Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.26772

Trace metal and nickel isotope evolution of ocean since the Cretaceous

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Nickel (Ni) isotopes, recognized as a promising tracer for understanding the biogeochemistry of the ocean, are now being applied to investigate the ancient oceans. In the modern ocean, seawater Ni isotopes ($d^{60}Ni_{sw}$) are heavy relative to the global input $d^{60}Ni$ ($d^{60}Ni_{input}$), driven by the preferential sorption of light Ni to Mn oxide and leading to an isotopically light sedimentary sink [1]. Modern organic-rich sediments from upwelling margins are unfractionated relative to the global seawater reservoir, potentially providing an archive of the past oceanic dissolved pool [2, 3], and thus the relative importance of deep ocean oxidizing conditions that produce Mn oxides. Here, we present an extensive record of trace metal abundances and Ni isotopes for organic-rich sediments, covering three oceanic anoxic events, OAE1 (Aptian-Albian), OAE2 (Cenomanian-Turonian) and OAE3 (Coniacian-Santonian), and through the Cenozoic, to track the biogeochemical and redox evolution of the ocean since the Cretaceous.

The contemporaneous $d^{60}Ni_{sw}$ recorded by authigenic Ni isotopes in organic-rich, open ocean sediments [2, 3] since the Cretaceous reveals two prominent features: 1) $d^{60}Ni_{sw}$ increased to the modern value of around +1.3‰ [4] only in the early Cenozoic, suggesting that the deep ocean has not been fully oxygenated until then, later than has previously been suggested [5]; 2) $d^{60}Ni_{sw}$ remained relatively constant across each OAE, but at lower than modern seawater, in contrast to the strong response implied by other metal isotope systems [6]. Coupled Ni and Mo mass balance models suggest that $d^{60}Ni_{input}$ under the Cretaceous greenhouse warming was most likely lower than modern, and that the areal fraction of the euxinic sink during the OAEs increased by up to a few percent.

[1] Fleischmann et al., 2023. *Earth and Planetary Science Letters.*

[2] Ciscato et al., 2018. *Earth and Planetary Science Letters*.

[3] He et al., 2023. *Geochimica et Cosmochimica Acta*.

[4] Takano et al., 2017. *Analytica Chimica Acta.*

[5] Lu et al., 2018. *Science.*

[6] McDonald et al., 2022. *Geochimica et Cosmochimica Acta*.