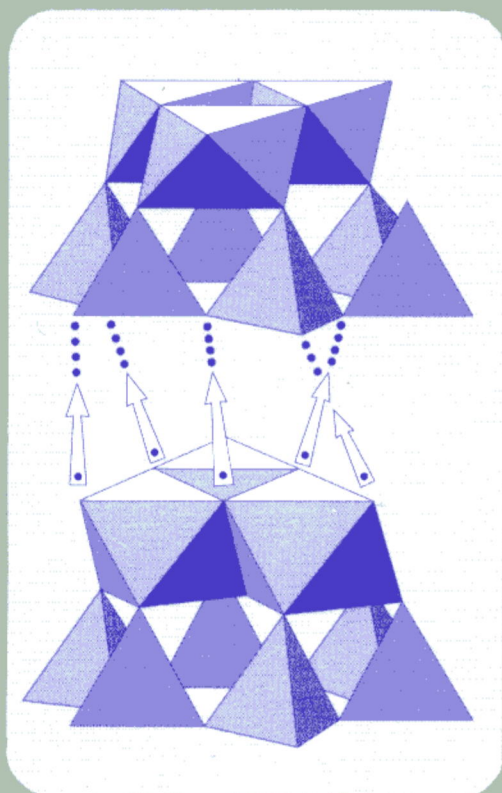


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Volume 11

# Teaching Clay Science

Audrey C. Rule  
Stephen Guggenheim  
*Editors*



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CMS WORKSHOP LECTURES

VOLUME 11

TEACHING CLAY SCIENCE

THE CLAY MINERALS SOCIETY

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DETERMINATION OF ILLITE CRYSTALLITE THICKNESS  
DISTRIBUTIONS USING X-RAY DIFFRACTION, AND THE RELATION  
OF THICKNESS TO CRYSTAL GROWTH MECHANISMS USING  
MUDMASTER, GALOPER, AND ASSOCIATED COMPUTER PROGRAMS

D. D. EBERL

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INTRODUCTION

These exercises involve determination of crystallite thickness distributions (CTDs) for illite by evaluation of X-ray diffraction (XRD) data using the MudMaster computer program. These data are used to infer crystal-growth mechanisms for the samples using the GALOPER computer program. The programs employed in this exercise, together with the instruction manuals, are available at: <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/> (no working). It is recommended that relevant sections of the instruction manuals (MudMan, p. 6-21; and GalopMan, p. 6-15) be read before the exercises below are undertaken.

Size distributions for crystallites can be measured by XRD because the widths of the XRD peaks broaden as crystallite size decreases. A detailed analysis of crystallite size is possible because the intensity function for XRD peaks can be represented as a Fourier series. Fourier analysis (a mathematical method used to determine the collection of cosine waves, differing in frequency and amplitude, that is necessary to approximate a function) of the interference function for illite yields Fourier coefficients for the various crystallite thicknesses that can then be treated according to Bertaut-Warren-Averbach (BWA) theory to yield crystallite-thickness distributions (Drits et al., 1998). These distributions are found by calculating the second derivative of a plot of the Fourier coefficients versus  $n$ , the number of illite layers in the crystallites. The interference function for an illite is found by dividing the intensity of its basal XRD peaks by the Lorentz polarization factor ( $L_p$ ) and by the layer scattering intensity ( $G^2$ ), both of which can be calculated independently (Moore and Reynolds, 1989). Additional corrections to experimental XRD data can be made by deconvolving the effects of instrumental broadening, of  $K_{\alpha 2}$  radiation, and of strain [as represented by small, random fluctuations in  $d(001)$ ]. These calculations are performed easily and automatically by the MudMaster computer program (Eberl et al., 1996). A key to successful BWA analysis of illite is in sample preparation. The illite XRD peak must not be broadened by swelling, but only by crystallite-thickness effects and by the other effects mentioned above.

Illite is a 2:1 dioctahedral clay mineral in which the 2:1 layers are joined by fixed interlayer potassium ions. Illite has a unit-cell-repeat distance perpendicular to the layers of about 1 nm for the 1M polytype. Although the

unit-cell thickness is 1 nm, the smallest thickness possible for a real illite crystal is about 2 nm, because two 2:1 layers are required to fix potassium between them. The other two basal surfaces of the 2:1 layers are exposed to solution, and therefore interlayer cations associated with these surfaces are exchangeable.

When thin illite crystals rest on each other on an X-ray slide, the exposed basal surfaces of the 2:1 layers, which contain H<sub>2</sub>O as well as exchangeable cations, may interact by forming a swelling interface. Two or more such illite crystals, forming a stack of illite crystals (a MacEwan crystallite), may thereby diffract coherently by interparticle diffraction to yield an XRD pattern for mixed-layer illite/smectite (I/S). To measure the thicknesses of such crystals by the BWA method, the effects of swelling must be eliminated. This can be accomplished by one of two methods: (1) The crystal surfaces and swelling interlayers can be dehydrated by heating (for example, to 300° C), resulting in a collapsed illite-like structure that is then analyzed by X-ray diffraction in dry air. In this case, the *00l* reflections yield thickness information about the stacks of illite crystals (about the thickness of MacEwan crystallites). (2) The illite crystals can be made to swell to the extent that they no longer diffract coherently by interparticle diffraction. This is accomplished by attaching a polymer (PVP-10) to the swelling illite basal crystal surfaces. In this case, the BWA method gives the thicknesses of the individual illite crystals (of the fundamental illite particles; see Nadeau et al., 1984).

The shapes of crystallite thicknesses measured by the BWA method can then be related to crystal-growth mechanisms according to the theoretical approach of Eberl et al. (1998a). To do this, the shapes of the CTDs, determined by MudMaster, are simulated using the GALOPER computer program (Eberl et al., 2000), and the simulated and measured CTDs are compared with a statistical test. If the calculated and measured CTDs match, one supposes that the crystal-growth mechanism used in the GALOPER calculation is the same as that which produced the measured illite CTD.

The ability to easily measure crystallite size distributions for minerals using XRD, and the interpretation of these distribution shapes in terms of crystal-growth mechanisms, are recent developments. These techniques have been applied to explore crystal growth mechanisms for illite and smectite (Srodon et al., 2000; Mystkowski et al., 2000), to the measurement of crystallite sizes of magnetic particles on computer disks (Li et al., 2000), to studies of weathering processes that have affected smectite and illite/smectite (Sucha et al., 2001), and to studies of crystallite-size changes undergone by pyrophyllite during grinding (Uhlík et al., 2000), among others. The exercises below, presented as a Learning Cycle with Exploration Phase, Explanation Phase, and Expansion Phase (Karplus and Lawson, 1974), offer a brief introduction to using these techniques. More information on the Learning Cycle can be found in the chapter in this volume titled "Learning Theory and National Standards Applied to Teaching Clay Science" by Audrey Rule.

## EXERCISES

*Exploration*

What can be learned from examining or measuring X-ray diffraction peaks? Discuss this with the people sitting near you and make a list of information about a clay sample that might be obtained from an X-ray diffraction pattern.

The crystallites in a particular clay sample are not always the same size. What inferences about the geologic setting might be made if a particular distribution is found? How do different crystallite-size distributions originate?

*Explanation*

*Exercise A: MUM's the word.* How much information is contained in a single X-ray diffraction peak? Figure 1 is a calculated 001 XRD peak for illite. The peak was calculated using the NEWMOD program (Reynolds, 1985) with a special crystallite-thickness distribution in the calculation. To make the peak more realistic, the pattern was calculated twice using wavelengths for Cu  $K_{\alpha 1}$  and  $K_{\alpha 2}$  radiation, and these peaks then were added together in the ratio of 2:1, as is found in most XRD patterns.

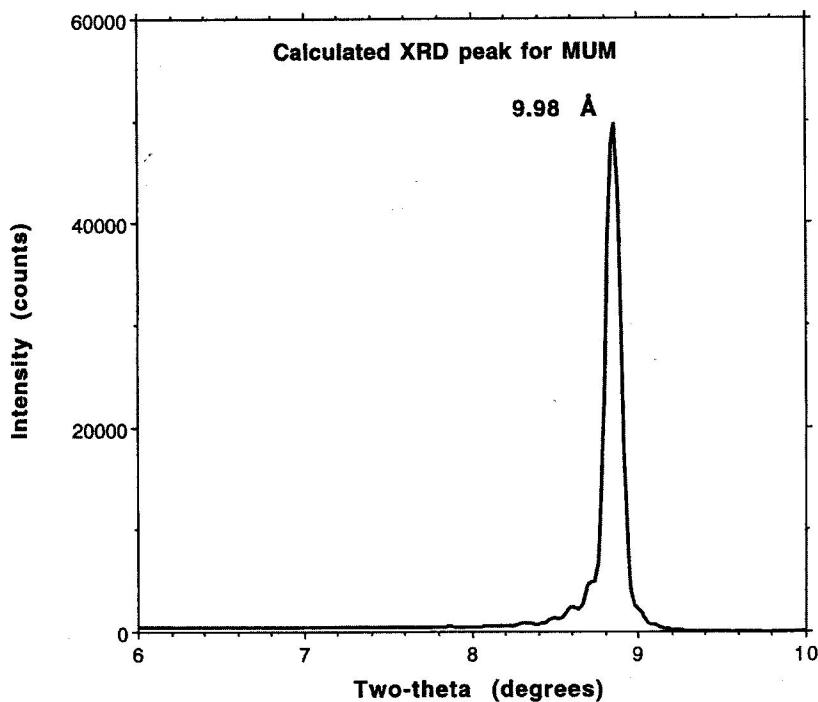


Figure 1. NEWMOD-calculated XRD pattern for illite.

In traditional analysis, two parameters can be determined from this XRD peak. (1) From the peak position ( $8.86^\circ$  two-theta),  $d(001)$  can be calculated using Bragg's Law. The spacing is 9.98 Å, indicating that the clay is probably a pure illite with very little or no mixed-layering (i.e., interstratification of smectite and illite). (2) The peak width at half height can be measured ( $0.11^\circ$  two-theta), and the mean crystallite thickness thereby determined using the Scherrer equation (e.g., Drits et al., 1997), which is a simple equation that relates peak breadth to crystallite size. This calculation gives a mean illite-crystallite thickness of 72 nm, which is incorrect. The mean thickness used in the NEWMOD calculation was 47.1 nm. The Scherrer equation gives the incorrect answer because a constant used in the Scherrer equation, usually taken to be 0.89, actually is not constant, but varies with the shape of the crystallite-thickness distribution (Drits et al., 1997). In deriving the Scherrer constant, it is assumed that the frequencies of all of the crystallite thicknesses are the same, which may never be the case with natural samples.

Much additional information can be extracted from the peak if it is analyzed by the BWA method (Drits et al., 1998), using the MudMaster (MM) computer program (Eberl et al., 1996). The BWA method makes no assumption concerning the shape of the CTD. In fact, the CTD shape is determined using this method.

To do this analysis, paste the XRD data for MUM, to be found in the file WkshpXRD.xls, into column E of the PeakPicker (the first) sheet of the MM program, and analyze the pattern according to methods described in the instruction manual (Eberl et al., 1996) or in the program itself. The resulting distribution (Fig. 2) spells the word "MUM", and almost exactly recovers the crystallite-size distribution used in the original NEWMOD calculation. The MM-determined mean thickness (48.5 nm) nearly matches that used in the NEWMOD model (47.1 nm). In other words, a wealth of precise and accurate information can be extracted from an XRD peak if it is analyzed by the BWA method.

Try to analyze higher-order peaks for this XRD pattern. To do this accurately,  $K_{\alpha 2}$  radiation must be removed from the pattern by setting cell B10 in Sheet 1 to a value of 1. Generally,  $K_{\alpha 2}$  does not need to be removed when analyzing natural clays, because clay peaks are very broad. Experiment with this pattern by not removing  $K_{\alpha 2}$ , or by not removing  $LpG^2$ , or by starting the analysis closer to the peak maximum than the recommended two-theta value.

This exercise has indicated that the BWA method can accurately recover CTD shapes from calculated XRD peaks. Words are not spelled out in the CTDs of natural illites. However, if one knows how to read them, the shapes of natural CTDs do offer insight into the crystal growth history of the clays, as will be shown in the following exercises.

Extra credit: Analyze the NEWMOD-calculated XRD patterns HUMPS (003 reflection) and Mt. Washington (which contains both  $K_{\alpha 1}$  and  $K_{\alpha 2}$  radiation), which also are located in the file WkshpXRD.xls. Why do these XRD patterns have these names?

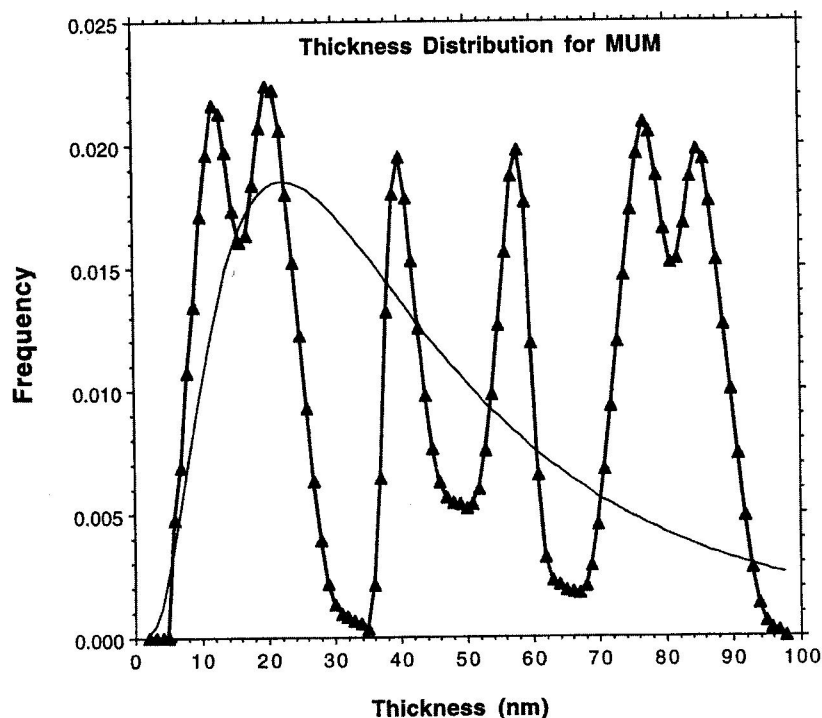


Figure 2. Crystallite-thickness distribution (CTD) determined for XRD peak in Figure 1 using the BWA method (MudMaster computer program). The smooth curve is the theoretical lognormal distribution calculated from the measured distribution (triangles).

*Exercise B: Determination of CTDs for natural illites.* Analyze three XRD patterns of natural illite; the data are to be found in WkshpXRD.xls. Le Puy is an illite from an ancient lakebed in France; RM30 is a hydrothermal illite from the Silverton caldera, Colorado; and MF1170 is a metasediment from the Glarus Alps, Switzerland. Na-saturated samples  $<2 \mu\text{m}$  in crystallite size were intercalated with the polymer polyvinylpyrrolidone (molecular weight = 10,000; PVP-10) to eliminate the effects of swelling (Eberl et al., 1998b), and analyzed by XRD on Si-wafers to eliminate scattering from the substrate. Therefore, XRD peak broadening is almost entirely related to crystallite-thickness effects.

The results of the calculations yield an asymptotically-shaped crystallite-thickness distribution for Le Puy, with a mean thickness of 4.8 nm (Fig. 3), and a lognormal distribution for RM30, with a mean thickness of 11.8 nm (Fig. 4). These shapes are the two most common shapes found for illite-thickness distributions.

Analysis of MF1170 is a little more complicated. After the XRD data for this sample are plotted in the PeakPicker sheet of MM, note that this sample contains a chlorite peak, which will interfere with the illite determination. Open the PkChopr.xls program; remove the offending chlorite peak as is obvious in



the program; and paste the resulting XRD pattern into MM prior to MM analysis. The CTD for this sample (Fig. 5) is neither asymptotic nor lognormal, but appears to be bimodal, yielding a mean thickness of 30.3 nm.

Extra credit: Analyze the two XRD patterns for the Zempleni illite, one of which is from a K-saturated and heated sample (K-Zemp-H), and the other of which is intercalated with PVP-10 (Zemp-PVP). Which sample should have the thicker crystals?

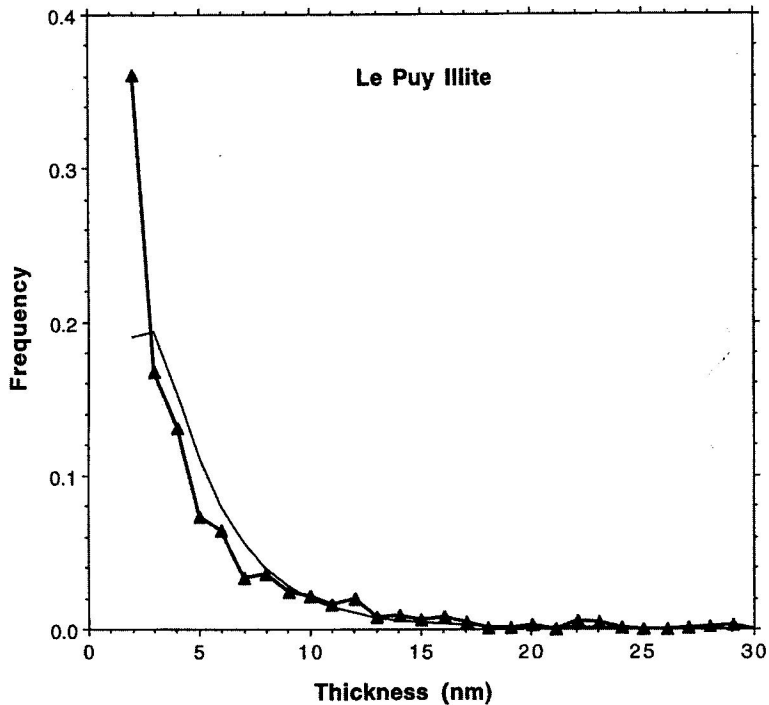


Figure 3. The asymptotic CTD shape for Le Puy illite is thought to be related to the crystal-growth mechanism of constant-rate nucleation with simultaneous, size-dependent growth. Detrital illites also may have this shape. The smooth curve is a lognormal fit to the measured distribution (triangles).

### Expansion

*Exercise C: Simulation of illite growth with GALOPER.* The GALOPER computer program simulates crystal-size distributions that are expected for a variety of crystal-growth mechanisms. The growth mechanisms of interest here are simultaneous nucleation and growth, and growth without simultaneous nucleation. During the first mechanism, new illite nuclei continue to form at a constant rate while previously nucleated crystals continue to grow. During the second mechanism, growth occurs on previously nucleated crystals, but no new nuclei are produced.

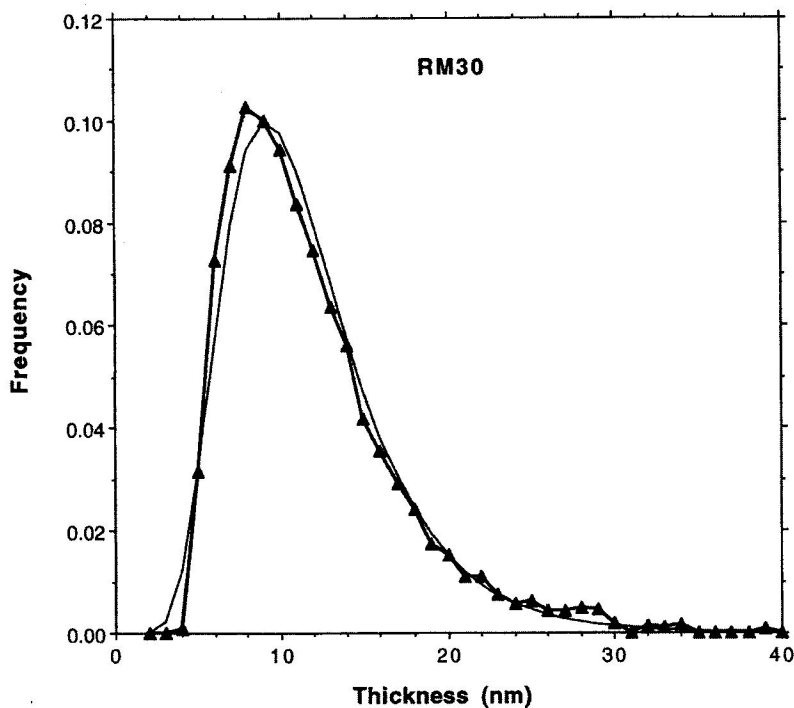


Figure 4. The lognormal CTD shape for RM30 is thought to be related to the crystal-growth mechanism of size-dependent growth, without simultaneous nucleation. The triangles are the measured CTD, and the smooth curve is the lognormal fit.

Using the GALOPER computer program, simulate the shape of the asymptotic distribution (Le Puy) using option 1, "simultaneous nucleation and growth," by consulting the instruction manual (GalopMan, p.10-12; Eberl et al., 2000) that accompanies the program. This CTD can be simulated approximately by nucleating 250 crystals per calculation cycle, with  $k = 1.06$ . Next simulate the shape of the lognormal CTD (RM30) using option 5. This shape can be simulated by using a  $k = 1.03$ , and setting the calculation to stop at a mean size of 10 nm.

From this exercise, one can conclude that the Le Puy illite grew by a different crystal-growth mechanism (simultaneous, constant-rate nucleation and surface-controlled growth) than did RM30 (surface-controlled growth without simultaneous nucleation). More generally, it has been found (D.D. Eberl, unpublished data) that the lognormal CTDs are found in metabentonites and in fissures in hydrothermal deposits, whereas the asymptotic shape is found in shales and in hydrothermally-altered wall rock. An asymptotic shape for illite CTDs also may be related to an origin by sedimentation as was found, for example, for illites deposited in sand bars in the Yukon River system (D.D. Eberl, unpublished data).

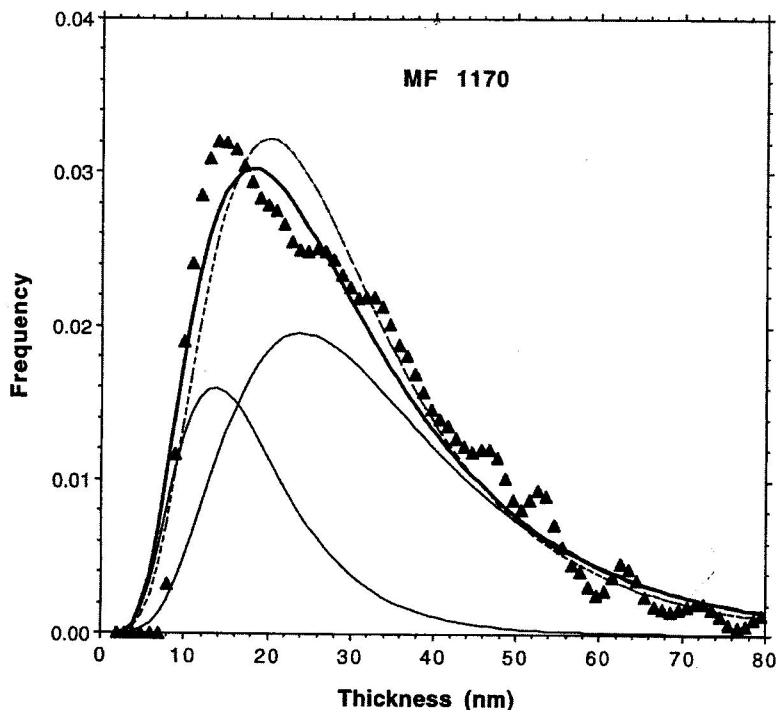


Figure 5. The CTD shape for MF1170 (triangles) is neither asymptotic nor lognormal (dashed line), but may be bimodal, being composed of the sum (thick curve) of two lognormal CTDs (thin curves).

Extra credit: Why do the crystal-growth mechanisms, and therefore CTD shapes, differ for illite in the different environments mentioned above (e.g., fissures versus wall rock)? Another question: What will happen if the Le Puy illite is overgrown subsequent to the time of its formation, without simultaneous nucleation? Try this calculation with surface-controlled overgrowth (option 5) and then with supply-controlled overgrowth (option 6), after first repeating the calculation to generate the asymptotic shape for the Le Puy illite. Be sure to set cell A28 to zero so that the new growth will overgrow the previously formed asymptotic CTD.

*Exercise D: Statistical comparison of calculated and measured CTD's.* The "goodness-of-fit" of the simulated to the measured CTDs can be determined by using either the ChiSq.xls or KSTest.xls computer programs. (The KSTest.xls is better to use if there are less than 10 size categories, and this type of analysis tends to be more lenient than chi-square analysis.) For example, paste the MM-determined frequency distribution for RM30 into column D in either ChiSq.xls or KSTest.xls. Next, simulate this CTD using GALOPER. Then, paste the numbers of crystals from column W in GALOPER into column C in one of the two statistical programs. All entries should start at 2 nm. The simulated CTD

matches the measured CTD very well, at chi-square significance levels >10 to >20%.

Extra credit: Try to match the Le Puy GALOPER calculation to the MM measurement of this sample using the KStest.xls program.

*Exercise E: Decomposition of illite CTD.* MF1170 does not have a simple thickness distribution, because it fits neither the asymptotic type (attributed to simultaneous, constant-rate nucleation and surface-controlled growth) nor the lognormal type (attributed to surface-controlled growth without simultaneous nucleation) (Eberl et al., 1998a). The thickness distribution appears to be bimodal. To check this possibility, open the UnMixer.xls program and paste the MM-determined thickness distribution for MF1170 into column H. Run the Solver option under the Tools menu, as directed.

The graph (Fig. 5) shows that the crystallite-thickness distribution for sample MF1170 can be decomposed into two lognormal curves, the means of which are 19.6 and 36.9 nm, having the area-weighted ratio of 0.28:0.72. These distributions may represent, for example, two separate metamorphic events that formed illite in the rock. The ratio of the two distributions may be used with other data to calculate, for example, the ages of metamorphic events from the mixed ages of metasediments.

Extra credit: Exactly how could the decomposed curves in Figure 5 be used in the determination of an age for a metamorphic event?

#### CAUTION AND CONCLUSION

Note that MM determines crystallite size (X-ray scattering-domain size) distributions, which may or may not be the same as crystal-size distributions. Based on a comparison of TEM, chemical, and MM data for illite (Drits et al, 1998; Eberl et al., 1998b; D.D. Eberl unpublished data), these two measurements for illite are the same. Other unpublished data indicate that they may not be the same for other minerals. Some kaolinites, for example, have thinner crystallites as determined by XRD than by TEM or AFM. In other words, some kaolinite crystals may be broken into two or more discretely diffracting domains, which X-ray experiments show as individual crystallites. Therefore, one should confirm MM measurements with another method.

Despite this problem, MudMaster and GALOPER analyses enable new areas of research, and may be used to help deduce the properties and origins of clay minerals.

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