate from evaporating seawater after the  $\text{CaCO}_3$  stage but before halite precipitation. Where there was halite, there also will have been gypsum.

In another direction, Simonson et al. (1993) report “zebraic dolomite cement” pseudomorphous after calcite in the Carawine Dolomite. Furthermore, they illustrate in their Figure 12 an oolitic arenite with geopetal matrix and dolomite spar filling the pore spaces between the ooids, these latter in turn show the characteristic radial fabric of primary calcite. Relevant to this feature is Sandberg’s (1975, Fig. 16) illustration of a Jurassic

calcite ooid with a classic radial fabric typical of “calcite sea” ooids that had nucleated on a gastropod aragonitic shell, which in turn has been replaced by blocky calcite spar. In this regard, Sandberg (1975, p. 532) notes that “a marked difference in textural preservation exists between calcite-replaced ancient shells known to have been aragonite and coexisting ooids presumed by analogy with modern equivalents to have been originally aragonite. Since organic matrix and paramorphic replacement arguments are untenable in this regard, no justification remains for ascribing an original aragonitic mineralogy to ancient calcitic ooids that retain fine texture. Those ooids must have been originally calcite.” In the sedimentological literature there are many well-illustrated examples of calcitic ooids with this primary radial fabric. Their occurrences dominate the periods of “calcite seas” during the Phanerozoic.

Sumner and Grotzinger (2000, p. 138–139) have argued that measurements of Sr concentrations in six samples of radiating pseudomorphs and one sample of fibrous calcite provide support for their interpretation of an aragonite precursor. They found that the calcite cement contained  $600 \pm 400$  ppm Sr, while the pseudomorphs in the same sample carried  $900 \pm 400$  ppm Sr, but that “most analyses were below the detection limit.” In only one sample (BT 20) did they find areas that yielded Sr values of 1800–3700 ppm. It is not clear that this is sufficient evidence to make the claim that all the radiating pseudomorphs in the Campbellrand-Malmani carbonates were originally aragonite.

Finally, there remains the vexing problem of distinguishing between pseudomorphs after gypsum (monoclinic) and pseudomorphs after aragonite (orthorhombic). Both minerals typically form as twins that yield pseudohexagonal crystals with very similar interfacial angles. I applaud Dr. Sumner for attempting to distinguish between gypsum and aragonite by measuring interfacial angles, and I am just as disappointed as I am sure she is that this approach was not helpful.

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