

Cd isotope fractionation between phases in Cambrian black shales: A case study from the Niutitang Formation, Southwest China

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The non-traditional Cd stable isotope system has been used extensively for examining nutrient uptake in the modern surface oceans. Based upon this premise, it is potentially useful as a paleo-bio-productivity proxy in marine sediments and the geological record. But interpretation of Cd isotope data from such archives is problematic due to a lack of basic understanding of Cd partitioning and isotope fractionation between the component phases present.

In order to understand better the Cd fractionation processes in marine sediments we performed a set of leaching experiments on shale lithologies from the Cambrian Niutitang Formation, Zunyi Section, Southwest China. We employed a double-spike TIMS method which has an external precision of ± 8 ppm. We found an overall Cd isotope variation in black shales of 6 $\epsilon^{112/110}\text{Cd}$ units, with the values obtained resembling previous published carbonate and black shale data from the Ediacaran and Permian.

Our sequential leachate dataset implies a preferential incorporation of light Cd isotopes in the order sulphides > organic matter > carbonates > silicates. Despite an extreme metal enriched ore layer, all analysed leachates exhibit a negative correlation of Cd concentrations and Cd/Zn vs. $\epsilon^{112/110}\text{Cd}$ in the carbonate leachates, arguing for a simple Rayleigh-type fractionation process. In contrast sulphides showed the opposite behaviour, with the lightest $\epsilon^{112/110}\text{Cd}$ values found in samples with low Cd concentrations, while silicates generally resembled upper crustal values. Within the ore layer there was enriched Ni and Mo/TOC, a high Y/Ho fractionation and the highest observed $\epsilon^{112/110}\text{Cd}$ (up to +2.7) in all leach phases. The origin of these metal enrichments, which are presumably accompanied by a loss of light Cd, may be a result of hydrothermal overprinting.