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Thallium isotope system: Unique global ocean paleoredox proxy but vulnerable to basin restriction effects

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The stable thallium (Tl) isotope system is a unique global ocean paleoredox proxy that is based on the sensitivity of seawater Tl isotope compositions ($\varepsilon^{205}Tl$) to the extent of manganese (Mn) oxide burial in well-oxygenated sediments ($\varepsilon^{205}Tl = 10000 \times [^{205}Tl/^{203}Tl_{sample} / {}^{205}Tl/^{203}Tl_{NIST\text{-}SRM\text{-}3158} - 1]$; NIST-SRM-3158 is isotopically identical to NIST-SRM-997). A key advantage of the Tl isotope proxy is the direct capture of seawater $\varepsilon^{205}Tl$ in anoxic sediments deposited from locally anoxic bottom waters or when O_2 penetration into sediments is limited. By comparison, other global ocean redox proxies, notably molybdenum (Mo) and uranium (U) isotopes, struggle to directly record seawater isotopic signatures in sediments. Thallium's lower oceanic residence time (~20 kyr today; compared to ~400-500 kyr for Mo and U) enables capture of high-resolution changes in seawater $\varepsilon^{205}Tl$ yet renders it vulnerable to the effects of basin restriction, which can prevent preservation of global seawater $\varepsilon^{205}Tl$ in anoxic sediments.

We report recently acquired Tl isotope data for Devonian and Ediacaran organic-rich mudrocks. The impact of basin restriction on Tl isotope ratios is illustrated by the Upper Devonian Kettle Point Formation (SW Ontario, Canada), deposited in an epicontinental setting. This formation exhibits an inverse correlation between Mo and U isotope ratios and a positive correlation between Mo and Tl isotope ratios; both reflect a change from a more restricted basin (less negative $\varepsilon^{205}Tl$) to a less restricted basin (more negative $\varepsilon^{205}Tl$). By contrast, no correlation is observed between Mo and U isotope ratios or between Mo and Tl isotope ratios for the end-Devonian Exshaw Formation (Alberta, Canada), deposited in an epicontinental setting during the Hangenberg Crisis. Initial Exshaw results reveal an upward stratigraphic trend from less negative to more negative $\varepsilon^{205}Tl$, which potentially records a recovery from expanded ocean anoxia. An undergraduate student project found more negative $\varepsilon^{205}Tl$ in the lower Brachina Formation, deposited in the Adelaide Rift Complex, than in the coeval Pertatataka Formation, deposited within the more restricted intracratonic Centralian Superbasin of Australia. The $\varepsilon^{205}Tl$ of the Brachina Formation provides further evidence for an early Ediacaran episode of globally increased ocean oxygenation shortly after the Marinoan glaciation.