

## Nickel isotope of paleo-seawater at the end-Ordovician

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Nickel (Ni) is a bioessential trace metal and shows a nutrient-like profile in the modern ocean [1]. This is evidenced in the oceanic cycle of Ni, where it is dominated by biological uptake in the photic zone and regeneration at depth [1,2]. Recent data suggest that where dissolved Ni is depleted in the surface ocean it can be accompanied by a shift in its isotopic composition, expressed as  $\delta^{60}\text{Ni}$ , from a homogenous interior towards heavier values at the surface, consistent with a metabolic requirement of phytoplankton for Ni [2]. Systematic relationships between Ni concentrations, TOC and Ni isotopes [3] suggest that the Ni contained in the organic-pyrite fraction extracted from modern ocean sediments in upwelling regions is derived from the photic zone, and delivered to the sediment relatively unmodified [3]. Bulk sediment authigenic  $\delta^{60}\text{Ni}$ , tracks Ni derived from the water column dissolved pool, and has the potential to track the evolution of whole-ocean  $\delta^{60}\text{Ni}$ .

Here we apply the same Ni-TOC systematics approach as above to ancient sediments from the Vinini Creek, formed prior to the Late Ordovician mass extinction [4]. The best estimate of  $\delta^{60}\text{Ni}_{\text{authigenic}}$  and thus contemporaneous seawater, for Vinini Creek sediments sampled thus far, is +0.74‰, much lower than the modern value of +1.31‰ [2]. Other metal isotope systems, such as Mo, have also seen a shift to a heavier oceanic isotopic composition from that of the early Paleozoic, thought to be driven by changes to surface Earth redox conditions [5,6]. We will further explore the potential mechanisms for the observed secular changes to seawater  $\delta^{60}\text{Ni}$ .

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