

IN-SITU NANOSCALE IMAGING OF CLAY MINERALS WITH ATOMIC FORCE MICROSCOPY

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Clay minerals play a key role in many concepts for high-level nuclear waste repository systems in deep geological formations. Various aspects related to the long-term safety of nuclear disposal are linked to their fundamental physical-chemical properties, in particular with respect to their reactivity in aqueous environments. Atomic Force Microscopy (AFM) allows high resolution imaging of clay minerals in-situ while they are exposed to an aqueous solution. The presentation is intended to provide an overview of examples of AFM studies on clay minerals:

1. AFM is an ideal tool to visualize the shape of individual clay particles down to molecular scales (Figure 1) including a quantitative description of for example their aspect ratio (Tournassat *et al.*, 2003). Furthermore, the particle size can be easily extracted from AFM data for individual particles as well as particle size distribution.

2. Surface area of clay minerals is a key issue when discussing heterogeneous reactions such as dissolution, adsorption or (surface) precipitation – total surface area, BET surface area, reactive surface area need to be distinguished. In particular reactive surface area is linked to specific reactive surface sites. AFM is of course able to identify such sites and consequently AFM data allow to characterize and to quantify reactive surface area.

3. The reactivity of clay mineral surfaces in aqueous environments controls the behaviour of clay minerals under repository conditions and also affects the migration/retention of radionuclides. It could be shown that the dissolution of smectite particles under acidic conditions at room temperature primarily occurs at (hk0) particle edges, whereas the reactivity of the (001) basal surfaces is very limited (Bickmore *et al.*, 1999, Bickmore *et al.*, 2001, Bosbach *et al.*, 2000, Brandt *et al.*, 2003, Köhler *et al.*, 2005, Metz *et al.*, 2005). The heterogeneous (surface) precipitation of secondary iron (hydr)oxides phase could be unraveled by AFM observations. Surface precipitation occurs preferentially at (hk0) edges surfaces (Charlet *et al.*, 2000, Charlet *et al.*, 2002). Ignoring the surface site specific reactivity may be misleading, especially when discussing kinetic aspects of heterogeneous reactions.

4. The adsorption of organic matter/molecules such as humic substances has been successfully imaged using a combination of AFM imaging modes (phase imaging), which allows to simultaneously measure locally the viscoelasticity of the sample surface. Since the viscoelasticity of clay minerals and humic substances is significantly different, the attachment of organic material to clay mineral surfaces can be studied down to molecular scales.

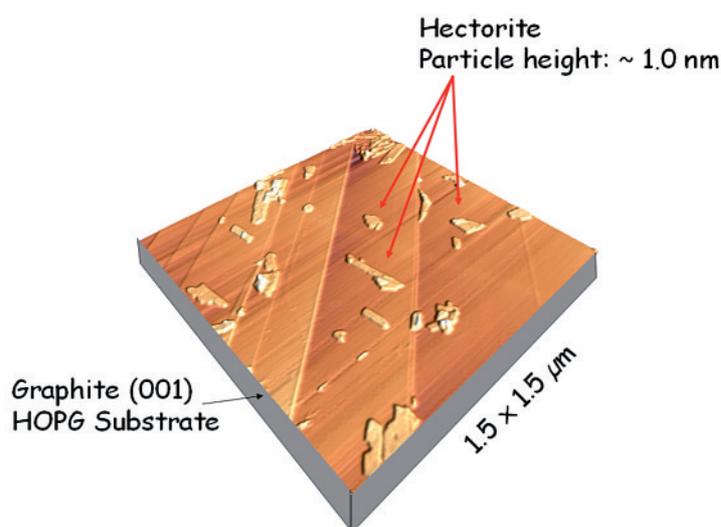


Figure 1: Hectorite particles attached to a graphite substrate. The height of the clay platelets is 1.0 nm, thus representing one TOT layer of the clay structure.

5. The swelling of clay minerals is also a property which may play a key role for the long-term safety of a nuclear waste repository system. Here, the swelling of clay mica due to Na⁺ exchange for K⁺ could be imaged time-resolved on (001) basal surfaces. Consequently, kinetic studies of ion exchange can be performed by AFM studies in-situ.

AFM has been demonstrated in the last 15 years to be an ideal tool to study the nanotopography of mineral surfaces and in particular of clay minerals in-situ in aqueous solution (or any other fluid) time-resolved down to molecular scales.

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