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Freezing and thawing of montmorillonite — A time-resolved synchrotron X-ray diffraction study

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ABSTRACT

The evolution of phases over time during freezing and thawing of unconfined Na- and Ca-montmorillonites (Wyoming, MX-80) was studied with time-resolved synchrotron X-ray diffraction. The clay samples were: (i) powder equilibrated to ambient atmosphere and (ii) pastes of 30 mass% montmorillonite in pure water. The phases were characterised in-situ using a stream of nitrogen gas for temperature control.

The behaviour of montmorillonite during freezing and thawing is important in final repositories for spent nuclear fuel that are using bentonite as a buffer material.

The Na-montmorillonite equilibrated to ambient atmosphere (one-layer hydrate) was unaffected by freezing down to −50 °C. The Ca-montmorillonite equilibrated to ambient atmosphere (two-layer hydrate) showed a minor decrease in basal spacing (0.11 Å) by freezing down to −50 °C. The magnitude of the decrease in basal spacing was high compared to the thermal contraction of the similar minerals muscovite and pyrophyllite and some dehydration of the clay was likely to be involved. Wet Na-montmorillonite in pure water was highly affected by freezing causing the osmotic phase to collapse during ice formation to 19 Å (three-layer hydrate) and later to a mixture of two and three-layer hydrates (−15 °C) and at lower temperatures to two-layer hydrate (16 Å, −50 °C).

The Ca-montmorillonite in pure water was present as a 19 Å three-layer hydrate at +20 °C and expanded upon cooling, producing two partly overlapping 001 reflections corresponding to three and four-layer hydrates prior to the ice formation. A mean *d*-value of the 002 peaks of the four-layer hydrate was determined to be 10.8 Å, which corresponded to a basal spacing of 21.6 Å. To our knowledge this is the first time a distinct four-layer-water hydrate is reported for Ca-montmorillonite in pure water. After the ice formation started, the montmorillonite was dehydrated to three-layer hydrate and at −15 °C to a mixture of two and three-layer hydrates. At −50 °C only two-layer hydrate was present.

The ice formation and the dehydration of the montmorillonite occurred simultaneously. The effects of freezing on the montmorillonite were shown to be reversible during the thawing.

The two dimensional diffraction rings gave information on the ice texture. The highly dispersed Na-montmorillonite (high surface area) in pure water facilitated the nucleation of the ice crystals and gave rise to uniformly sized crystals, while the Ca-montmorillonite (not dispersed, lower surface area) gave rise to non-uniformly sized ice crystals.

1. Introduction

Around 50 years ago it was shown by X-ray diffraction that the freezing of montmorillonite-containing pastes led to dehydration and shrinking of the montmorillonite interlayer distance (Norrish and Rausell-Colom, 1962; Ahlrichs and White, 1962; Anderson and Hoekstra, 1965). They showed that the process was rapid and reversible. This behaviour should be of importance when swelling clays containing montmorillonite (bentonites) are used as engineered barriers for toxic or radioactive waste repositories. The closer to the ground level these deposits are situated, the more likely they are to be exposed to freezing temperatures and to freeze–thaw cycles during subsequent glaciations. For final repository of spent nuclear fuel, a time scale of 10^5 years is applied for performance assessment and the possibility of one or more glaciations must be taken into account for areas situated sufficiently close to the Earth's poles (SKB, 2006). Also, surface drill holes used for the investigation of the rock and parts of the shaft are planned to be backfilled with smectite rich clays. Smectites such as montmorillonite are common minerals in some soils and are likely to have an impact on the soil properties upon freezing and thawing with respect to moisture transport and volume change. This makes enhanced understanding of freezing and thawing behaviours of smectites important for many different fields. The effect of freezing on montmorillonite has received

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little attention in connection with clay barriers, until recently, when Birgersson et al. (2008) investigated its effect on the swelling pressure of saturated and confined montmorillonite systems and showed that freezing decreased the swelling pressure. Access to synchrotron X-rays makes it possible to get much higher signal to noise ratios compared to traditional X-ray diffraction. Additionally, time-resolved data can be captured and this makes it possible to analyze this important process further. In the present study, we have investigated the evolution of phases over time during the freezing and thawing of unconfined Na- and Ca-montmorillonites in the dry state equilibrated to ambient atmosphere and as pastes with pure water. We describe the basal spacing of the montmorillonite in terms of the number of water layers. This is a simplified model. Using 3 Å as the approximate size of a water molecule (thickness of one layer), one can predict most observed basal spacings of smectite–water mixtures (Bradley et al., 1937). For simplicity we label these layer hydrates as: W1 (one-layer hydrate), W2 (two-layer hydrate), W3 (three-layer hydrate), W4 (four-layer hydrate) and WX (unknown number of water layers). A more detailed picture of the interlayer structure of smectite hydrates has emerged based on neutron scattering experiments and computer simulations, see for example Sposito et al. (1999). Basal spacings of smectites deviating from the ideal ones have also been reported (van der Gaast et al., 1986).

2. Experimental

2.1. Preparation of samples

The montmorillonite samples used in the present study were obtained by courtesy of Clay Technology AB, Lund. The Wyoming type of bentonite (MX-80, American Colloid Co.) consisted of around 80 mass% montmorillonite (mainly sodium form). Homo-ionic and dialyzed clay fractions (<2 µm diameter) were carefully prepared. The detailed procedure of sample preparation was reported elsewhere (Karnland et al., 2006, p. 11). The analyses showed the clay fraction to consist almost exclusively of montmorillonite, with the following approximate layer composition per unit cell: $(Al_{3.1}Fe_{0.4}Mg_{0.5})(Si_{7.9}Al_{0.1})O_{20}(OH)_4$ and either Na- or Ca-ions in the interlayer positions (Karnland et al., 2006, p. 116). The cation exchange capacity (CEC) of the dried material (105 °C, 24 h) was determined to be 86 cmol(+)/kg (Karnland et al., 2006, p. 23).

2.2. Mounting of specimens

(i) Montmorillonite samples equilibrated at ambient atmosphere were ground in an agate mortar, and the powder was used to partly fill a soda–lime–glass capillary (outer diameter 1.5 mm), which was then closed at both ends using modelling clay. The water content (mass of water divided by mass of solid hydrate) in the samples was estimated from the X-ray diffractograms by using the position of the montmorillonite 001 reflection, the unit cell parameters $a = 5.21$ and $b = 8.97$ Å and unit cell mass 734 g/mol (Karnland et al., 2006, p. 63). The approximated values were 6 and 17 mass% for the sodium and calcium montmorillonites respectively. This was equivalent to water ratios of 0.07 and 0.21 (defined as mass of water divided by mass of anhydrous solid).

(ii) Ground montmorillonite was mixed with deionized water to form a paste with 30 mass% of solid (25–27 mass% anhydrous solid), corresponding to a water content of 82–83 mass% (water ratio of 4.6). A capillary was partially filled with the paste using a syringe and the capillary was sealed with modelling clay. The samples used were thus essentially unoriented.

2.3. Synchrotron X-ray diffraction

Time-resolved X-ray powder diffraction data were collected on the beam-line I711 at MAX-lab, Lund (Cerenius et al., 2000) using a Mar system with a flat CCD detector (Mar 165, 2048 × 2048 pixels). The X-ray beam had a wavelength of 1.09994 Å, as refined using a LaB_6 reference sample, and a size of 1 × 1 mm. The capillary was not rotated during the measurements and was kept in a stream of flowing nitrogen with adjustable temperature (Cryojet, Oxford Instruments). After setting of the target temperature, the data collection was started. No continuous temperature monitoring was performed during the experiment. Each frame was monitored for 20 s with subsequent saving of data until the diffraction pattern did not change further. Before and after each run, the absence of any ice on the outside of the capillary was checked visually. The integrated intensity, scattering angle and width of the recorded diffraction rings were evaluated using the software Fit2d (A.P. Hammersley, ESRF). The minimum scattering angle that was measured was approximately $2\theta = 1.7°$, depending on the exact position of the beam stop in each experiment. This corresponded to a maximum observable d-spacing of 38 Å.

3. Results and discussion

3.1. Montmorillonite equilibrated at ambient atmosphere

In the two dimensional diffraction patterns of air-dry montmorillonites at +20 °C (Fig. 1a) the diffraction ring of the 001 reflection was closer to the central beam position in the Ca-montmorillonite compared to the Na-montmorillonite, indicating higher water content in the Ca case. The integrated diffractograms of dry montmorillonite at +20, −15 and at −50 °C (Fig. 1b) indicated a W1 hydrate for Na-montmorillonite and a W2 hydrate for Ca-montmorillonite in the samples, as would be expected for montmorillonite equilibrated at normal in-door environment (Brindley and Brown, 1980, p. 203). The first montmorillonite hk reflection was present at $d = 4.48$ Å (Fig. 1b,

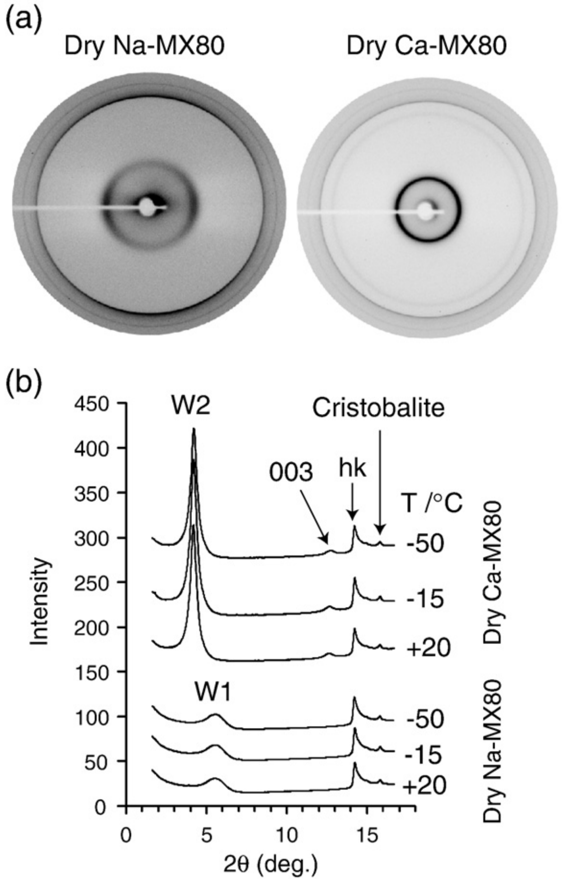

Fig. 1. (a) Two dimensional X-ray diffractograms of dry montmorillonite at +20 °C. (b) Integrated diffractograms of dry montmorillonites at +20, −15 and −50 °C. W1 and W2 denote one-layer and two-layer hydrates, respectively.