The chromium isotopic composition of organic-rich marine sediments as a potential paleoredox archive

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It has been suggested that the oxygenation of Earth's atmosphere acted as an environmental trigger for the appearance and radiation of metazoans during the late Precambrian/Early Cambrian. However, the evolution of surface oxygen levels has to be further constrained to better understand the possible link between oxygen availability and the emergence of more complex lifeforms. Chromium (Cr) stable isotopes can be used as a proxy for tracking paleoredox change. Recent studies used black shales as an archive of oceanographic Cr isotope changes in Precambrian-aged strata. As shales comprise of a number of potential Cr-bearing phases (e.g. clays, organic matter, phosphates) it is critical to understand 1) which mineral phases host Cr and 2) variations and degree of fractionation in δ^{53}Cr of different mineral phases. To investigate this issue and to develop a method to recover the authigenic Cr component associated with organic-rich marine sediments, this study analysed black shale and other selected samples (e.g. phospates) from the Early Cambrian Jiumenchong Formation, South China, in bulk and leachates. In addition, batch absorption experiments of Cr(IV) onto organic matter (active charcoal) were conducted to test the reliability of δ^{53}Cr values obtained from the organic phases of black shales. The bulk analyses resulted in δ^{53}Cr values of -0.09‰ ±0.03‰ for a black shale sample to 0.86‰ ±0.04‰ for a chert sample. Results from the leachates suggested that the majority of Cr is hosted in iron-rich, phosphate and clay minerals. The δ^{53}Cr value of these mineral phases was within error to the bulk δ^{53}Cr values. The role of the organic phases as a Cr host varied depending on the sample. The δ^{53}Cr values of the organic phases were up to 0,3‰ lighter than the bulk values, which was in good agreement with the results of the absorbtion experiments onto organic matter. These showed a shift to heavier δ^{53}Cr values for the liquid phase, indicating a preferred absorption of ^{52}Cr onto the active charcoal. This may have implications for studies relying on organic-rich sediments to reconstruct redox fluctuations in past oceans.