Cd isotopic variations in Ediacaran carbonate rocks from south China: Biogenic or abiogenic isotope fractionation?

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The use of Cd isotopes as proxy for modern ocean nutrient utilization by phytoplankton has become an important tool in marine geochemistry. Of particular interest is the applicability of Cd isotopes as tracer of past marine bio-productivity. However, the detailed fractionation processes of cadmium isotopes in the marine realm are still debated. Most studies favour substitution for Zn atoms in carbonic anhydrase of Diatoms as the main driver for the fractionation. Cd isotopic data of carbonate leachates from the Ediacaran Xiaofenghe section on the Yangtze Platform, S-China have been analysed together with trace element concentrations, N and C isotopic compositions. The data, obtained by using the double spike method and TIMS ($\varepsilon^{112/110}$Cd relative to NIST SRM 3108, external precision: ± 8ppm) show εCd of +0.06 to +1.07 in the cap carbonates and in the lower Doushantuo, but significantly lighter values (-3.53 to -0.79) in the overlying Doushantuo and Dengying strata. Neither Cd concentrations, nor isotopic compositions correlate with P or Zn abundances. Given the experimentally derived $\alpha_{CaCO3\text{-}Seawater}$ of 0.99955 for the fractionation of Cd into carbonate, seawater in equilibrium with these carbonates should have εCd between 0.97 and 5.57, which is in the range of modern surface water. However the trend to lower values in the upper Ediacaran does not represent the signal expected for increased bio-productivity. The upper Doushantuo displays substantial fluctuations of Y/Ho_{PAAS}, Pr/Sm_{PAAS}, N and C isotopic compositions, presumably caused by mixing of seawater with freshwater masses. Carbonates with negative εCd in this part of the section show negative Ce/Ce* anomalies and high $\delta^{13}C_{carb}$, which may indicate carbonate precipitation in shallow oxic water subjected to increased evaporation and variable salinity. Our data suggest that the variations in the Cd isotope composition of Ediacaran carbonates at Xiaofenghe are most likely a result of kinetic fractionation of Cd into inorganic carbonates and may be solely controlled by salinity rather than by bio-productivity.