Water diffusion in the dehydroxylation reactions in dioctahedral phyllosilicates by *ab initio* molecular dynamics simulations

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High temperature transformations of dioctahedral 2:1 phyllosilicates are interesting in geosciences and technological processing of ceramics and material design. However, there is a lack of knowledge at atomistic and nanoscale level of the mechanism and the role of the water molecules in this process. The dehydroxylation of pyrophyllite involves the reaction of OH groups forming water molecules throughout two possible mechanisms: on-site and cross. However, some discrepancies exist about both mechanisms and the limiting steps of this reaction. Therefore, a deeper insight about the mechanism, structural rearrangements and the diffusion of the water molecules during this process at high temperature are necessary for a better a better understanding of this process.

We apply quantum mechanical Car-Parrinello molecular dynamics simulations with the Metadynamics algorithm for simulating these reactions. Different reaction paths and the critical points of the FES are found for both possible mechanisms, reproducing the activation energy (Ea) found experimentally (60 kcal/mol). The water loss mechanism is not concerted but it is performed in at least two steps with intermediates. Besides, the apical tetrahedral oxygens are also implicated in the dehydroxylation mechanism forming intermediate silanol groups detected experimentally. For all mechanisms, the limiting step is the formation of water molecule, although it is trapped in the ditrigonal cavity and, during its release along the interlayer space (Ea = 17 kcal/mol), it reacts with other residual oxygens producing successive rehydroxylation-dehydroxylation processes justifying the wide temperature range needed in this reaction.

Parallel factor analysis for time-resolved laser fluorescence spectroscopy: A powerful tool for speciation studies

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Time-resolved laser fluorescence spectroscopy (TRLFS) is a speciation technique, allowing us to determine the number of different fluorescent components of a fluorescent metal ion and to obtain their relative abundance and structural information. Regardless of its popularity in geochemistry and environmental chemistry, the reliability of the information obtained from TRLFS seems sometimes doubtful due to strongly overlapped spectra and very close fluorescence lifetimes among different species. Parallel factor analysis (PARAFAC) is a multi-mode factor analysis (FA) method explicitly assuming a trilinear structure in analyzed data, as is the case for TRLFS data [1]. Compared with most conventional 2D FAs, the PARAFAC utilize an entire data set defined in more than three variables (wavelength, lifetime and chemical conditions, etc.) to separate the contributions of statistically different factors (species) and is free of rotational ambiguity inherent to 2D FAs, both of which makes the PARAFAC rather robust.

We have been used the PARAFAC to extract spectral, temporal and chemical information of different species of UO_2^{2+} and Eu^{3+} from the TRLFS data collected in aqueous complexation systems as well as surface sorption systems. Europium complexation by acetate ligand was studied for the introductory purpose [2]. The PARFAC provided the relative abundance of factors, which well agrees with the known speciation of the Eu^{3+}/acetate system. Both the pure spectra and fluorescence decays of the obtained factors also in line with the stoichiometries of the corresponding Eu^{3+} complexes. The UO_2^{2+}/gibbsite and Eu^{3+}/kaolinite sorption systems are being studied by the TRLFS-PARAFAC. The results will be discussed to demonstrate the applicability of the PARAFAC for TRLFS data analyses.

[1] Bro (1997) *Chemom. Intell. Lab.* **38**, 149–171. [2] Saito *et al.* (2010) submitted for *ES&T.*