

Copper chemostratigraphy of the Ediacaran and Early Cambrian in the Three Gorges area, South China: Concentrations of copper in different phases of sedimentary rocks

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Copper is one of bioessential elements, and is incorporated into various proteins such as hemocyanin. The hemocyanin transports oxygen throughout bodies of some invertebrate animals such as arthropods and molluscs; thus secular change of copper contents of seawater may correlate with appearance and evolution of the metazoans.

We selected the samples of 9 shale and 11 carbonate rock samples, whose TOC (total organic carbon) and sulfur contents are available, from the drill core samples with the Ediacaran to Early Cambrian ages in Three Gorges area of South China, to more comprehensively analyze the transition element contents together with the TOC and S contents. We dissolved the powdered samples at four steps: CH₃COOH, HNO₃, HClO₄, and HF acid digestion methods to dissolve carbonate, sulfide, organic matter, and silicate, respectively. We analyzed Na, Mg, Al, P, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn and Mo contents with ICP-MS at Gakushuin University. We added Indium to analytical solutions as an internal standard, and determined the chemical compositions of four fractions of carbonate, sulfide, organic matter, and silicate, using calibration curves of standard solutions with four different concentrations.

Copper contents of the carbonate, sulfide and organic matter fractions are highly fluctuated from the Doushantuo (Member I–IV) through the Dengying, Yanjiahe, Shuijintuo, and Shipai to Tianheban formations in ascending order. The Ediacaran–Cambrian boundary is identified in the lower Yanjiahe Formation, and the Member IV of the Doushantuo Formation corresponds to the late Shuram excursion of the terminal Ediacaran. The Cu contents of the carbonate fractions basically range from 1.33 to 11.4 ppm in the Member I–III, but are quite high up to 24.5 ppm in the Member IV and up to 20.5 ppm in the Shuijintuo Fm. The Cu contents of the sulfide fractions are varied from 1.60 to 38.3 ppm, but also are quite high up to 127 ppm in the Member IV and up to 23.5 ppm in the Shuijintuo Fm. The organic matter fractions are extremely low in the Cu contents from 0.01 to 0.08 ppm, but are also high up to 2.13 ppm in the Member IV and up to 1.47 ppm in the Shuijintuo Fm.

We calculated chemical compositions of pure carbonate, sulfide, and organic matter to avoid influence of contamination of silicate on the carbonate fraction, carbonate and silicate on the sulfide fraction, and carbonate and sulfide on the organic matter fraction, respectively. The amounts of contaminants were estimated from Ca, Fe, and Ti contents for carbonate, sulfide, and silicate, respectively. Because their Ti contents are very low, the influence of silicate contamination is negligible. However, a carbonate fraction (0.97 ppm in Cu content) with a quite low Ca content (23 ppm) from black shale in the Shipai Fm., two sulfide fractions with very low sulfur contents, and two organic matter fractions with quite low TOC

contents are possibly influenced by contamination of other phases. Hereafter, we use the corrected chemical compositions of pure carbonate, sulfide and organic matter except for the above mentioned five exceptions to estimate ancient seawater compositions.

The Cu x1000/Ca ratios of the carbonate fractions range from 0.005 to 0.046, but are very high up to 1.35 in the Member IV and 0.694 in the Shuijingtuo Fm. The Cu x1000/S ratios of the sulfide fractions range from 0.28 to 3.06, and are also high up to 5.98 in the Member IV and up to 1.30 in the Shuijingtuo Fm. The organic matter fractions range from 0.003 to 0.026 in Cu x1000/TOC ratios for the Member I to III, and are high, ranging from 0.074 to 0.203, for Member IV to Tianheban Fm.

The carbonate, sulfide and organic matter fractions have similar trends of the Cu/Ca, Cu/S and Cu/TOC ratios, respectively. They increase in the Member IV, suggesting increase in the marine Cu content around 550 Ma. The increase may be correlated with the first appearance of molluscs (*Kimberella*) and arthropods (*Spriggina*) around 550 Ma.

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