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Post-depositional redistribution of chromium in black shales and implications for paleo-redox reconstructions based on chromium isotopes

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Chromium (Cr) isotope compositions of black shales have been widely used to trace the oxygenation of Earth's oceans and atmosphere. Cr in black shales consists of detrital Cr and authigenic Cr, only the latter originated from seawater and can reflect paleo-redox conditions. However, the host phase of authigenic Cr in black shales remains poorly understood. Here we studied the Cr species in black shales from three sections with various geologic ages, using synchrotron-based micro-X-ray fluorescence (μ-XRF) mapping and micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy, sequential leaching, and Cr isotope analysis.

Our results reveal that most authigenic Cr in black shales is not associated with typical authigenic phases, such as organic matter or iron-rich components, but instead resides in silicate minerals. μ-XANES spectra further indicate that Cr is incorporated or adsorbed onto clay minerals. These findings contrast with studies of modern organic-rich sediments (evolve into black shales in the future), in which authigenic Cr was suggested to be associated with typical authigenic components such as organic matter. We propose that the maturation of organic matter during post-depositional diagenetic processes can induce the migration of authigenic Cr from the original organic phase to silicate minerals within black shales. This process likely involves Cr isotope fractionation, significantly altering the isotope compositions of the remaining organic phase. Additionally, we provide evidence that similar post-depositional effects may influence other trace elements, such as vanadium. These findings highlight the need to take into account the post-depositional processes when using trace elements and their isotope compositions in black shales to study the paleoenvironments.