

Understanding Zn(II) Sorption on Palygorskite at the molecular scale: A coupling XAFS and Zn stable isotope approach

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Sorption reactions at the mineral-water interface control the fate and transport of trace metals in aqueous geochemical environments. While surface complexation theory is well established, the understanding of surface-induced precipitation at mineral/water interfaces, especially the kinetic process of sorption/precipitation, is still limited. The development of advanced synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy has improved understanding of interfacial geochemical processes to the molecular-atomic level, however, there are still constraints for normal XAFS to investigate the kinetic process and in particular, the initial stage owing to the time gap. Given that the *in-situ* Quick-scanning XAFS technique can achieve monitoring the sorption processes in real time, and Zn stable isotope is widely-used as a tracing tool, we employed a coupling XAFS and Zn isotope approach to elucidate the sorption mechanisms of Zn at palygorskite/solution interfaces.

In this work, the macroscopic and spectroscopic results indicate that at equilibrium, at low pH (e.g., below pH 7.0), Zn(II) is predominantly sorbed as an outer-sphere surface complex in octahedral coordination at low ionic strength (e.g., below 0.01 M), whereas at higher ionic strength (e.g., above 0.1 M) the sorption mechanism is dominated by the inner-sphere complexation in octahedral coordination along with a possible minority of tetrahedral inner-sphere complexation. At higher pH (e.g., pH 7.5), the formation of Zn phyllosilicate precipitate is observed. In addition, the *in-situ* real-time QXANES results in flow cell corroborate the finding of isotopic evolution in the sorption process at pH 7.5, where the magnitude of fractionation ($\delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$) changes from $0.53 \pm 0.05 \text{ ‰}$ to $0.05 \pm 0.04 \text{ ‰}$. The combined results indicate that the predominant mechanism evolves from tetrahedral surface inner-sphere complexation in the initial stage to octahedral surface inner-sphere complexation in the later stage, followed by polymerization and/or nucleation and the formation of Zn-phyllosilicate precipitates occurs.

The findings presented in this study improve not only the current understanding of surface sorption/precipitation but also try a novel application of metal stable isotope for tracing the sorption kinetic process at mineral-water interfaces.

