

The constraints of cadmium isotopes on primary productivity and environmental perturbations during the Late Ordovician mass extinction

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The Late Ordovician mass extinction (LOME) constitutes the second largest of the “Big Five” extinctions of the Phanerozoic. The LOME comprised two extinction pulses associated with sea level changes linked to the Hirnantian glaciation. Although climate change has been implicated as a potential driver of the mass extinction, uncertainty remains as to its precise impact relative to the concurrent development of ocean anoxia. Here, we investigate the behavior of the oceanic cadmium (Cd) cycle, as a key element involved in a number of biological processes, across the LOME and into the Early Silurian. Our focus is on the Wangjiawan section in South China, which is the Global Stratotype Section and Point section marking the base of the Hirnantian Stage. Our $\delta^{114}\text{Cd}_{\text{auth}}$ data display a gradually decreasing trend from the late Katian to the Katian–Hirnantian boundary, suggesting enhanced biological assimilation of isotopically light Cd followed by export to the sediments. This interpretation is supported by an increase in organic carbon isotope compositions, as well as a progressive decrease in P/Al ratios and increase in C_{org}/P ratios in the early part of the late Katian. A slight increase in Cd isotope values in the early Hirnantian was likely caused by drawdown of light Cd in euxinic shallower seawater settings. During glacial melting in the late Hirnantian, organic carbon burial declined, consistent with lower Cd/Al, Zn/Al, and Ni/Al ratios. However, $\delta^{114}\text{Cd}_{\text{auth}}$ values remain low across this interval, possibly due to an increase in the supply of isotopically light Cd from enhanced weathering and rising sea levels, as supported by elevated Al contents and chemical index of alteration (CIA) values. Elevated $\delta^{114}\text{Cd}_{\text{auth}}$ values subsequently occurred in the Early Silurian (Rhuddanian), alongside a decline in CIA and Al values, suggesting that the Cd sink was gradually balanced by a decline in the weathering input of Cd and lower rates of primary productivity. Our data provide new insight into the Cd cycle through the Late Ordovician to Early Silurian, and suggest that elevated marine productivity drove enhanced burial of organic matter, which likely contributed to CO₂ drawdown and the initiation of the Hirnantian glaciation.