

Extending the utility of the Tl isotope paleoredox proxy to carbonates

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Thallium isotope ratios ($^{205}\text{Tl}/^{203}\text{Tl}$) recovered from ancient marine shales are able to provide novel information about Earth's ocean oxygenation history [1]. Here we demonstrate the potential to extend this utility to the ancient carbonate record. We present Tl concentration and isotope ratio data for modern and geologically recent carbonates from the Great Bahama Bank that capture both initial carbonate deposition and diagenesis on multiple scales. Young carbonates from bank-top cores reveal bulk Tl isotope values that are essentially indistinguishable from today's globally homogenous seawater Tl isotope value. Older carbonates from the deeper and diagenetically altered cores also oftentimes capture Tl isotope compositions within error of modern seawater values. Carbonates with high dolomite contents are the most reliable archives, revealing with only minor exception Tl isotope compositions within analytical error of modern seawater. Meteoric diagenesis drives carbonate Tl isotope compositions towards values akin to the average composition of global rivers, suggesting significant modification of the original marine Tl isotope values. Our findings suggest that properly screened ancient carbonates can be viable archives of past seawater isotope compositions. These seawater values are set by past marine Tl isotope mass-balance, which is sensitive to Mn oxide burial on the seafloor and hence past levels of global bottom water ocean oxygenation.

[1] Owens, J.D., et al., *Geochim. Cosmochim. Acta.*, 2017. 213: 291-307.