

A TECHNIQUE FOR MAINTAINING TEXTURE AND PERMANENT EXPANSION OF SMECTITE INTERLAYERS FOR TEM OBSERVATIONS

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Abstract—A process for treating smectite-bearing rock samples that utilizes LR White resin; allows TEM observation of expanded smectite interlayers and therefore preservation of original rock textures. Examples of several lattice fringe images are shown, including: (1) Dioctahedral smectite layers from a shale (1388.9 meter depth, Texas Gulf Coast) give fringes that consistently have spacings of 1.2–1.3 nm, yet duplicate other features previously observed in collapsed samples. (2) Packets of illite layers give fringes with 1.0-nm spacings coexisting with packets of (dominantly) R1 I/S having 2.1-nm lattice fringe spacings in a Gulf Coast shale from 4742.1 m. (3) Rectorite from Garland Co., Arkansas gives 2.3-nm lattice fringes. Samples with wide ranges of I/S ratios and lithologies have been found to be permanently expanded with retention of original textures, commonly leading to unambiguous identification of illite and smectite interlayers in lattice fringe images.

Key Words—Illite, LR White resin, R1 I/S, Rectorite, Smectite, Transmission electron microscopy (TEM).

INTRODUCTION

One of the most perplexing problems in TEM analysis of clay minerals concerns the dehydration and collapse of smectite layers to $d(001)$ -values of approximately 1.0 nm, resulting in ambiguity in differentiation between illite- and smectite-like lattice fringes. Even though contraction does not occur in all cases (Ahn and Peacor 1986a), 1.0-nm layers cannot be identified either as smectite-like or illite-like with certainty. Smectite and illite also form mixed-layer structures, and it is difficult and usually impossible to distinguish between layers of these two clay minerals. Identification of individual layers of I/S as being smectite- or illite-like is critical to determination of the mechanisms by which smectite transforms to illite. For example, by examining sequences in which the proportions of layers change, it should be possible to differentiate between replacement of individual layers or dissolution and crystallization of packets.

Ahn *et al* (1983) and Ahn and Peacor (1984) characterized material from the Gulf Coast, showing that smectite-rich material from shallow sediments and illite-rich material from deep sediments could be readily differentiated. Individual layers could not be identified, however, and material at intermediate depths remained poorly characterized. Guthrie and Veblen (1989a, 1989b) and Veblen *et al* (1990) showed that lattice fringe images of illite- and smectite-like layers were different for special focus conditions. However, Ahn and Peacor (1989) and Freed and Peacor (1989a) subsequently found that even for those focus conditions, a given operator could observe contrast differences between smectite- and illite-like layers in 1:1,

R1-ordered I/S of Gulf Coast shales only with great difficulty, whereas the same operator consistently and easily observed contrast differences for some other kinds of R1-ordered I/S (e.g., Ahn and Peacor 1986b, Jiang *et al* 1990, Alt and Jiang 1991), even for a wide range of focus conditions. The difficulty in identifying individual layers has therefore been a matter of continuing concern for at least some I/S of diagenetic sedimentary origin.

Yoshida (1973) treated smectite layers with laurylamine hydrochloride so that they remained expanded during TEM observations. However, observations could only be made on curled edges of flakes. Lee and Peacor (1986) found that although most layers were expanded, the expansion was variable and could be inconsistent even for adjacent layers. The principal problem that they encountered, however, was that stress resulting from expansion of smectite caused the surface to progressively spall away, destroying the original rock textures. Bell (1986), Vali and Köster (1986), Vali and Hesse (1990), and Vali *et al* (1991) successfully developed methods for permanent expansion of interlayers using *n*-alkylammonium ion treatment, but this method can only be used for separates. Murakami *et al* (1993) described a freezing technique that permits characterization of I/S without contraction of smectite layers at liquid nitrogen temperatures. They used a Gatan cryotransfer system to freeze carbon-coated TEM specimens at liquid nitrogen temperatures. However, this technique is apparently only applicable to separates, and the method requires expensive equipments.

Tessier (1984) developed a method of impregnation of moist samples that maintains layer stacking se-

quences and causes smectite to be permanently expanded for TEM observations. The samples are prepared at low suction pressures (3.2 kPa, generally) in order to saturate specimens fully with water. The interlayers and the pore space separating packets are then completely expanded but the samples retain their shape and texture. After saturation with water, the samples are immersed in a solvent, generally methanol, and then exposed to an epoxy resin. This procedure causes the pores to remain open during impregnation, and the various solvents can easily penetrate into the sample, especially between expandable interlayers. Satisfactory impregnation was shown to occur with low magnification ($\sim 5000\times$) images. The methanol is used as an intermediate solvent for water and resin. As shown by Annabi-Bergaya *et al* (1980), the layer spacings expanded with water remain at 1.3 nm after methanol exchange and about 1.35 nm after resin infiltration (Srodon *et al* 1990). The layer spacings correspond to the presence of the methacrylic component of the LR White resin as provided by Taab laboratories. The resin is composed of aliphatic chains with carboxylic groups. Its polar character allows the components of the resin to penetrate into the layer. The thickness of the methacrylate molecules is about 0.35 nm. The method has been used to better understand hydration and swelling mechanisms as well as for mineralogical characterization. It has been used for embedding samples which have various cation-exchange capacities and concentrations of Ca or Na (Tessier and Pédro 1983, 1987), for samples subjected to varying stress (Ben Rhaïem *et al* 1987, Tessier *et al* 1992), and for various clay minerals, i.e., kaolinite and halloysite (Delvaux *et al* 1992, Romero *et al* 1992), and illite and smectite (Tessier *et al* 1992). The technique was also adapted for examination of smectite prepared with reduction of Fe(III) to Fe(II), the embedding procedure being carried out under an N_2 atmosphere. TEM observations showed that there was a significant increase in packet thicknesses and degree of stacking order (Stucki and Tessier 1991).

A variant of the technique was used by Srodon *et al* (1990) for original rock chips, resulting in observations that showed that XRD measures of relative proportions of illite and smectite in I/S were in agreement with TEM observations. However, the general utility of the method, and its power to promote expansion of smectite vis-a-vis illite interlayers with retention of unperturbed mineral and rock textures, has not been described and therefore is not generally recognized. We have therefore developed a variant of the technique and utilized it to expand smectite interlayers for samples from a variety of environments. It has been successful in all cases, including well indurated shales and friable mudstones, smectite-rich and illite-rich packets, and ordered I/S. It seems to be the "magic bullet" for which we have searched for many years. The purpose

of this paper is therefore to bring the method and examples of its use to the attention of other clay mineralogists, so that it can be generally used for observations of I/S.

METHODS

The samples used in these studies were Gulf Coast shales having I/S, with $>85\%$ smectite and $<15\%$ smectite from depths of 1388.9 m and 4742.1 m, respectively, from the Pleasant Bayou No. 1 well, Brazoria Co., Texas, and rectorite (R1 I/S) from Garland Co., Arkansas. Samples from the Pleasant Bayou No. 1 well have been thoroughly characterized by XRD and TEM (Freed 1980, 1989b), whereas the rectorite is a well-characterized Clay Mineral Society standard (R-Ar-1).

The impregnation process involves three steps: rehydration, embedding, and polymerization. It utilizes LR White resin (LRW), a polymer that is of lower viscosity than even the commonly-used Spurr resin. Those steps are:

1. Rehydration—Air dried rock chips (less than 2-mm thickness and 6-mm width) that lay on a porous membrane (0.025-m pore diameter) are rehydrated by capillarity in an ultrafiltration cell at an applied air pressure of 3.2 kPa. The size of rock chips should be as small as possible, so that they will be impregnated homogeneously, but keeping in mind that they must be large enough to yield 3-mm diameter TEM samples. They must not be in direct contact with water as that would cause smectite-rich samples to spall during rehydration.
2. Embedding—Water in the clay is replaced by solvent exchange, starting with 100% methanol and progressively adding medium grade LRW: (a) Rock chips are immersed in 100% methanol for two h and then immersed again in freshly prepared 100% methanol for four h. The samples are then transferred to a flask containing freshly prepared methanol and stored overnight in a refrigerator. (b) The solvent is progressively modified by mixtures of methanol and LRW with volume ratios $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ each for two h and the samples are immersed in pure LRW for six h. (c) Pure LRW is changed every two h (four times) and the samples are then placed in a refrigerator overnight. (d) Pure LRW is again changed for two h.
3. Polymerization—(a) The samples are transferred to casting molds and freshly prepared LRW is added. They are then placed in a vacuum desiccator to remove any bubbles in the LRW. (b) Finally, samples are placed in an oven at 60°C for 24 h to polymerize and harden the LRW.

An ordinary thin section can then be prepared using "sticky wax" or other low-melting point or solvent-soluble resin as an adhesive. A selected area of the thin

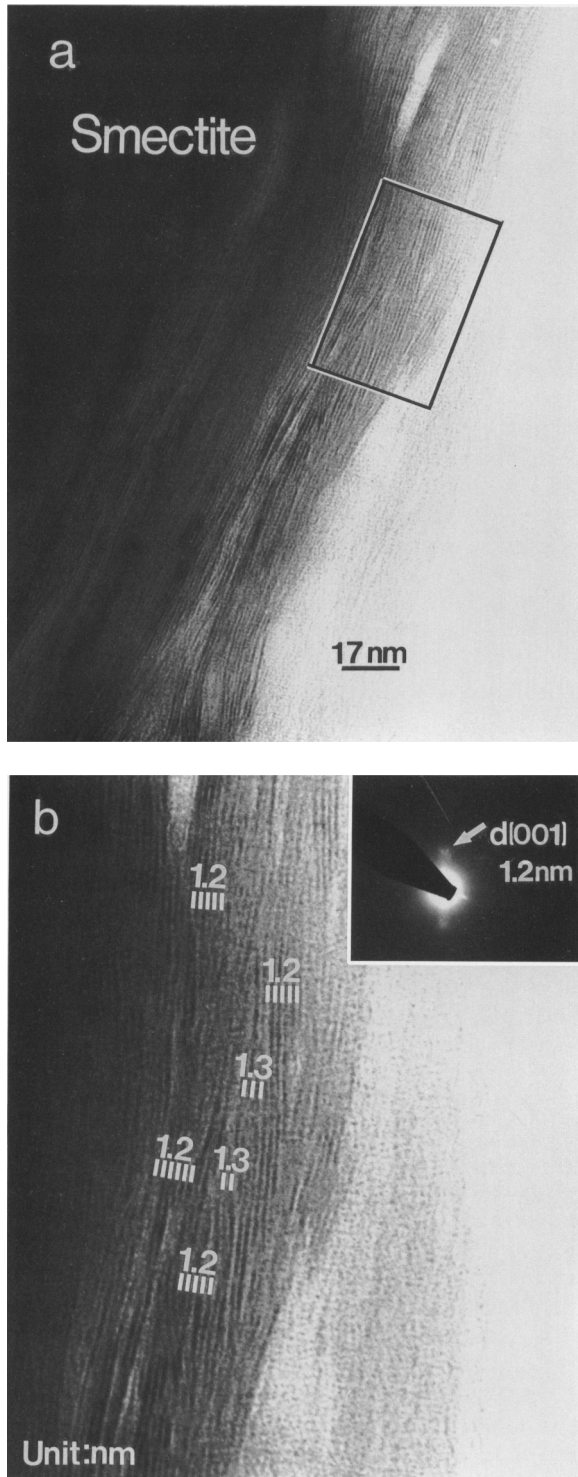


Figure 1. TEM lattice fringe images of an embedded sample having >85% smectite at a depth of 1388.9 m from the Pleasant Bayou No. 1 well, Brazoria County, Texas. (a) Intermediate-magnification TEM lattice fringe images displaying the typical continuous smectite matrix extending over a broad area. Fringes are wavy and anastomosing with a lack of par-

allelism. The original rock texture is well preserved. (b) Enlarged area outlined in Figure 1a, showing expanded smectite fringes with spacing ranging from 1.2 to 1.3 nm at high magnification. Discontinuous, interfingered fringes have abundant dislocations (layer terminations). The inset SAED pattern shows 001 reflections with $d(001)$ -values of 1.2 nm. Diffuseness along c^* is due to variable layer thicknesses and diffuseness normal to c^* is caused by variable layer orientation.

section can be pre-thinned using a dimpler, if desired, and a 3-mm diameter Al washer attached with epoxy. The selected area is then detached, ion-milled, and carbon-coated.

These procedures represent our initial attempt to apply techniques developed for soil samples to coherent rocks. It may be possible to modify this scheme substantially. We present this recipe simply because it has proven to work. Further experimentation may lead to considerable refinement, however.

TEM observations were made with a PHILIPS CM 12 scanning-transmission electron microscope (STEM) fitted with a Kevex Quantum solid-state detector and computer system in the Electron Microbeam Analysis Laboratory at The University of Michigan. The STEM was operated at 120 kV and a beam current of ~ 20 A, and images were obtained at $75,000\times$ magnification with an objective aperture 20 μm in diameter. In order to obtain the strongest contrast differences between illite- and smectite-like layers, images were obtained under overfocus conditions as defined by Guthrie *et al* (1989a, 1989b), following slight adjustments in tilting of (001) layers relative to the electron beam.

RESULTS AND DISCUSSION

Figures 1a and 1b are TEM lattice fringe images for the LRW-treated samples from the Gulf Coast having >85% smectite. Figure 1a is an intermediate-magnification image chosen to illustrate the typical smectite texture over an extended area, whereas Figure 1b is an enlarged image of the outlined portion of Figure 1a. Figure 1b displays smectite layers with spacings varying from 1.2 to 1.3 nm, similar to those of hydrated smectite layers, but clearly different from the 1.0-nm spacing of illite. Smectite layers imaged as 1.2-nm lattice fringes are prevalent in most areas and smectite layers with 1.3-nm spacing are observed as one or two layer units. There are abundant dislocations (layer terminations) resulting in branching and interfingered layers. There is a general lack of parallelism in anastomosing layers, the spacings between fringes appearing to vary slightly along layers. The textural relations have an appearance identical to those observed by Ahn and Peacor (1986a) for smectite-rich I/S in Gulf Coast samples that were untreated, and for which all fringes had spacings of approximately 1.0 nm; this demonstrates that the textures are preserved even after LRW treat-

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allelism. The original rock texture is well preserved. (b) Enlarged area outlined in Figure 1a, showing expanded smectite fringes with spacing ranging from 1.2 to 1.3 nm at high magnification. Discontinuous, interfingered fringes have abundant dislocations (layer terminations). The inset SAED pattern shows 001 reflections with $d(001)$ -values of 1.2 nm. Diffuseness along c^* is due to variable layer thicknesses and diffuseness normal to c^* is caused by variable layer orientation.

ment. Ahn and Peacor (1986a) also observed some lattice fringe spacings as large as 1.3 nm. However, spacings varied continuously along the layers, with most layers having collapsed to 1.0-nm spacing. As shown in Figure 1b, all smectite layers of the sample treated with LRW have constant spacings of 1.2 to 1.3 nm, demonstrating that smectite interlayers can readily be differentiated from illite interlayers. The discontinuous, anastomosing smectite layers form a more or less continuous array that constitutes a continuous matrix that envelopes detrital grains of other minerals (not shown here), and for which Ahn and Peacor (1986a) coined the term “megacrystal”. That is, a smectite-rich mudstone can be viewed as having a crystallographically-continuous matrix of defect-rich smectite.

The inset selected area electron diffraction pattern that corresponds to the lattice fringe image of Figure 1a shows basal reflections that are very diffuse in all directions. The component of diffuseness normal to c^* is a consequence of non-parallelism of layers. The diffuseness parallel to c^* is caused by the presence of variable layer spacings. Vali and Hesse (1990) observed two kinds of expandable layers having spacings of 1.6–1.7 nm and 2.4–2.5 nm, respectively, and concluded that they are caused by differences in interlayer charges. Similarly, Ahn and Peacor (1986a) concluded that small variations in spacings of smectite-like interlayers of the sort observed here for the 1388.9 m sample may be due to heterogeneity in composition and therefore in interlayer charge.

The XRD data for shallow Gulf Coast samples, including those for this sample (Freed 1980), imply the presence of R0 smectite-rich I/S having a small proportion of illite interlayers. Most material has been interpreted to have up to 30% illite layers, but in the case of the sample studied here, Freed concluded that there is <15% illite. However, we have been unable to detect the presence of any fringes with spacing of 1.0 nm. This may indicate that indeed there are no random I/S mixed layers existing in the natural samples. Ransom and Helgeson (1993) concluded that on the basis of thermodynamic studies, illite and smectite do not form a solid solution corresponding to I/S mixed layers. Separate packets of mica having the characteristics of detrital material (Ahn and Peacor 1986a) consisting of 10 to 20 straight, defect-free layers were observed, for which the fringe spacings had characteristic 1.0-nm values. These data are preliminary and represent only a small volume of material and we can therefore offer no definitive explanation for the lack of illite-like interlayers. However, we tentatively speculate that the difference between XRD data on samples for which standard polar organic liquids were used, and those for LRW, may be due to differences in the ability of those substances to cause expansion of clay minerals with variable layer charge, i.e., the lack of expansion of all layers as detected by XRD data may

be caused not by illite-like interlayers, but by relatively high-charge smectite interlayers.

Figures 2a and 2b are TEM lattice fringe images at different magnifications for the LRW-treated samples having <15% smectite. Figure 2a displays the well-preserved texture of illite-rich sediments recovered from a depth of 4742.1 m, the overall texture duplicating the general features observed by Ahn and Peacor (1986a) for untreated samples. Thin (approximately 10 nm thick), subparallel packets of illite-rich material are defined by relatively straight, defect-free lattice fringes, giving an overall impression that is similar to that of the smectite-dominated texture of the shallow samples shown in Figure 1 except that here it consists of discrete interfingering packets rather than being a continuous array of anastomosing layers.

Figure 2b illustrates packets of two types, and is representative of other images for these preliminary results. There are two distinctly different materials, however. One consists of packets dominated by layers of 1.0-nm spacing that we interpret as illite, *sensu strictu*. The other, which we interpret as 1:1, R1-ordered I/S, is imaged as having broad, dark lattice fringes which alternate with narrow, bright fringes. The periodicity is 2.1 nm, with the weaker subfringes displaced slightly from the midline between darker fringes. Guthrie and Veblen (1989b) and Veblen *et al* (1990) demonstrated that darker black fringes correspond to smectite interlayers whereas the lighter black fringes correspond to illite interlayers, when imaged under special overfocus conditions. The expansion of R1 I/S to only 2.1 nm is surprising in light of expansion of rectorite (see below) to 2.3 nm. Possible explanations include differences in interlayer charge or porosity of the samples, factors that are now being investigated.

Figures 3a and 3b display intermediate and high resolution TEM lattice fringe images, respectively, of LRW-treated rectorite from Garland Co., Arkansas, showing lattice fringes with 2.3-nm spacings. The inset selected area electron diffraction pattern of Figure 3b displays $d(001)$ -values of 2.3 nm, corresponding to lattice fringes of Figure 3b. Figure 3a shows well-preserved textures of rectorite coexisting with goethite, again demonstrating that the technique appears to have no effect on both extended and local textures. Figure 3b demonstrates that the rectorite fringes have 2.3-nm periodicity and, like the R1 I/S described above, are defined by alternating dark, broad and lighter, narrow fringes.

The LRW-embedding technique has also been used in our laboratory to obtain lattice fringe images of several other samples, including I/S from the Antrim formation of the Michigan Basin, I/S from the 1.1-Ga Nonesuch Shales from near the White Pine copper mine, Michigan, and smectite-rich bentonite from Kaka Point, New Zealand. In all cases, illite and smectite layers were apparently successfully identified.

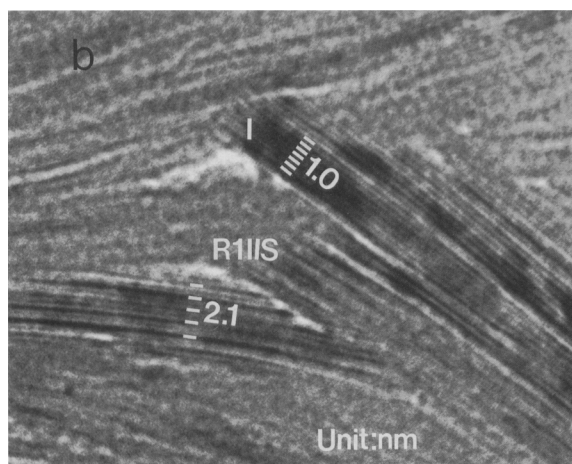
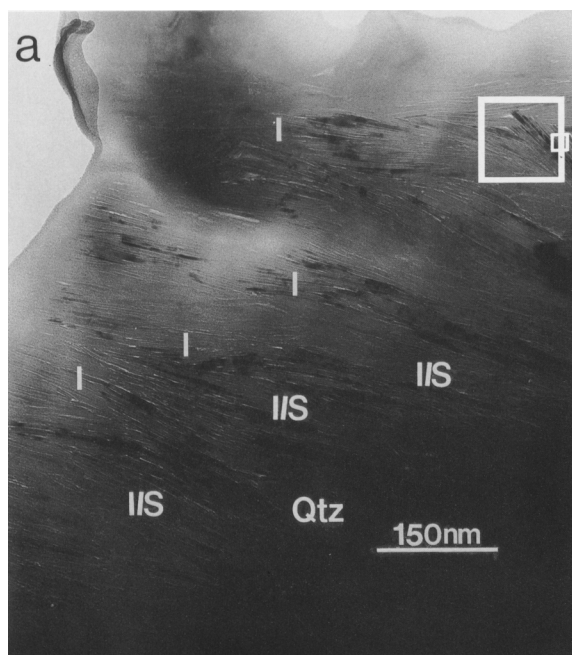


Figure 2. TEM lattice fringe images of samples with <15% smectite from a depth of 4742.1 m from the Pleasant Bayou No. 1 well, Brazoria County, Texas. (a) Intermediate-magnification TEM lattice fringe images showing an array of interlocking packets of illite-rich material, each packet being approximately 9–11 layers thick. (b) Enlarged area outlined in Figure 2a showing thin packets consisting of relatively straight, defect-free layers. The packet on the left consists largely of R1 I/S with 2.1-nm periodicity, whereas the larger packet is dominated by 1.0-nm illite.

These results can be interpreted on the basis of the interaction between clay layers, water, and the solvents used in this method. Preparation of samples at 3.2 kPa of suction pressure produces a relatively open porous system by which the resin can penetrate layers easily. Saturation with water causes extensive swelling of smectite layers. Nevertheless smectite layers are de-

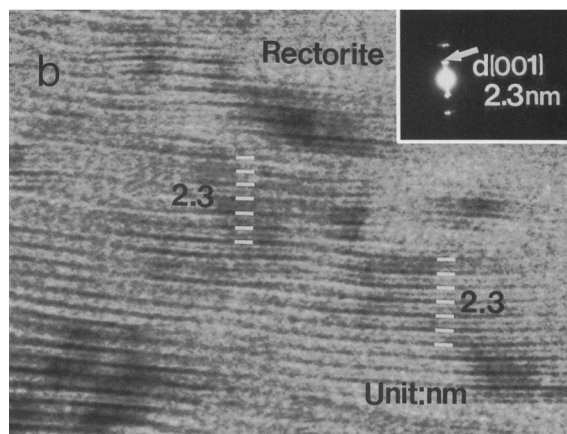
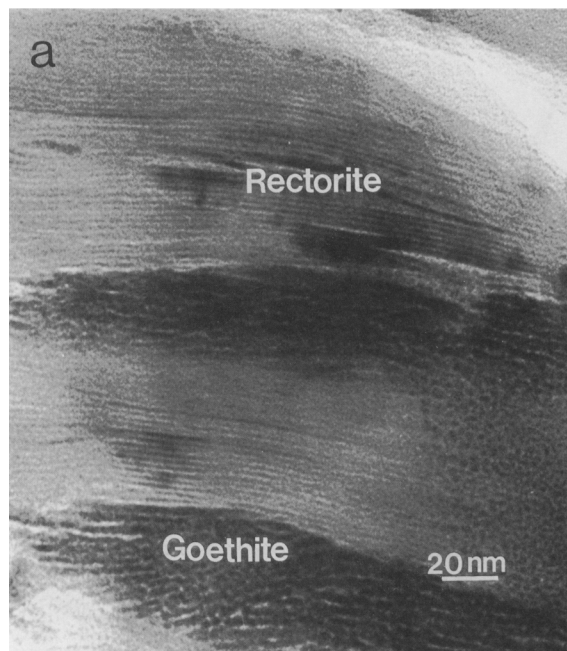


Figure 3. TEM lattice fringe images for rectorite from Garland Co., Arkansas. (a) Intermediate-magnification TEM lattice fringe images displaying the unperturbed original rock texture defined by goethite and rectorite. (b) High resolution lattice fringes of rectorite with 2.3-nm periodicity defined by alternating broad, dark and narrow, lighter subfringes. The inset SAED pattern shows 001 reflections with $d(001) = 2.3$ nm.

hydrated with methanol, and limited layer expansion is subsequently maintained by remaining water molecules in the interlayer even after dehydration with methanol. The expansion of smectite layers depends on the layer charge as well as the nature of the interlayer cation. For the low-charge Na-smectite impregnated with LRW or Spurr resin (Tessier 1984, Stucki and Tessier 1991), $d(001)$ is about 1.26 nm but for the Ca-smectite, $d(001)$ is close to 1.5 nm. We speculate that

the difference in expandibilities of R1 I/S of diagenetic origin (2.1 nm) and rectorite of hydrothermal origin (2.3 nm) may be caused by differences in interlayer charges, perhaps as related to Al/Si distributions (Ahn and Peacor 1986b), implying that such materials may not be identical. Because of the strong cohesive forces between illite-like layers as compared with smectite-like layers, neither methanol nor methacrylic components can cause expansion of the 1.0 nm spacing, which Srodon *et al* (1992) confirmed by comparing XRD and HRTEM results of interstratified clay minerals. Future studies should emphasize variation in spacings as functions of interlayer charge, interlayer cations, and geologic origin.

The main advantage of this embedding technique is that resin can penetrate layers easily after preliminary saturation of clays with water which promotes open space. Because the components of LRW are characterized by polar molecules, they are adsorbed on clay surfaces. The configuration of the molecules depends on the selectivity of the clay surfaces for the various components used during sample preparation, which can differ from one sample to another. Degree of penetration of the chemical components also depends on several factors, especially pore continuity as related to the nature of the clay matrix, cation exchange capacity, salt concentration, and confining pressure. Attention should be paid to the influence of sample size and duration of sample preparation to be sure that chemical components reach all clay surfaces. We are currently working on a wider range of samples, including a closely-spaced sequence from the Gulf Coast, as a further test of the method. It does appear, however, that the Tessier technique is indeed the "magic bullet" for which we have searched for several years.

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