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Evidence for oxygenation at ~1.65-1.64 Ga from authigenic thallium isotopes in McArthur Basin shales

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Authigenic thallium isotopes ($\varepsilon^{205}Tl_{auth}$, Eq. 1) in black shales are a tool for investigating ocean oxygenation and could be useful to evaluate the relationship between ocean redox conditions and early eukaryotic evolution. Seawater (sw) Tl isotopes are mainly fractionated during adsorption–oxidation and burial with manganese (Mn)-oxides under well-oxygenated conditions, favouring removal of ^{205}Tl from seawater. In the well-oxygenated modern oceans, Mn-oxide burial shifts $\varepsilon^{205}Tl_{sw}$ (-6‰) to lower than the average input composition (-2‰). Organic-rich sediments deposited under anoxic conditions (i.e., black shales) commonly preserve $\varepsilon^{205}Tl_{sw}$. Thus, black shale $\varepsilon^{205}Tl_{auth}$ chemostratigraphy should track variations in the extent of Tl burial with Mn-oxides in well-oxygenated marine environments.

We present $\varepsilon^{205}Tl_{auth}$ data from a late Paleoproterozoic succession in the intracratonic McArthur Basin (northern Australia) (Figure 1), which closely temporally coincides with the earliest known multi-cellular eukaryotes [1]. Samples in the Mallapunyah (~1.65 Ga, core MCDD0005) and Barney Creek (BCF; ~1.64 Ga, core McA5) formations likely record contemporaneous $\varepsilon^{205}Tl_{sw}$ based on anoxic iron speciation or passing a geochemical decision tree [2]. Mallapunyah $\varepsilon^{205}Tl_{auth}$ features two apparent excursions to -5.2 ± 0.5‰ from a baseline of -3.5 ± 1.2‰. One excursion is situated immediately below occurrences of eukaryotic *Valeria lophostriata* [3], which at face-value suggests a potential link between increased oxygenation and basinal proliferation of this species. The BCF shows no clear $\varepsilon^{205}Tl_{auth}$ excursions, although the uppermost samples are isotopically lighter (-3.9 ± 0.3‰) than deeper samples (-2.7 ± 0.4‰). The lower BCF shows evidence for basin restriction, with a progressive increase in circulation up-section [4]. Hence, $\varepsilon^{205}Tl_{auth}$ in the lower BCF may capture the $\varepsilon^{205}Tl$ of local Tl inputs (-2‰), whereas $\varepsilon^{205}Tl_{auth}$ of the upper BCF better captures regional or global $\varepsilon^{205}Tl_{sw}$. A widely anoxic global ocean is expected to have $\varepsilon^{205}Tl_{sw}$ of -2‰. By contrast, both formations host samples with lighter $\varepsilon^{205}Tl_{auth}$, suggesting Mn-oxide burial under well-oxygenated conditions in at least some regions of the oceans at 1.65-1.64 Ga.

[1] Miao et al. (2024). *Sci Adv* 10(4), eadk3208.
[2] Wang et al. (2022). *GCA* 333, 347-361.
[3] Riedman et al. (2023). *Pap Palaeontol* 9(6), e1538.
[4] Johnston et al. (2008). *GCA* 72(17), 4278-4290.

(Eq. 1) $$\varepsilon^{205}Tl\ (‰) = \left(\frac{^{205}Tl/^{203}Tl_{sample}}{^{205}Tl/^{203}Tl_{NIST3158}} - 1\right) \times 10000$$

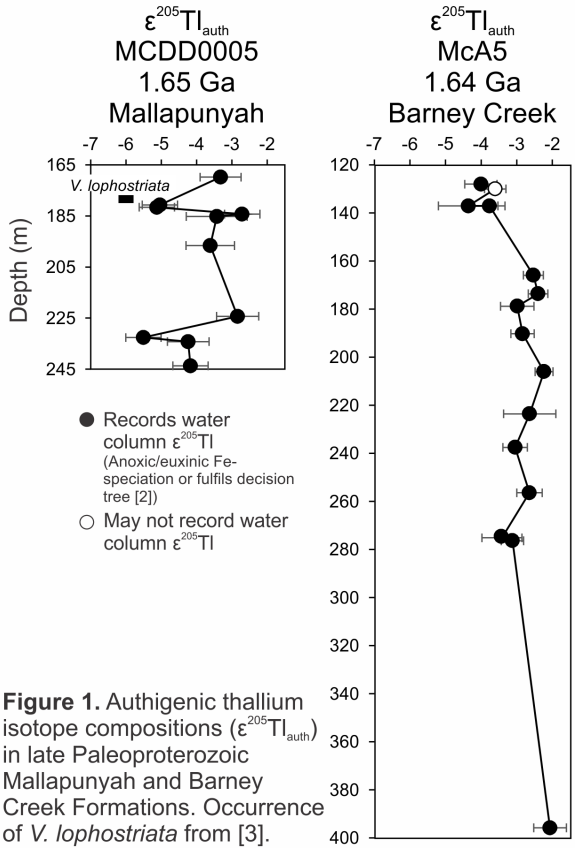

Figure 1. Authigenic thallium isotope compositions ($\varepsilon^{205}Tl_{auth}$) in late Paleoproterozoic Mallapunyah and Barney Creek Formations. Occurrence of *V. lophostriata* from [3].