

Novel calcite-aragonite sea transition in the terminal Proterozoic

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Tectonically driven fluctuations in seawater Mg/Ca are thought to have caused changes in the polymorph mineralogy of platform carbonates throughout Phanerozoic time (Mg/Ca < 2 = calcite seas; Mg/Ca > 2 = aragonite seas) [1]. Previously published elemental analyses of micritic limestones from the terminal Proterozoic Nama Group (552-544 Ma), southern Namibia, show a threshold increase in Sr/Ca (by a factor of 6-7) from 549 to 547 Ma and a decrease in Mg/Ca ratio (by a factor of 5) from 552 to 544, which are both consistent with a transition from primary calcite limestones (Sr-depleted, Mg-enriched) to primary aragonite limestones (Sr-enriched, Mg-depleted) across this interval [2].

To further investigate this potentially novel calcite-aragonite sea transition, we measured the Sr and Mg isotope compositions of the Nama Group carbonates (552 – 544 Ma) at Yale University. ⁸⁷Sr/⁸⁶Sr ratios are elevated from 0.7090 to 0.7105 between 552 and 549 Ma, and then decline to a relatively stable value of 0.7086 between 549 and 544 Ma. The bulk $\delta^{26}\text{Mg}_{\text{DSM3}}$ values of the carbonates increase steadily from ~ -2.5 to -1.2‰ between 552 and 544 Ma, with a brief excursion down to -3.5‰ at ca. 549 Ma, which coincides with peaks in ⁸⁷Sr/⁸⁶Sr and Mg/Ca ratios.

Theoretical work and empirical observations of modern carbonates show that ²⁶Mg is enriched in the following order: low Mg calcite < high-Mg calcite < dolomite < aragonite [3]. Thus, the increase in $\delta^{26}\text{Mg}$ from 552 to 542 Ma is consistent with an increase in the proportion of primary aragonite with time. Likewise, the decline in ⁸⁷Sr/⁸⁶Sr across the interval is consistent with a transition from a lower-Mg/Ca calcite sea characterized by increased hydrothermal flux of radiogenic Sr (higher ^{87/86}Sr), to a higher-Mg/Ca aragonitic sea characterized by decreased hydrothermal flux of radiogenic Sr (lower ^{87/86}Sr). High-frequency incremental leaching of a set of limestone samples also suggests that the anomalous peaks in ^{87/86}Sr and Mg/Ca around 549 Ma may have resulted from localized diagenetic alteration.

[1] Hardie, LA, 1996, *Geology* 24: 279-283. [2] Ries, J *et al.*, 2009, *Geology* 37: 743-746 [3] Wang *et al.*, 2013, *GCA*, 102: 113-123

Oxygen isotope equilibrium between sulfite and water

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Application of the oxygen isotopic composition of sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) is complicated by rapid equilibration between sulfoxyanions and water. Specifically, the apparent relationship that develops between $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{water}}$ during microbial sulfate reduction is thought to result from rapid equilibrium between water and aqueous intracellular sulfite (SO_3^{2-}) – a reactive intermediate in the sulfate reduction network. Here, we describe the oxygen isotope equilibrium effect between SO_3^{2-} and water, based on experiments conducted over a range of pH (4.5 to 9.8) and temperature (2 to 90°C). Experimental results are consistent with predicted values based on *ab initio* estimates of oxygen isotope equilibrium values among S(IV) species and water and changes in speciation. We find that $\epsilon_{\text{sulfite-water}} = 13.61 - 0.299 \cdot \text{pH} - 0.081 \cdot \text{T}^\circ\text{C}$ such that at a pH (7.0) and temperature (25°C) typifying common experimental conditions of sulfate reducing bacterial cultures, SO_3^{2-} is enriched in ¹⁸O by 9.5‰ ($\pm 0.8\%$) relative to ambient water. By evaluating previously published data within an updated sulfate reduction network, results prove consistent with high enzyme reversibility in the sulfate reduction biochemical network. We show that intracellular SO_3^{2-} exchanges with water up to 3 orders of magnitude faster than internal recycling and that kinetic isotope effects upstream of SO_3^{2-} are required to explain previous laboratory and environmental studies of $\delta^{18}\text{O}_{\text{SO}_4}$ resulting as a consequence of sulfate reduction.