Cr isotope fractionation during sorption on kaolinite and its implications for using black shales as a paleoredox archive

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It has been suggested that the oxygenation of Earth's atmosphere triggered the evolution of more complex life forms. Chromium (Cr) stable isotopes have been used to better constrain the changes in surface oxygen levels. Recent studies have focused on chromium records in black shales to investigate their potential use as marine archives tracking paleoredox changes. However, most isotope fractionation processes determining the final Cr composition of complex marine sediments/rocks with multiple components, such as black shales, are not well understood. Silicate-phases (e.g. feldspars and clays) of black shales are expected to show unfractionated δ^{53}Cr values, comparable to the range of Igneous Earth inventory (-0.124‰ ±0.101‰), but sequential leachates of organic-rich marine sediments from the Jiumenchong Formation, South China, identified positively fractionated silicate phases with values of up to 0.97‰ ±0.08‰. Cr(VI) adsorption on clay minerals could be one process explaining the fractionated silicate signals observed. To investigate and constrain this further, Cr(VI) batch adsorption experiments on kaolinite were performed. Two sets of experiments were conducted, in which kaolinite was reacted 1) with synthetic Cr(VI) solutions buffered at a ph of 8 and 2) with Cr(VI) doped seawater. The kaolinite record Cr isotope values that are offset by -0.15‰ ±0.08‰ from the signature of the original solution. Thus, our experiments show that the removal of Cr(VI) from solution results in more positively fractionated δ^{53}Cr values in the solution, which indicates that a reduction of Cr(VI) happens during adsorption. Considering that δ^{53}Cr values of up to 1.6‰ have been reported for modern ocean waters, the positively fractionated δ^{53}Cr silicate values of sediments deposited in marine environments can be tentatively explained by sorption processes of Cr on clay minerals, which potentially mask the Cr isotope signatures of the detrital phases. Our results encourage the use of Cr isotopes in black shales to track paleoredox fluctuations in the marine realm.