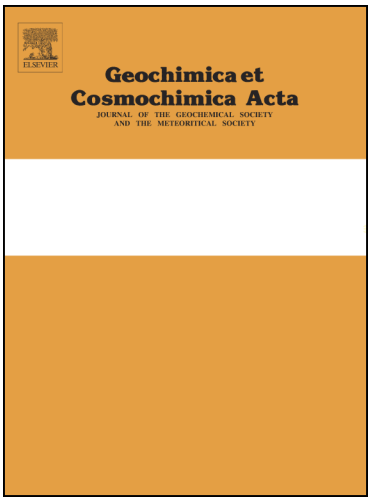

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Chromium isotope fractionation in ferruginous sediments

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ABSTRACT: Ferrous Fe is a potent reductant of Cr(VI), and while a number of laboratory studies have characterized Cr isotope fractionation associated with Cr(VI) reduction by ferrous iron, the expression of this fractionation in real-world ferrous Fe-rich environments remains unconstrained. Here we determine the isotope fractionation associated with Cr(VI) reduction in modern ferrous Fe-rich sediments obtained from the previously well studied Lake Matano, Indonesia. Whole core incubations demonstrate that reduction of Cr(VI) within ferruginous sediments provides a sink for Cr(VI) leading to Cr(VI) concentration gradients and diffusive Cr(VI) fluxes across the sediment water interface. As reduction proceeded, Cr(VI) remaining in the overlying lake water became progressively enriched in the heavy isotope (^{53}Cr), increasing δ^{53}Cr by 2.0 ± 0.1‰ at the end of the incubation. Rayleigh distillation modelling of the evolution of Cr isotope ratios and Cr(VI) concentrations in the overlying water yields an effective isotope fractionation of ε_{eff} = 1.1 ± 0.2‰ (^{53}Cr/^{52}Cr), whereas more detailed diagenetic modelling implies an intrinsic isotope fractionation of ε_{int} = 1.80 ± 0.04‰. Parallel slurry experiments performed using anoxic ferruginous sediment yield an intrinsic isotope fractionation of ε_{int} = 2.2 ± 0.1‰. These modelled isotope fractionations are corroborated by direct measurement of the δ^{53}Cr composition on the upper 0.5 cm of Lake Matano sediment, revealing an isotopic offset from the lake water of ε_{eff} = 1.1 – 1.5‰. The data and models reveal that effective isotope fractionations depend on the depth at which Cr(VI) reduction takes place below the sediment water interface—the deeper the oxic non-