Copper isotopes as an ocean-atmosphere redox indicator through geological time

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The emergence of appreciable amounts of free molecular oxygen (O_2) in the Earth's atmosphere at c. 2.45 billion years ago (Ga) is perhaps one of the major events that changed Earth's redox history. This so called "Great Oxidation Event" (GOE) had strong implications not only on the evolution of life, but also on the development of geochemical processes that still continue to shape the surface of modern Earth.

Cu and Fe are considered here as robust indicators of oxygen levels since they are redox-sensitive elements and the coupling of sedimentary dynamics of Cu and Fe to organic C systematics may provide patterns of biological behaviour, since both are key to microbial metabolism. We hypothesize that prior to the GOE, ^{65}Cu was scavenged and buried along with Fe(III)(oxyhydr)oxides. The dissolved ^{63}Cu became enriched in biomass and was preserved as C_{org}-rich shales. After the GOE, increased continental weathering of pyrite, delivered heavy dissolved ^{65}Cu to the oceans, which we hypothesized changed the Cu isotope signatures of C_{org}-rich shales to heavy ^{65}Cu. To test this hypothesis, well constrained black shale samples before the GOE transition (2.6 Ga), the Lomagundi event (2.3-2.1Ga) and the Shunga-Francevillian Event (2.1–2.084 Ga) were analysed for their Cu, Fe, C_{org} and S isotope signatures. As predicted light ^{63}Cu shales show a trend towards enrichment of heavy ^{65}Cu at 2.3 Ga, coinciding with the GOE. Fe isotope signatures also show the effects of oxidative weathering after the GOE, which can be directly correlated to Cu. We observe a marked correlation between Cu and C isotopes, establishing the idea of either metal sorption into buried organic matter or the use of Cu as an important metabolic element. The data suggests that Cu isotopes may serve as a redox proxy for tracking Earth's redox history.