Effect of bioavailability restrictions on Chromium isotope fractionation during microbial Cr(VI) reduction

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Chromium isotope fractionation analysis is an emerging tool for monitoring the extent of microbial Cr(VI) reduction in groundwater. Understanding the mechanism and factors controlling the Cr isotope fractionation is critical to this application. The major Cr isotope fractionation during Cr(VI) reduction is caused by the cleavage of Cr-O bond. However, when the mass transfer process preceding the bond cleavage step become rate-limiting or the bioavailability of Cr(VI) become lower, the observed isotope fractionation may be significantly affected. Here, we investigated the influence of bioavailability on observed Cr isotope fractionation during Cr(VI) reduction by *Shewanella oneidensis* strain MR1 under different conditions. In the temprature-control experiments, The Cr isotope fractionation showed a two-stage behavior: at Stage I, Cr isotope fractionation factors (ε) were 2.81±0.19‰ and 2.74±0.13‰ at 18°C and 34°C, respectively; at stage II, as the reaction of Cr(VI) reduction progressed, Cr isotope fractionation was significantly masked and the isotope fractionation factors decreased to 0.98±0.49‰ and 0.96±0.05‰ at 18°C and 34°C, respectively. Similar results with two-stage isotope fractionation were found in experiments under different pH and with or without nitrate. The masking of isotope fractionation at stage II indicated bioavailability restrictions of Cr(VI) and/or mass-transfer limitations by steps prior to reconfiguration of Cr-O bond. In additon, the extent of Cr isotope fractionation was not affected by changes in the tested conditions, such as different temperature and pH conditions, and with or without nitrate.