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

JINHUA LIU, YU JIAO AND LIAN ZHOU
China University of Geosciences (Wuhan)
Presenting Author: liucug2010@163.com

The North American Midcontinent Sea (NAMS) covered a vast area during Late Pennsylvanian glacio-eustatic highstands, providing a laboratory for analysis of the internal water mass dynamics of large cratonic seas (of which few exist in the Recent). A novel proxy, copper isotopes ($\delta^{65}$Cu), was used to gain a better understanding of NAMS water mass 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 $\delta^{65}$Cu and other geochemical proxies. The gray shale facies yielded $\delta^{65}$Cu of $+0.02 \pm 0.06\%$ (2σ, n = 14), similar to detrital Cu in modern marine sediments ($\delta^{65}$Cu = $+0.08 \pm 0.20\%$; 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 $\delta^{65}$Cuauth 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 $\delta^{65}$Cu, and low values (indicative of brackish conditions) linked to high Mo/U and heavy $\delta^{65}$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 $\delta^{65}$Cu by Fe-Mn cycling is supported by the results of a sequential extraction experiment showing that organic $\delta^{65}$Cu is positively correlated with Mo/U. These findings provide evidence of large fluctuations in water mass salinity and sea-level elevation within the NAMS at timescales of $\sim 10^4$ yr during core shale deposition, as previously inferred but not conclusively demonstrated until now.