Adsorption mechanism of Co(II) on hectorite and its consequences on the dissolution process: Insight from polarized EXAFS and kinetic chemical studies

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Smectites are widespread minerals of soils, weathering formations and sediments. They possess an important surface reactivity which allows them to dominate many of the physicochemical properties of the natural systems in which they are present. Owing to this widespread occurrence and importance, the properties of the smectite-water interface, and specifically the smectite surface stability and sorption properties, deserve a particular interest.

The high surface reactivity of smectites is a consequence of their lamellar and defective structure. Smectites are built of layers made by the condensation of one central (Mg, Li, Al) octahedral sheet and two (Si, Al) tetrahedral sheets. Heteroionic cationic substitutions in these layers impart to smectites a negative structural charge, which results in cation exchange properties. Truncation of the bulk structure at the layer edges leads to unsaturation of surface oxygens, which can promote both pH-dependent sorption or surface dissolution. However, no definite evidence for the adsorption of cations on layer edges has been reported today. Furthermore, whereas it has been observed that the dissolution rate of smectites decreases in presence of metal cations, the exact

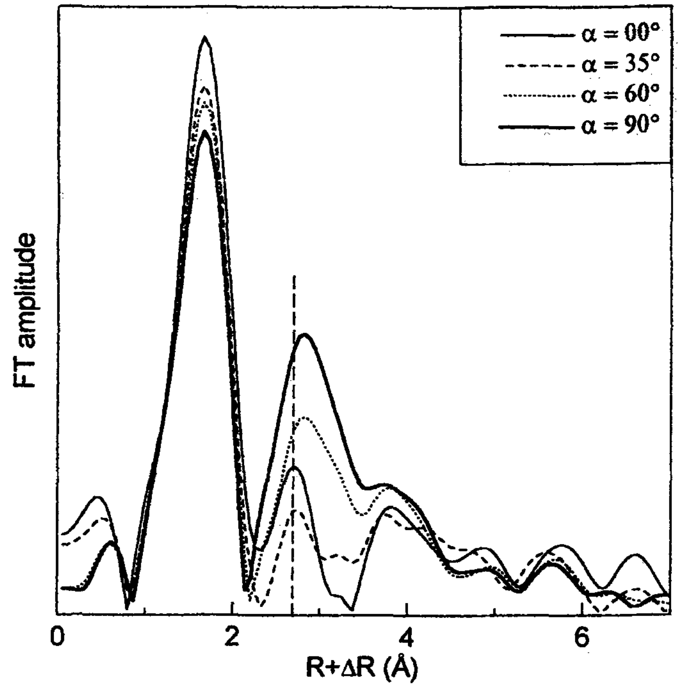

FIG. 1. Angular dependence of the radial distribution functions for Co(II) sorbed on hectorite.

mechanism for this dissolution inhibition has not been determined yet.

The present study aims at clarifying the mechanism of cation sorption on hectorite ($Na_{0.45}(Mg_{2.65}Li_{0.35})Si_{3.9}Al_{0.1}O_{10}(OH)_2$), and its influence on the dissolution kinetics of this mineral. It is shown by combining polarized-EXAFS spectroscopy (P-EXAFS) (Manceau *et al.*, 1998) and kinetic chemical studies that sorbed Co(II) forms inner-sphere surface complexes on (Li, Mg) structural positions of the layer edge. This adsorption mechanism correlates with a long-term inhibition of the hectorite dissolution.

Materials and methods

1.95 $g.l^{-1}$ suspensions of hectorite with a specific surface area of 114 $m^2.g^{-1}$ and a cation exchange capacity of 84 meq.100 g^{-1} were purged with Ar and kept at pH 6.5 during all sorption and dissolution experiments. A high ionic strength (I = 0.3 M) was chosen to supress Co(II) adsorption on exchangeable sites. Combined hectorite dissolution-Co(II) sorption experiments were performed with initial Co(II) concentrations from 20 to 200 μM. t_0 refers to the moment of Co(II) introduction in the suspension.

The sample for P-EXAFS spectroscopy was prepared by slowly filtering a suspension of Co-sorbed hectorite (Co(II) surface coverage = 37 $\mu mol.g^{-1}$) on a cellulose nitrate filter. The film was rinsed with bidistilled water, air-dried, and mounted on a rotating sample holder. P-EXAFS spectra were obtained by varying the angle α between the normal of the film and the incident X-ray beam. Quantitative analysis of EXAFS spectra was performed with theoretical reference functions calculated with FEFF7.02 (Rehr *et al.*, 1992)

Mechanism of Co(II) sorption on hectorite

Co K-edge P-EXAFS spectra obtained for different values of α were clearly dissimilar. These differences come from the occurence of different backscattering atomic shells having distinct orientations with respect to the sample plane. This structural anisotropy was confirmed by comparing the radial distribution functions (RDF) obtained by Fourier-transforming EXAFS spectra (Fig. 1). We observe that the amplitude and the position of the structural peak located at $R+\Delta R$ = 2.7 Å change with α which indicates that at least two atomic subshells do contribute to the second RDF peak. Quantitative analysis indicated that the first RDF peak at 1.7 Å originates from the contribution of the nearest oxygen shell at R = 2.07 (± 0.02) Å, whereas the second RDF peak near 2.7 Å originates from the contribution of two cationic subshells containing 1.4 (± 0.4) Mg at 3.03 (± 0.02) Å and 2 (± 0.5) Si at 3.27 (± 0.02) Å. $R_{Co\text{-}O}$ = 2.07 Å is symptomatic of 6-fold coordinated divalent Co, as 4-fold coordinated Co(II) or 6-fold coordinated Co(III) would have resulted in shorter distances of 1.9-2.0 Å. $R_{Co\text{-}Mg}$ and $R_{Co\text{-}Si}$ are typical of edge-sharing linkages between Mg and Co(II) octahedra, and corner-sharing linkages between Co(II) octahedra and Si tetrahedra, respectively. The angular dependence of Mg and Si contributions indicated that the Co-Mg pairs are oriented parallel to the film plane, whereas the Co-Si pairs are not. These results allow us to conclude that sorbed Co(II) forms inner-sphere surface complexes located at structural Mg positions on the edges of hectorite platelets, in the prolongation of the magnesian octahedral sheet.

Impact of Co(II) adsorption on hectorite dissolution

In pure suspensions, hectorite was found to dissolve uncongruently, with a preferential release of octahedral Mg over tetrahedral Si (Mg to Si ratio between 0.93 and 1.00 at t_0). This non-congruency suggests that hectorite dissolution is initated by acidic attack on octahedral surface sites. Adsorption of Co(II) dramatically changed this dissolution behaviour. During the first 12 h of Co sorption, the release rate of Mg was much enhanced. The additionnal amount of released Mg relative to $t < t_0$ (i.e. before Co(II) addition) was quite equal to the amount of sorbed Co. For $t > t_0 + 12$ h, the release of Mg and Si were inhibited. For example, the Si release rate decreased from 0.61 ± 0.11 $\mu mol.g^{-1}.h^{-1}$ at $t < t_0$ to 0.25 ± 0.14 $\mu mol.g^{-1}.h^{-1}$ at $t = t_0$ 120 h. The kinetic of Co(II) adsorption and its effects on mineral dissolution could be adequately described assuming two types of edge reactive sites. Both Co(II) adsorption on surface Mg sites and hectorite dissolution were supposed to occur on each of these sites.

References

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