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Nanoscale Adsorbed Water Layer and Macroscopic Soil Properties

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Objective

Use of atomic force microscopy (AFM) to measure thickness of the adsorbed water layer in montmorillonite clay platelets.

Approach and Procedures

An instrument combining AFM with confocal optical microscopy has been used to measure the thickness of the adsorbed water layer in montmorillonite clay platelets. This instrument allows AFM from the top of an exposed sample surface, while simultaneously providing for confocal optical microscopy through a thin, transparent sample support from below (Lulevich et al., 2006).

We have succeeded in reproducibly generating surfaces of clean, stable platelets and small stacks of platelets on atomically flat substrates, such as mica. While impurity features such as those that were problematic to previous researchers are sometimes observed in our studies, most of our samples (a commercially distributed natural sodium-montmorillonite) have been free of this complication and are well suited for such studies.

Results

We used a sharp AFM tip to obtain a high-resolution topographic image of the clay platelets using minimum applied normal force (Eggleston 1994).This allows one to develop a map of useful features: single, isolated platelets and stacks of two or more platelets. An example from our initial studies is shown in figure 1a (left), which shows a 2 μm x 2 μm AFM image of cleaved mica after allowing brief contact with a sonicated dilute aqueous solution of montmorillonite, followed by wicking of excess solution. The mica surface is observed to be atomically smooth with very few impurities. Clearly visible in the center of the image is a group of platelets, the largest of which lies directly on top of the mica and measures approximately 500 nm x 250 nm in lateral dimension. Also easily observed is a second layer platelet on top of the first. Its lateral dimensions are smaller (~200x200 nm) than the first, but its vertical dimension is actually somewhat larger. The terrace of the larger platelet is measured to be 1.52 ±0.02 nm above the mica surface; the height of the second level terrace of montmorillonite is 1.79 ± 0.02 nm above the first, shown in figure 1b (right).

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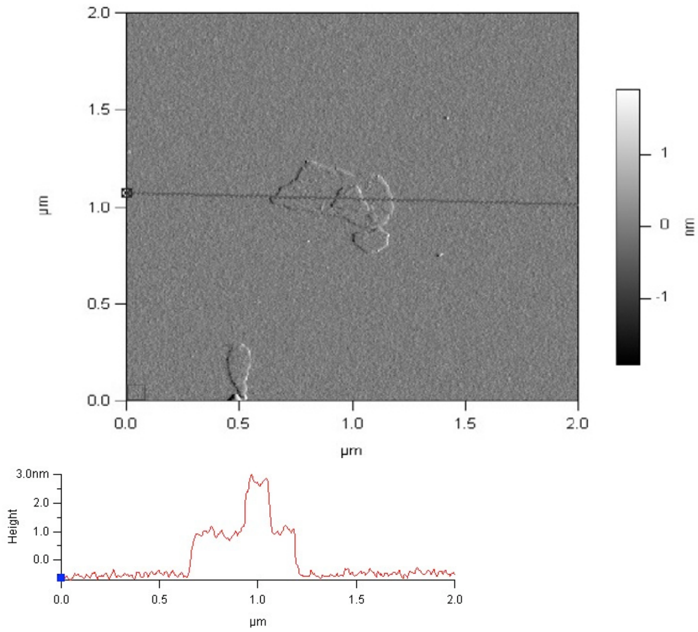
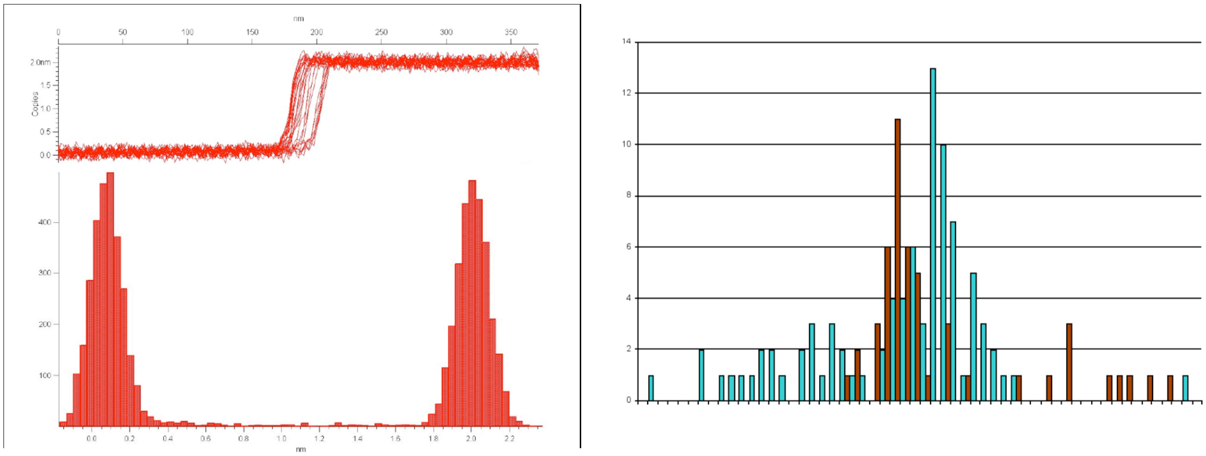


Figures 1a and 1b

The quantitative measurement of interlayer thickness requires a stable hydration state. This is best achieved by measuring the platelet stacks while immersed in water, since particles exposed to reduced relative humidity start to dry out. However, platelets immersed in water can move under influence of the AFM tip when imaging in direct contact mode. Thus, non-contact, or tapping mode is used to image immersed platelet stacks. In this imaging mode, the tip is positioned slightly away from the surface and vibrated vertically so that the tip makes intermittent, low-force contact with the surface. The top portion of figure 2a shows 30 superimposed scan lines of about 400 points each from a stack of two montmorillonite platelets. At left is the lower platelet and at right is the upper with a clear step up at 180-210 nm on the upper scale. Below these are two red histograms of the heights of each point in the line scans.



Figures 2a and 2b

The distribution is clearly bimodal with the lower terrace centered at 0.04±0.01 nm and the upper terrace at 2.01±0.01 nm. The difference between these two means is 1.97±0.01 nm and represents the interlayer spacing, which includes one montmorillonite platelet plus intercalated water. Figure 2b (right) shows a histogram of the interlayer thickness measured for more than 100 platelet stacks measured using tapping mode while submerged in water. Two different types of stacks are displayed. In brown are the height of single montmorillonite platelets relative to the mica substrate. In blue are the interlayer heights for montmorillonite platelets on top of another montmorillonite platelet. Both populations show a strongly spiked distribution. It appears that the interlayer distance is slightly smaller for the former (1.90 nm) than for the latter (1.98 nm). This might be attributed to the fact that although mica and clay platelets are very similar in their geometric structure, they are different in their electrochemical properties that mainly arise from the disparity in charge deficiency in the internal layers of the particles (Mitchell 1993).

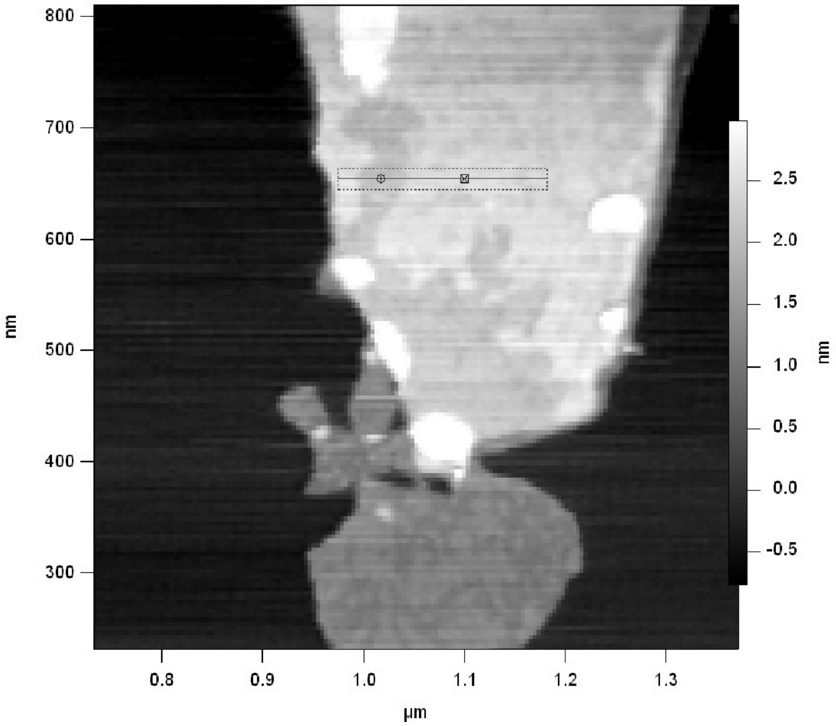


Figure 3. Montmorillonite platelets on a mica surface after partial drying. Height mode: lighter features are higher. The darkest areas are the mica substrate. A stack of two clay platelets is observed extending from the upper edge down about three quarters of the way to the bottom. The fact that this is a stack of two particles can be discerned by observing the extension of the lower platelet, particularly at the right edge, and also by comparison with the single ellipsoidal platelet directly below it. Small brighter regions are a third level of platelets. The upper terraces of both the single platelet and the stack show a mottled appearance. This is due to incomplete loss of two of the three water layers that separated the platelets from the mica surface when fully hydrated. The horizontal line near the top indicates a height trace that yields a difference in the slightly darker and lighter regions to be 0.51 nm – two water layers.

An example of a stack of two clay platelets in the process of drying is shown in figure 3 (preliminary results). Near the bottom of the imaged stack of two platelets (the large, bright feature that occupies the region from 400 nm to the top in "y" and from 0.95 to 1.3 µm in "x"), it is evident that the loss of water takes place at different rates on different regions of the samples. The low regions of the upper clay platelet are 0.51 nm below the higher regions. This is the expected height of two water layers. Thus, the low regions have a single layer of water between subsequent platelets, and the higher regions are still in the fully saturated state, with three layers of water. As yet, no images have been observed where there are only two layers of intercalated water. Theoretical molecular dynamics modeling has indicated that the first layer of water is very tightly bound, but that the second and third layers are bound much less tightly with about the same energy. (Suzuki and Kawamura 2004) These are the first images showing this behavior, and we are early in the process of modeling the dynamics, but this clearly has implications in the prediction of the swelling and drying behavior of clays.

Discussion

For oven-dried tactoids, the total layer height is reported to be 0.955 nm. After hydrating in a low relative humidity environment for an extended time, the tactoid platelets were estimated to contain one layer of water of hydration, and the total layer height was estimated to have expanded to 1.249 nm. Hydration to the level of two layers of intercalating water resulted in an estimate of 1.555 nm, and full hydration led to estimates of three layers of water and a total layer height of 1.81 nm. Thus, our measurement of 1.79 ± 0.02 (95% confidence limits) is in excellent agreement with other estimate (Cases et al. 1992) for a fully hydrated tactoid with three layers of water separating neighboring platelets.

Our results with standard topographic image and the corresponding phase signal obtained simultaneously during the same scan indicate that higher stacks of hydrated platelets have a smaller Young's modulus. This result must be a consequence of the intercalated water layers, since the Young's modulus for dry Montmorillonite has been estimated to be approximately the same as that for dry mica. (Chen and Evans 2006)

Our ability to measure plate heights to less than 0.02 nm with 95% confidence allows us to easily measure the nanoscale effects of swelling and to distinguish between the various hydration states observed and characterized by others

References

Cases, J.M., I. Berend, G. Besson, M. Francois, J.P. Uriot, F. Thomas, and J.E. Poirier. 1992. Mechanism of adsorption and desorption of water vapor by homoionic Montmorillonite. 1. The Sodium-Exchanged form. *Langmuir* 8: 2730-2739

Chen, B., and J.R.G. Evans. 2006. Elastic Moduli of clay platelets. *Scripta Materialia* 54: 1581-1585.

Eggleston, C.M. 1994. High-resolution scanning probe microscopy: Tip-surface interaction, artifacts, and applications in mineralogy and geochemistry. In, *Scanning*

Probe Microscopy of Clay Minerals. K.L. Nagy and A.E. Blum, (eds.) Boulder, The Clay Minerals Society. 7.

Lulevich, V., T. Zink, H.-Y. Chen, F.-T. Liu and G.-Y. Liu. 2006. Cell Mechanics Using Atomic Force Microscopy-Based Single Cell Compression. *Langmuir* 22: 8151-8155.

Mitchell, J.K. 1993. *Fundamentals of Soil Behavior 2nd Edition*. New York. John Wiley & Sons, Inc.

Suzuki, S., and K. Kawamura. 2004. Study of Vibrational Spectra of Interlayer Water in Sodium Beidellite by Molecular Dynamics Simulations. *Journal of Physical Chemistry B* 108: 13468-13474.

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