

Water mobility in smectite

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The hydrogen in smectite can be broadly separated into five major types according to the association with (i) structural hydroxyl groups, (ii) interlayer water bonded directly to the interlayer cations as nearest neighbours, (iii) interlayer water that does not directly interact with the cations, but instead with other waters and is thus next nearest neighbours to the cations, (iv) water that is loosely H-bonded to the interlayer clay surface and/or (v) inter-particle water. Because of the unique scattering length of hydrogen, neutron scattering can give unique insights into the motion of hydrogen, and thus water mobility can be studied. Obviously the amount of water in a smectite depends on the amount of water in the atmosphere, the cations present, and the layer charge of the clay. In this project we contrast the mobility of the water in the clay at partial pressures of 0.33 or 0.55, in the presence of either Ca or Na cations, and as a function of layer charge (1.05 or .46 or 0.26 eq/(Si Al)₈O₂₀). The source clay used was SAz-1 which was exchanged by Ca or Na. Charge reduction was induced following the reduced-charge (RCM) techniques described by Komadel et al (2002).

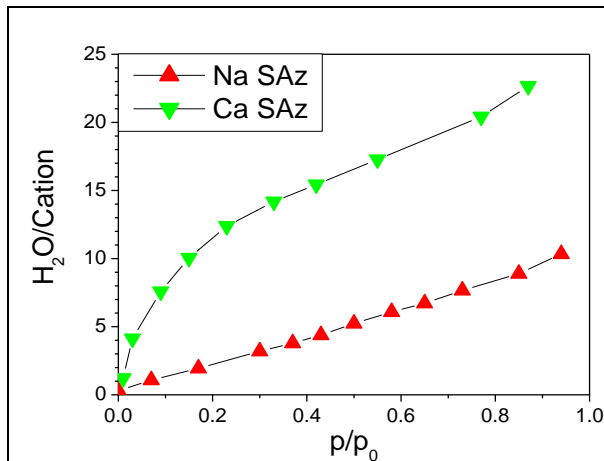


Fig. 1. Amount of water as a function of water partial pressure. Results recalculated from Chiou and Rutherford (1997) for Na SAz and Ca SAz. The original data was calculated in mg water/g of dry clay.

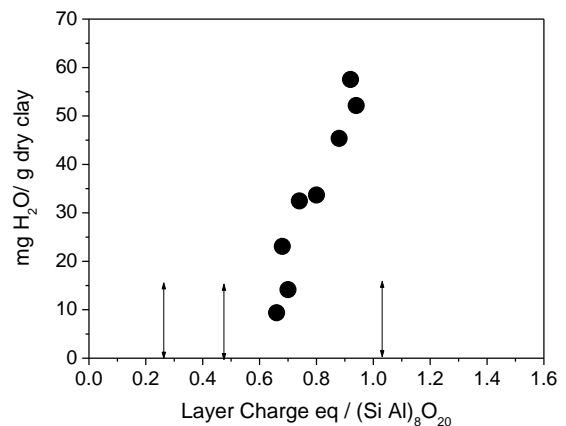


Fig. 2. Excess inter-particle water in Mg smectite conditioned at P/P₀ 0.54 as a function of layer charge Laird (1999). Lines indicate layer charges of samples used in this paper.

The amount of water adsorbed by a smectite at different water concentrations is well known. For example Chiou & Rutherford (1997) have measured the water adsorbed in (mg H₂O)/(g dried clay) as a function of the partial pressure of water vapour for Na or Ca exchanged SAz-1 clay. While the amount of water in SAz is well documented (Figure 1) the differentiation of this water into the different categories has not been generally attempted. It is well known that differences in water behaviour occur when the amount of water or the cation content or the layer charge are varied. For example both Komadel et al (2002) and Laird (1999) have indicated that increases of clay layer charge increases the amount of inter-particle water (Figure 2).

In this study we investigate the effect of environment on the mobility of water. Previously we had used quasi-elastic neutron scattering on a Jelšovský Potok montmorillonite to probe the mobility of water as a function of temperature (Bordallo et al., 2008, 2010), but the results should be very similar to those used by Chiou & Rutherford (1997). It was known that the mobility of the water was dependant on the resolution of the instrument reflecting the time scale that water mobility was detected. Thus a resolution of 1 μ eV detects water motion faster than 7 ns while resolutions of 25 & 100 μ eV indicate water mobility as less than 250 and 70 ps respectively. From the data it was possible to estimate that at the 7000, 250, & 70 ps time scales, respectively 100%, 40% and 20% of the water was mobile. Furthermore following Zanotti et al (2005) it is possible to differentiate the water mobility between translation and rotational components by measuring the fraction of the elastic scattering of neutrons as a function of temperature. The elastic scattering is shown in Figures 3 & 4. From the slope of the line it is possible to subdivide the scattering from 0 to 180K as arising from the vibrational motion and hydroxyl rearrangements while the increased loss of elastic intensity from 180-220K can be attributed to rotational motion and the increased loss of elastic intensity from 220-300K can be attributed to the translational motion. It is likely that the translational motion below 280K is mainly due to translational motion from within interlayer water while above this temperature the translational motion from inter-particle water contributes to this signal.

Thus quasi-elastic neutron scattering allows us to distinguish between different types of water motion, which combined with the previous work highlights the time dependant nature of water dynamics, should further allow us to differentiate between the different water states in smectite. In reality all forms of water will form a continuum of dynamic exchange where it is envisaged that individual water molecules will go from one state to another. However it must be recognised that water motion must vary over periods of nanosecond to fractions of a picosecond and that the characterisation of the mobility will depend to a large extent on the time window that the characterising instrument sees.

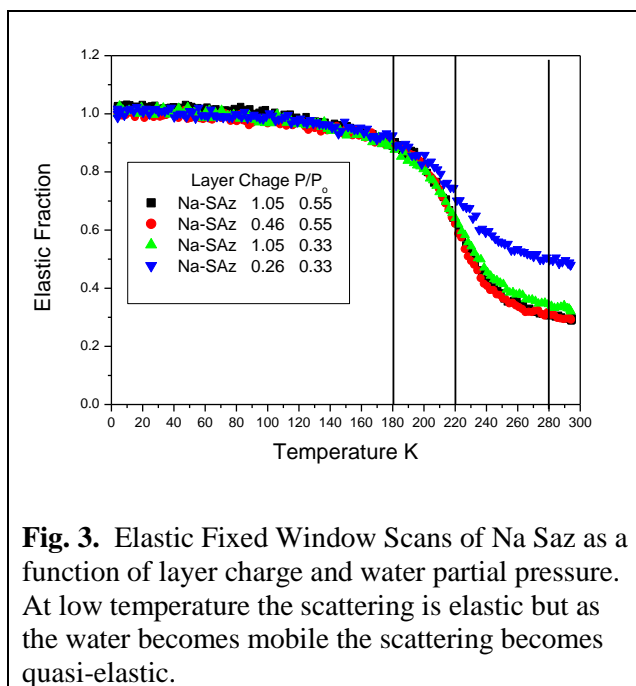


Fig. 3. Elastic Fixed Window Scans of Na SAz as a function of layer charge and water partial pressure. At low temperature the scattering is elastic but as the water becomes mobile the scattering becomes quasi-elastic.

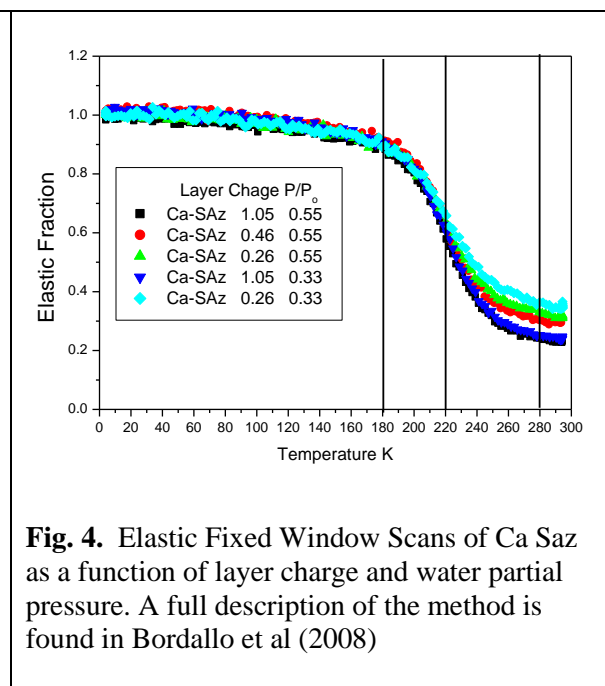


Fig. 4. Elastic Fixed Window Scans of Ca SAz as a function of layer charge and water partial pressure. A full description of the method is found in Bordallo et al (2008)

From the work presented here and previously (Bordallo et al 2008, 2010) we would claim that it should be possible to differentiate between the different categories of water using a combination of neutron scattering instruments of different resolutions and samples that encompass different water contents and layer charges. However it is obvious that effective resolution depends on careful sample choice. Much of our present work is designed to determine what samples are needed to highlight the difference in water mobility. Indeed we were surprised to see that differences in Figures 3 and 4 between the Ca exchanged clay were so small. However the changes in the gravimetric water (the results which have been submitted to another journal) does reflect a similar trend to the neutron data presented here. We do suggest that the marked difference between the Na Clay at low layer and higher layer charge reflects the difference in water / cation ratio.

We suggest that only by combining results from backscattering instruments (with resolution of 1 μeV) with the time of flight (with resolution 25- 100 μeV) is it possible to examine the spectra of all the water. It should be noted that Sposito and Prost (1982) previously highlighted the different time scales of water mobility. We suggest that water bonded directly to the interlayer cations as nearest neighbours would be the most tightly bound water that can only be seen with resolution of 1 μeV while the most loosely bound water can be seen at resolution of 100 μeV . Even though we have defined the water to be in 4 states (neglecting OH) we must expect that it can have a range of dynamic motions in each state and that spectrum is an average of this range. The deconvolution of this motion including the range of speed, translational diffusion, and rotational diffusion is complicated. However the studies that we have carried out suggest that the motions can in fact be separated.

Although this work on water mobility seems only of academic interest it arose from a consideration of barriers for low level nuclear waste repositories where the wastefoms which are generally encased in concrete and are separated from the environment by a number of barriers. These barriers are designed to limit the mobility of the water during the designed 300 year service life of the repository. Two commonly used barriers are concrete and compacted clay. In an earlier paper we considered that water transmission through concrete barriers would be minimized if there were no significant cracks in the concrete (Bordallo et al 2010). This has lead us to consider the interaction between water with both concrete and clay barriers. In particular we must consider the cracking induced by the volume changes of clay when exposed to the environment. Such cracking can easily occur. For example even in the Australian desert at depths of one meter the moisture content of soil expressed as relative humidity would be higher than 88% (Peter, 2000) while at the surface the relative humidity of both the clay and concrete would be significantly lower during most of the year. Australian deserts do have occasional severe rain events so that over a three hundred year service life it would be expected that there would be significant wetting and drying. During the wetting and drying cycles (1) alkalis and calcium are leached from the concrete that modify the clay and (2) clay is dried. Both can lead to such significant changes on the volume of the clay that cracking would be expected to take place. For example, of the kinds of changes Laird (2006) has highlighted the influence that Na replacement for Ca has on the breaking up the quasi crystallites. Our interest in water mobility in clay arose from a consideration of how the mobility of water in clay would change during the three hundred year period that the clay was acting as a barrier in a nuclear or a waste repository.

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