Zinc adsorption on clays inferred from atomistic simulations and EXAFS spectroscopy

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Supporting information

3 Supplementary

1 Table

1 Figure

5 Pages

Supplementary 1

The structural formulas of the montmorillonite samples used in this work are[1]:

Milos: $(Si_{7.76}Al_{0.24})(Al_{3.0}Mg_{0.54}Fe(II)_{0.02}Fe(III)_{0.44})O_{20}OH_4\,Na_{0.79}$ (MW = 750.3 [g/mol])

STx-1: $(Si_{7.91}Al_{0.09})(Al_{3.12}Mg_{0.75}Fe(III)_{0.14})O_{20}OH_4\,Na_{0.84}$ (MW = 742.1 [g/mol])

Milos and STx-1 contain 1.26 wt% and 0.56 wt% Fe, respectively. Based on an XRD characterization of the montmorillonites used, no indications for crystalline Si-phases were detected. The < 0.5 μm montmorillonite fraction used in this study was obtained in purification and conditioning processes. Briefly, the clay was thoroughly washed three times with 1 M $NaClO_4$ to convert the clay into a homo-ionic Na form. The < 0.5 μm size fraction was selected by successive washing with de-ionized water, combined with centrifugation and finally soluble hydroxyl-aluminum compounds and traces of amorphous iron were removed.

Supplementary Table S1: Experimental data and the chemical analysis of the filtered solutions for the samples prepared for P-EXAFS studies in 0.2 $NaClO_4$.

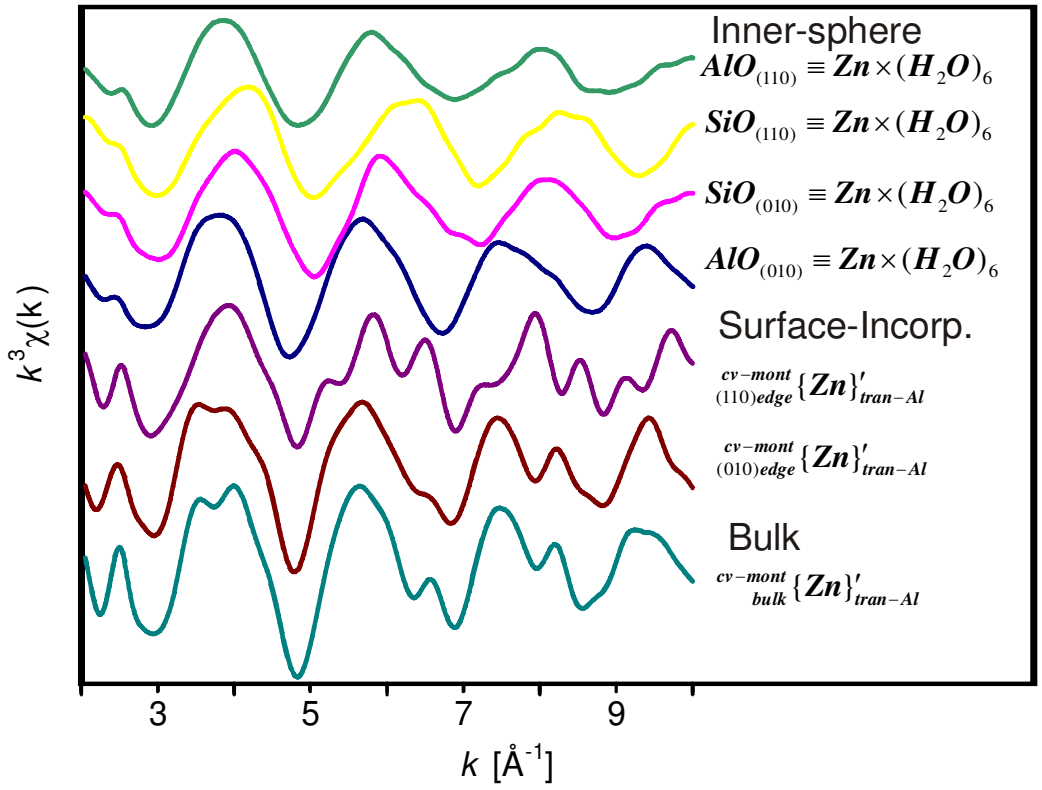
Sample	S:L ratio ($g\ L^{-1}$)	Initial Zn conc. (M)	Final Zn conc. (M)	Total Zn sorbed ($mol\ kg^{-1}$)	Si (M)	Al (M)
Milos-low	2.0	5.0×10^{-6}	8.0×10^{-7}	2.7×10^{-3}	2.8×10^{-5}	3.9×10^{-6}
STx-1-low	1.85	4.0×10^{-6}	4.6×10^{-7}	2.3×10^{-3}	1.0×10^{-4}	2.8×10^{-7}

STx-1-medium	2.25	2.4×10^{-4}	1.7×10^{-4}	3.2×10^{-2}	1.1×10^{-4}	3.3×10^{-7}

Supplementary 2

In the GAPW method implemented in the QUICKSTEP module of the CP2K package, the Kohn–Sham orbitals are expanded using a linear combination of atom-centered Gaussian type orbital functions. In this study "short range" double-ζ polarized valence basis sets for all atoms in the systems were used[8]. This basis set was optimized for large scale simulations in condensed matter systems and was proved to give accurate structural results. The "soft" part of the electron charge density was expanded using an auxiliary basis set of plane waves up to a 200 Ry cutoff. The PBE exchange and correlation functional[9] used in this work is known to reproduce the structural properties of water accurately[10]. The dual space norm-conserving pseudopotentials[11] were applied to avoid explicit consideration of core electrons. Ab initio MD simulations based on the Born-Oppenheimer approximation were performed with a time step of 1.0 fs at 350K using the Nose-Hoover thermostat[12, 13]. Before each force evaluation step, the energy was converged to within a value of 6×10^{-10} au/atom using a single k-point in the origin of the Brillouin zone (Γ-point sampling only).

Supplementary 3



Supplementary Figure S1. *Basis components used for the fit of experimental spectra at low and medium loading.*

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