

Relation between cis- or trans-vacant character of 1M illite and crystal morphology. Implications for metal sorption

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Sorption of pollutants like heavy metals in contaminated soils or sediments is controlled in part by their strong interactions with micro-crystalline minerals such as phyllosilicates, and numerous studies have been devoted to the determination of possible fixation sites for these adsorbed cations on phyllosilicates. These sites can be located on accessible edges, basal planes and interlayer planes, the relative abundance of which depends on the crystal morphology. In addition the configuration of the edge sites varies as a function of the layer structure.

Among the reactive minerals, natural illite (2:1 phyllosilicate of the mica family) crystals were found to occur with several morphologies ranging from 1D "hairy" illite to more isometric pseudo-hexagonal 2D plates. This morphological variability has been correlated with a structural modification from a 1M polytype with the octahedral *trans* site vacant to a 1M polytype with the octahedral *cis* site vacant using X-ray diffraction. However, no direct link has been demonstrated between morphology and structure because only populations of particles were investigated and statistically correlated.

In the present work, Selected-Area Electron Diffraction (SAED) patterns along the [001] zone axis were recorded on individual illite particles exhibiting contrasting morphologies to assess the validity of the hypothesized link. While the position of *hk0* reflections is similar for all illite polytypes, their relative intensity distribution was found to be very sensitive to the nature of the polytype and the *cis- versus trans*-vacant character of the octahedral sheet. Theoretical electron diffraction patterns were calculated and compared with the experimental SAED patterns to identify for individual crystals the polytype and the structure of building layers.

Nucleation and epitaxial growth of Zn phyllosilicate on montmorillonite

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Introduction

Zn retention by phyllosilicates has been documented in heavily contaminated soils. This retention can occur either by adsorption on clay surface or by neoformation of Zn phyllosilicates (e.g., Zn-kerolite), depending on physico-chemical conditions. This study aims to clarify the mechanism of Zn sorption on montmorillonite, the most common phyllosilicate in soils.

Materials and methods

Suspensions of purified MX80 montmorillonite (3.6 g L⁻¹ of solid, 0.5 M NaCl) were reacted with 500 μM Zn at pH 7.3, and with either "low" or "high" concentrations of dissolved Si ([Si]_{aq} = 70 and 500 μM, respectively). Self-supporting films of Zn-sorbed montmorillonite were obtained by slowly filtering suspension aliquots on 0.01 μm cellulose nitrate filters. Zinc K-edge polarized EXAFS (P-EXAFS) spectra of the self-supporting films were collected in fluorescence mode on the FAME beamline (ESRF, France). P-EXAFS data were reduced, and analyzed using standard procedures.

Results and interpretation

Strong angular dependences were observed for all P-EXAFS spectra, meaning that the binding environment of Zn is anisotropic. At low [Si]_{aq} and after 216 h contact time, the magic angle (powder) EXAFS spectrum resembled that of Zn-sorbed hectorite, a magnesian smectite [1] in which Zn is sorbed on layer edges. This same configuration was confirmed for montmorillonite, with Zn being surrounded by 0.6(4) Al at 3.00(2) Å in the film plane, and 0.5(4) Si at 3.21(2) Å in the perpendicular direction.

At high [Si]_{aq}, and t = 4 h, Zn was surrounded by in-plane Zn and Al, and out-of-plane Si, indicating the formation of clay nuclei on layer edges. At t = 313 h, Zn was surrounded on average by 3.7(7) in-plane Zn at 3.10(2) Å and by 3.6(4).4 out-of-plane Si at 3.27(2) Å, as in small Zn-kerolite particles [2]. These results collectively support the nucleation and epitaxial growth of Zn-kerolite on montmorillonite.

References

- [1] M.L. Schlegel, et al. *Am. J. Sci.* **301**, 798-830 (2001).
- [2] M.L. Schlegel, et al. *Geochim. Cosmochim. Acta* **65**, 4155-4170 (2001).