Molybdenum isotopic composition of Wafangzi ferromanganese oxide deposit and its paleoceanographic implications

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The Wafangzi ferromanganese oxide deposit in North China Craton is the only sizable sedimentary manganese ore deposit in the Mid-proterozoic around the world, which provides a unique opportunity to constrain the ocean redox state in the Mid-proterozoic.

Ferromanganese ores were collected from an underground mine, and eleven fresh samples were selected for this study. $\delta^{98/95}$Mo (relative to NIST 3134) of ferromanganese ores ranges from -2.50‰ to -0.50‰ with an average of -1.35‰.

The Mo isotope composition of Mid-proterozoic seawater has been inferred from blacks to be $\delta^{98/95}$Mo ≥1.0‰, (Arnold et al., 2004), and $\delta^{98/95}$Mo of hydrothermal fluid to be ~0.8‰ (McManus et al., 2002). The adsorption of Mo on MnO_2 and hematite results in a negative fractionation of 2.7‰ (Barling et al., 2002) and 1.80~2.00‰ (Goldberg et al., 2009). Mo isotope of ferromanganese ores may be the product of adsorption of dissolved Mo in seawater or hydrothermal fluid to Mn oxide (MnO_2) and Fe oxide (hematite).

If the Wafangzi ferromanganese oxide deposit formed in a restrict basin, massive Mn oxid and Fe oxide would remove all Mo in seawater and hydrothemal fluid, and the $\delta^{98/95}$Mo of ferromanganese ores should be same to the $\delta^{98/95}$Mo of seawater or hydrothemal fluid, which is opposite to the result of this study. Therefor, Wafangzi ferromanganese oxide deposit might formed in a basin with full connectivity to the open ocean.

Mo isotope fractionation between Mo adsorpted on Fe, Mn oxides and Mo in seawater is roughly constant. Therefor $\delta^{98/95}$Mo of mid-Proterozoic ocean was ~1.35. This result suggests that the ocean was predominantly anoxia during the mid-Proterozoic.

Overall, Wafangzi ferromanganese oxide deposit might formed in basin with full connectivity to the open ocean and widespread anoxia existed during the mid-Proterozoic.