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Measurement of Young's modulus of clay minerals using atomic force acoustic microscopy

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[1] The presence of clay minerals, hydrous aluminosilicates that are smaller than 2 μm can alter the elastic and plastic behavior of materials significantly. We have used Atomic Force Acoustic Microscopy (AFAM) to measure elastic properties of clay minerals. We demonstrate the AFAM technique for measuring elastic properties of soft materials. Using this technique, we present first-ever quantitative measurements of Young's modulus in clay. The Young's modulus of dickite was measured as 6.2 GPa. *INDEX TERMS:* 5102 Physical Properties of Rocks: Acoustic properties; 3909 Mineral Physics: Elasticity and anelasticity; 5112 Physical Properties of Rocks: Microstructure; 3994 Mineral Physics: Instruments and techniques

1. Introduction

[2] Presence of clay minerals, hydrous aluminosilicates with grain size smaller than 2 μm, alters the elastic and plastic behavior of materials significantly. Using acoustic microscopy images of sandstones, *Prasad* [2001] has shown that the clay in contact zones has significantly lower impedance than the quartz it cements. Ultrasonic velocities are reduced in clay-rich sandstones when the clay is load-bearing [*Tosaya*, 1982; *Han et al.*, 1986]. As pore filling materials, they block hydraulic pathways and decrease permeability. In the presence of water, clay minerals can swell and cause considerable formation damage. Despite their ubiquitous presence, measurements of the elastic properties of clay minerals remain a challenge.

[3] Since clay minerals are an integral part of many formations and seismic measurements are the main tools for identification of subsurface lithologies, knowledge about the elastic properties of clays is essential for interpretation and for modeling the seismic response of clay-bearing formations. However, elastic properties of clay minerals are almost unknown [*Alexandrov and Ryzhova*, 1961]. Until now, estimates of single crystal elastic properties have been either theoretical [*Katahara*, 1996], or based on extrapolations from measurements on clay-epoxy mixtures [*Wang et al.*, 2001].

[4] Recent studies have shown that it is possible to make measurements of dynamic Young's modulus at nanometer resolution on various materials using Atomic Force Acoustic Microscopy (AFAM) [*Kester et al.*, 2000; *Rabe et al.*, 2001; *Amelio et al.*, 2001]. We have investigated the feasibility of such measurements on clay minerals. We describe the methodology for making quantitative measurements of stiffness and elastic moduli using AFAM and show results of such measurements on clay samples.

2. Atomic Force Acoustic Microscopy

[5] In scanning Atomic Force Microscopy (AFM), the topography of the sample surface is measured from deflections of the cantilever tip from its equilibrium position. AFAM is an enhancement of the AFM technique in which ultrasonic transducers are used to insonify the contact zone between the cantilever tip and the sample surface. To this end, either the sample or the cantilever holder might be excited by an ultrasonic transducer [*Rabe et al.*, 1996; *Yamanaka et al.*, 1999]. The dynamic Young's modulus is determined by measuring the difference of the cantilever contact-resonance frequencies relative to its free resonances. The resonance frequencies of the flexural modes of the cantilever will depend, amongst other parameters, on the stiffness of the tip-sample contact, which in turn is a function of the Young's modulus of the sample and the tip, their Poisson's ratios, the cantilever tip radius and shape, the load exerted on the tip, and the geometry of the sample surface. In an isotropic material, if the elastic modulus of the tip and its radius are known, the Young's modulus of the sample can be determined if the Poisson's ratio is either known or assumed [*Kester et al.*, 2000; *Rabe et al.*, 2001]. In the anisotropic case, the so-called indentation modulus [*Vlassak and Nix*, 1993] is determined. For reliable measurements, the sample surface must be of nanometer smoothness over an area of tens of nanometers where the measurements are taken. The Young's modulus is measured with a spatial resolution of a few tens of nanometers.

[6] In an actual measurement, an area with low topographic variations is first selected with an AFM. Then, the free and contact resonances of the cantilever are measured. The excitation frequency is varied and the cantilever vibration amplitude is measured as a function of frequency. The frequency range used (10 kHz to about 3 MHz) covers typically the first three flexural modes of the cantilever in contact. The procedure is repeated with different normal forces on the tip in order to obtain information on the tip shape and to check whether a Hertzian contact prevails. For a complete set of measurements on an unknown sample, a standard sample is first measured with AFAM to determine the tip radius. The unknown sample is measured next. Finally, the standard sample is measured again to ascertain that the tip remained intact during the measurement. An averaged value between both standard measurements is used as tip radius for the calculation of the Young's modulus in the unknown sample [*Kester et al.*, 2000; *Rabe et al.*, 2001].

[7] *Kester et al.* [2000] give an accuracy of the Young's modulus from the average of the scatter and considerations of the simplifications mentioned above to be about 40%. By comparing indentation moduli of silicon, *Rabe et al.* [2001] have shown that it is possible to differentiate between indentation moduli of Si (100) and Si (111) crystals, that differ only by 4%. However, our

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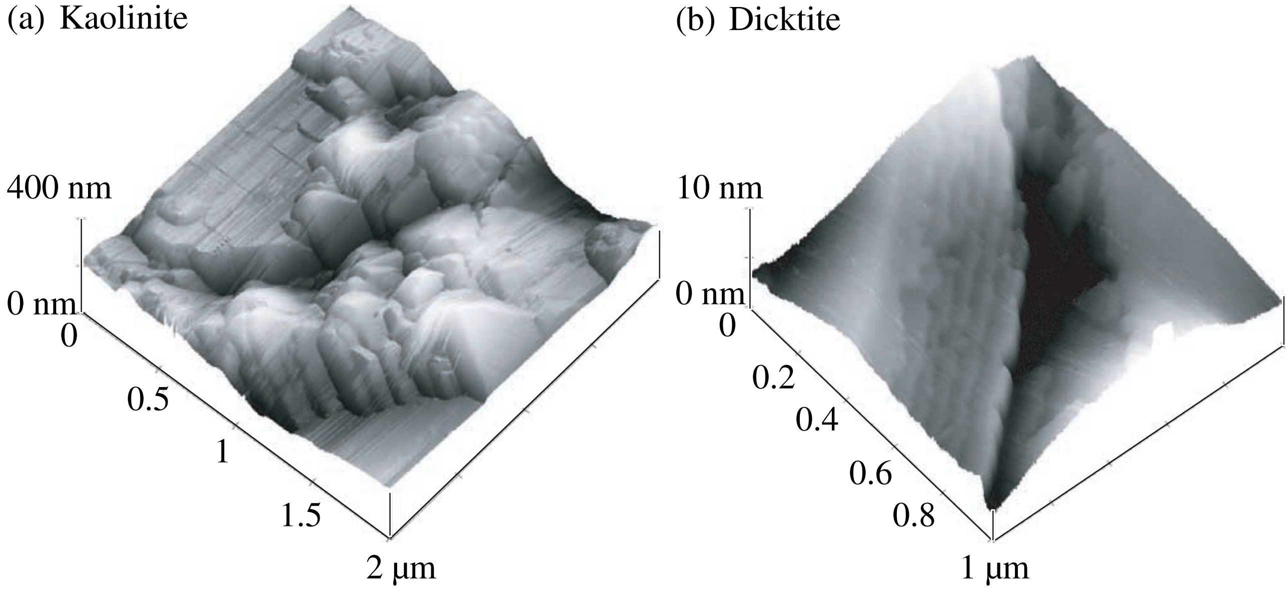


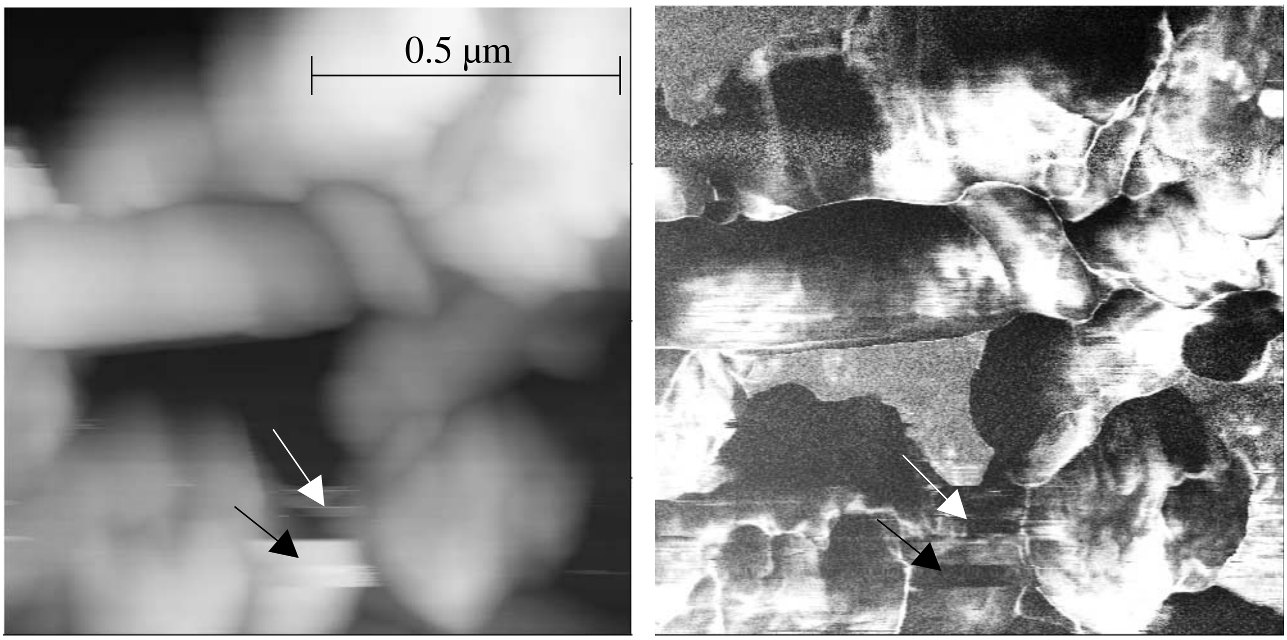
Figure 1. Contact mode AFM image of kaolinite (a) and dickite (b) powders. The topography is coded with gray colors: white = highs, black = lows. Although topography on each stack of grains is not large, the cantilever position on the sample is not stable, most probably due to the small grain size. Kaolinite grains show a typical rosette texture. Typical clay booklets with topography variations below 10 nm can be observed in the dickite sample.

measurements on a softer material, polystyrene, showed that an accuracy of at least 40% can be expected for such materials. We present here initial results of AFM and AFAM measurements for clay minerals and the Young' modulus derived from them.

3. Samples and Sample Preparation

[8] Clay mineral powders were used in this study. Fused silica, mica and polystyrene served as the standard samples with known Young's modulus [*Amelio*, 2000]. The Young's modulus of polystyrene measured with ultrasonic pulse-echo was 3.5 GPa.

[9] Kaolinite, dickite, and mica powders were immersed in distilled water and insonified for 30 minutes. After allowing the larger particles (mainly silts) to settle, a dilute water-clay mixture was extracted from the top of the container. This suspension was diluted further, mixed, and allowed to settle for 5 minutes. The water-clay mixture taken from the top of this solution was put on a glass slide heated by a glass lamp. In this manner thin layers of



(a) Topography image, scale 500 nm (b) AFAM image at 987 kHz

Figure 2. Contact mode AFM of image of dickite powder showing mineral texture (left image). Topography variations, color coded as in Figure 1 are below 500 nm. The right-side image is an acoustic image with AFAM: It is made with contact mode AFM after insonifying the sample at a resonance frequency of the sample-tip system. Although, topographic effects are small, the AFAM image has some noise and disturbances marked by arrows probably due to sample movements on the glass slide.

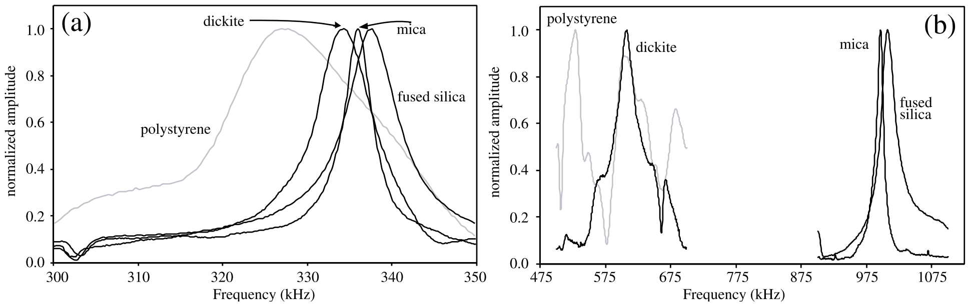


Figure 3. Contact-resonance spectra in polystyrene, dickite, mica, and fused silica. While there is a small shift in first contact-resonance towards lower frequencies (a) in the low impedance polystyrene and clay, a clear impedance based separation in frequency is observed in the second contact-resonance (b). The resonance spectra are broader in the low impedance materials, possibly due to attenuation in the sample.

kaolinite and dickite samples were obtained. Mica particles were co-mingled with the clay. With this method, the clay minerals were aligned with their C-axis perpendicular to the glass slide.

4. AFM Imaging

[10] AFM images of the kaolinite and dickite samples are shown in Figures 1a and 1b, respectively. In these images, as in all AFM images, the topographic differences are originally color coded and then converted to a gray scale (black = dips and white = highs). The kaolinite image shows grain stacks with a typical rosette structure of the kaolinite. Each mineral stack is less than 1μm wide. Although the topography varies only by a few tens of nanometers within each stack, the image shows numerous disturbances caused mainly by movement of the sample with respect to the cantilever. The dickite sample with slightly larger grain size shows the typical clay booklets observed in SEM studies. The topography of this stack of about 7 layers is less than 10 nm. The measurements were made in contact mode with a stiff triangular cantilever. This mode of operation was found to create disturbances in the imaging mode due to sample movement and grain deformation. The so-called tapping mode [*Zong et al.*, 1993] gave better resolution and imaging results. Using this mode, we ascertained that the texture shown in Figure 1b is repeated at random locations throughout the dickite sample.

Table 1. Calculated Effective Stiffness (k^*) and Young's Modulus (E) for Various Positions on the Dickite Sample

Sample	k^*		E1 (GPa)		E2 (GPa)	
	30	45	30	45	30	45
			(load in nN)			
Polystyrene	56	58	3.2	3.7		
Mica	301	300	56.9	60.2		
Position 1	81	76	5.99	5.69	6.7	6.13
Position 2	72	100	4.99	8.75	5.58	9.45
Position 3	81	83	5.99	6.52	6.7	7.04
Position 4	80	83	5.88	6.52	6.57	7.04
Position 5	78	75	5.65	5.57	6.32	6.0
Position 6	76	77	6.08	6.26	5.16	5.78
Position 7	77	78	6.19	6.38	5.26	5.9
Position 8	80	81	6.57	6.77	5.56	6.25
Position 9	78	59	6.32	4.14	5.37	3.83
Position 10	77	85	6.19	7.3	5.26	6.74

E1 corresponds to the tip radius obtained from measurements on the standard sample **before** measurements on clay and E2 corresponds to the tip radius obtained from measurements on the standard sample **after** the measurements on clay. The mean value of E is 5.9 Gpa at 30nN and 6.4 Gpa at 45nN static loads and the standard deviation for each Load step is 0.54 Gpa and 1.27 Gpa, respectively.

5. AFAM Quantitative Analyses

[11] Despite the good quality AFM images, quantitative AFAM of clay measurements were more difficult to obtain. The AFAM image (Figure 2) often had disturbances in the scanning mode. However, good repeatability was observed in the single-location contact-resonance spectra obtained at random clay locations with a rectangular cantilever (stiffness = 1.5 N/m). Quantitative analyses were made at 10 different clay locations. A typical spectra sequence is shown in Figure 3 for different materials. The contact-resonance spectra for polystyrene are at a lower frequency than mica and fused silica. The second contact-resonance spectra are as much as 500 kHz apart. Note that the relative frequency difference of the contact resonances on different materials depends on the mode of the cantilever vibrations [*Turner et al.*, 1997]. The contact-resonance spectra in polystyrene and clay also appear to be broader, possibly due to internal friction losses in the sample. Young's modulus for dickite was calculated from the spectra shown in Figure 3 by assuming a Poisson's ratio of 0.3. The values obtained for all 10 locations are given in Table 1 along with the standard deviation for the calculations at different locations (0.54 GPa and 1.27 GPa for 30 nN and 45 nN static load, respectively). The mean value for Young's modulus from our measurements is 5.9 GPa at 30 nN and 6.4 GPa at 45 nN static load.

[12] The Young's modulus was calculated by assuming a spherical tip and Poisson ratio = 0.3 for the dickite. The average value according to Table 1 is 6.2 ± 1.0 GPa. Although the values show a high reproducibility, a larger error of about 40% (± 2.5 GPa) needs to be assessed for the absolute values at present. This error arises from uncertainties in the theories required to model the cantilever vibration modes and the contact area between tip and sample. The input parameters for these calculations, such as beam geometry and tip shape, are only known to a certain approximation. The Young's modulus is calculated by comparing the vibration modes of the AFM cantilever on a known reference sample with those on the unknown sample. The error can be relatively small if the elastic constants of the calibration sample are close to those of the unknown sample. A future set of measurements will improve the precision of our measurement by using new reference samples. Furthermore, the complex clay-tip interactions will be modeled to account for deviations from the assumed model. For example, surface tension forces of clay might lead to higher lateral forces than assumed. Elastic moduli in the c_{11} and c_{33} directions in sheet silicates can differ by a factor of 3 to 3.5 [*Alexandrov and Ryzhova*, 1961]. Future work will improve accuracy and resolve the issue of anisotropy in these samples.

6. Conclusions

[13] Our analyses of the AFAM measurements and comparisons with measurements on similar materials give Young's modulus values of 6.2 GPa (± 2.5 GPa) in dickite in the c_{11} direction. This

value is in agreement with the theoretically derived bulk modulus value of 10 – 12 GPa by *Berge and Berryman* [1995]. Our study resolves the controversy surrounding elastic modulus values of clay minerals. Various values have been suggested for bulk modulus of clay minerals. For example, extrapolation from shale measurements [*Tosaya*, 1982; *Castagna et al.*, 1985; *Han et al.*, 1986], theoretical models using measured values on other sheet silicates [*Katahara*, 1996], and extrapolation from measurements on clay-epoxy mixtures [*Wang et al.*, 2001] gives bulk modulus values of kaolinite, which has a similar structure and mineralogy as dickite, between 21 and 55 GPa - much higher than our measured value of 6.2 GPa. We also demonstrate for the first time how the AFAM technique can be used for soft materials. Implications of this study go beyond the applications for earth sciences.

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