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Copper isotope evidence of particulate shuttle dynamics in the Late Pennsylvanian North American Midcontinent Sea, with implications for glacio-eustatic magnitude

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The North American Midcontinent Sea (NAMS) covered a vast area during Late Pennsylvanian glacio-eustatic highstands, providing a laboratory for analysis of the internal watermass dynamics of large cratonic seas (of which few exist in the Recent). A novel proxy, copper isotopes (δ^{65}Cu), was used to gain a better understanding of NAMS watermass dynamics. We analyzed the 63-cm-thick Stark Shale (Dennis Formation, Missourian Stage, Upper Pennsylvanian) in the Iowa Riverton core (IRC) at a centimeter scale in order to reconstruct secular variations in δ^{65}Cu and other geochemical proxies. The gray shale facies yielded δ^{65}Cu of +0.02 ± 0.06‰ (2σ, *n* = 14), similar to detrital Cu in modern marine sediments (δ^{65}Cu = +0.08 ± 0.20‰; 2σ, *n* = 42). In contrast, the black shale facies, in which the proportion of authigenic Cu hosted by the organic fraction is 50-100% of total Cu content, exhibits heavier $\delta^{65}Cu_{auth}$ values, mostly between +0.09 and +0.43‰. In modern marine systems, one of the main processes leading to ^{65}Cu-enriched sediment compositions is adsorption of aqueous Cu onto Fe-Mn particulates. The black shale facies of the Stark Shale exhibits four peaks in Mo/U ratios that are indicative of an active particulate shuttle because of the tendency of Mo to adsorb more strongly than U to Fe-Mn particulates. The Sr/Ba ratio, a paleosalinity proxy, shows correlated variations, with high values (indicative of more fully marine conditions) linked to low Mo/U and light δ^{65}Cu, and low values (indicative of brackish conditions) linked to high Mo/U and heavy δ^{65}Cu. These considerations suggest that the flux of isotopically heavy Cu to the sediment-water interface via Fe-Mn cycling was enhanced during brackish intervals, with subsequent reductive dissolution of Fe-Mn particulates allowing transfer of hydrogenous Cu to the organic fraction of the sediment. Control of δ^{65}Cu by Fe-Mn cycling is supported by the results of a sequential extraction experiment showing that organic δ^{65}Cu is positively correlated with Mo/U. These findings provide evidence of large fluctuations in watermass salinity and sea-level elevation within the NAMS at timescales of ~10^4 yr during core shale deposition, as previously inferred but not conclusively demonstrated until now.