Can carbonate hardgrounds serve as a seawater chemistry proxy?

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Systematic changes in seawater chemistry over the Phanerozoic have been linked to changes in biomineralization and global climate change. These changes are measured primarily in biogenic carbonate, evaporite minerals, or calcite veins in the oceanic crust. Each has its limitations. This study explores the use of trace element and isotopic ratios in authigenic carbonate as a new proxy for seawater chemistry.

As carbonate hardgrounds form rapidly in shallow marine settings, their composition should reflect that of seawater. Carbonate hardgrounds from seven time intervals over the Phanerozoic were investigated for magnesium/calcium (Mg/Ca) and strontium/calcium ratios (Sr/Ca), strontium isotopes, carbon and oxygen isotopes, and limited clumped isotopic analysis. All seven studied intervals fall on the strontium isotope curve for the Phanerozoic and clumped isotope analysis supports the lack of meteoric or later stage diagenesis in these samples.

Our results show that the most pristine authigenic carbonate within the carbonate hardgrounds records changes in seawater Mg/Ca throughout the Phanerozoic, with low Mg/Ca in the Mesozoic and early Paleozoic, transitional values during the Carboniferous, and higher Mg/Ca in the modern ocean. Sr/Ca ratios are consistent with other proxies back to the mid Mesozoic and remain low during the Carboniferous, Ordovician, and Cambrian. These results support the measurement of authigenic carbonates, particularly in carbonate hardgrounds, as an exciting new proxy to extend our records of seawater chemistry.