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**Title: Calcite Growth-rate Inhibition by Fulvic Acid and Magnesium Ion at 25 C and Calcite Supersaturation of 4.5 -- Potential Calcite Formation Rate Reduction in Marine Calcifying Organisms**

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**Abstract:** (392 words)

Field and laboratory studies demonstrate that increasing ocean surface water dissolved carbon dioxide concentration is negatively influencing marine organisms forming calcium carbonate skeletons by reducing the driving force for calcite formation -- calcite supersaturation. In addition to calcite supersaturation changes due to increasing ocean surface water dissolved carbon dioxide concentrations, natural organic acids, a large reactive global carbon reservoir, are implicated in biocalcification processes and may be involved in changes in the rates of calcification (calcite crystal-growth rates are markedly reduced by specific natural organic acids). Moreover, trace metal incorporation during carbonate mineral growth, used for reconstructing past ocean chemistry and paleoclimate (for example, the magnesium-to-calcium ratio of calcifying marine organisms is a proxy for past sea surface temperatures) is strongly growth-rate dependent. Here we report calcite seeded crystallization rates at constant temperature and calcite supersaturation, characterized in the absence and presence of a natural organic acid (a fulvic acid isolated from the Florida Everglades, FA), in the presence and absence of  $10^{-4}$  M magnesium (Mg) ion and in the presence of both FA and  $10^{-4}$  M Mg ion. Both FA (0.5 mg/L) and  $10^{-4}$  M Mg reduce calcite crystal-growth rates at pH=8.5 and calcite supersaturation of

4.5 by 47 % and 38 %, respectively, compared to control experiments containing no added substances. Organic matter adsorbed from the air onto the seed crystals has no influence on the measured calcite crystal-growth rates. Growth-rate experiments in the presence of both FA and Mg reduce the calcite growth rate to 5 % of the control rate; a calcite growth-rate reduction of almost ten times greater reduction than either individual inhibitor. Mg inhibits calcite by substitution of Mg for calcium ion at a growth site. In contrast, polycarboxylate acid anions inhibit calcite growth rates by binding multiple carboxylate groups on the calcite surface. Since both FA and Mg inhibit calcite growth rates by different adsorption mechanisms involving growth sites on the mineral surface, it seems plausible that adsorbed FA and Mg interact in solution and/or on the growing calcite surface dramatically increasing their combined calcite growth rate inhibition effectiveness. These results suggest that organic acid and Mg concentrations at biocalcification sites in marine calcifying organisms may regulate the calcite crystallization rates and thus the metal ion partitioning impacting use of these organisms as paleoclimate proxies and a global carbon dioxide sink.

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