

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band: 83 (2003)
Heft: 3

Artikel: Comment on "Evaluation of X-ray diffraction methods for determining the crystal growth mechanisms of clay minerals in mudstones, shales and slates," by L. N. Warr and D. R. Peacor
Autor: Eberl, Dennis D. / rodo, Jan / Drits, Victor A.
DOI: <https://doi.org/10.5169/seals-63156>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 27.01.2026

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

Comment on “Evaluation of X-ray diffraction methods for determining the crystal growth mechanisms of clay minerals in mudstones, shales and slates,” by L. N. Warr and D. R. Peacor

Dennis D. Eberl¹, Jan Šrodoň² and Victor A. Drits³

Abstract

A recent paper by Warr and Peacor (2002) suggested that our use of the Bertaut-Warren-Averbach technique (MudMaster computer program) for studying changes in crystallite thickness distributions (CTDs) of clay minerals during diagenesis and very low-grade metamorphism is not reliable because it is dependent on many variables which can not be fully controlled. Furthermore, the authors implied that the measured shapes of CTDs cannot be used with confidence to deduce crystal growth mechanisms and histories for clays, based on our CTD simulation approach (using the Galoper computer program). We disagree with both points, and show that the techniques are powerful, reliable and useful for studying clay mineral alteration in rocks.

Keywords: Bertaut-Warren-Averbach, MudMaster, crystal growth, illite, clay minerals.

1. Introduction

The MudMaster computer program (Eberl et al., 1996) uses a version of the Bertaut-Warren-Averbach (BWA) method, adapted to study clay minerals having a periodic structure at least along the *c* axis (Drits et al., 1998), to analyze X-ray diffraction (XRD) peak shapes for 00*l* clay mineral reflections to calculate crystallite thickness distributions (CTDs). The shapes of these CTDs then are used to infer crystal growth mechanisms undergone by the clays during alteration by applying a simulation technique (Galoper computer program) proposed by Eberl et al. (1998a). Both techniques have been used and tested in recent studies. For example, Uhlik et al. (2000) studied the evolution of pyrophyllite particle size changes during dry grinding; Šucha et al. (1999) examined kaolinite crystallite thicknesses; Šucha et al. (2001) studied the weathering of smectite and illite/smectite; Šrodoň et al. (2000) determined smectite illitization mechanisms; Brime and Eberl (2002) determined growth mechanisms for low-grade illites in Spain; Bove et al. (2002) followed reaction paths for hydrothermal illites in the San Juan Mountains, Colorado; Dudek et al. (2002) compared the MudMaster technique with high-resolution transmis-

sion electron microscope (HRTEM) measurements of the same samples; Kotarba and Šrodoň (2000) tracked diagenetic changes in illite-smectites from the Carpathian foredeep; Mystkowski et al. (2000) measured crystallite thickness distributions for smectites; Šrodoň et al. (2002) interpreted K–Ar dates for illite-smectites in bentonites; Dudek and Šrodoň (2003) interpreted the mechanism of smectite illitization in shales; and Shang et al. (2003) compared BWA measured illite thicknesses to those found by small angle X-ray scattering (SAXS).

Warr and Peacor (2002; hereafter WP) implied that three important requirements for use of the techniques have not been addressed adequately: (1) X-ray scattering domain size distributions must be calculated accurately; (2) X-ray domain boundaries must correspond directly to crystal growth surfaces; and (3) changes in the shapes of CTDs need to be correlated to known mechanisms of crystal growth. This discussion is welcome, because every technique has its limitations and should be used within these limitations. In the present paper we will discuss cases in which all three criteria have been addressed to such an extent that the techniques may be applied with some confidence to future studies.

¹ U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303, USA. <ddeberl@usgs.gov>

² Institute of Geological Sciences PAN, Senacka 1, 31002 Krakow, Poland.

³ Institute of Geology RAN, Pyzhevsky 7, 109017 Moscow, Russia.

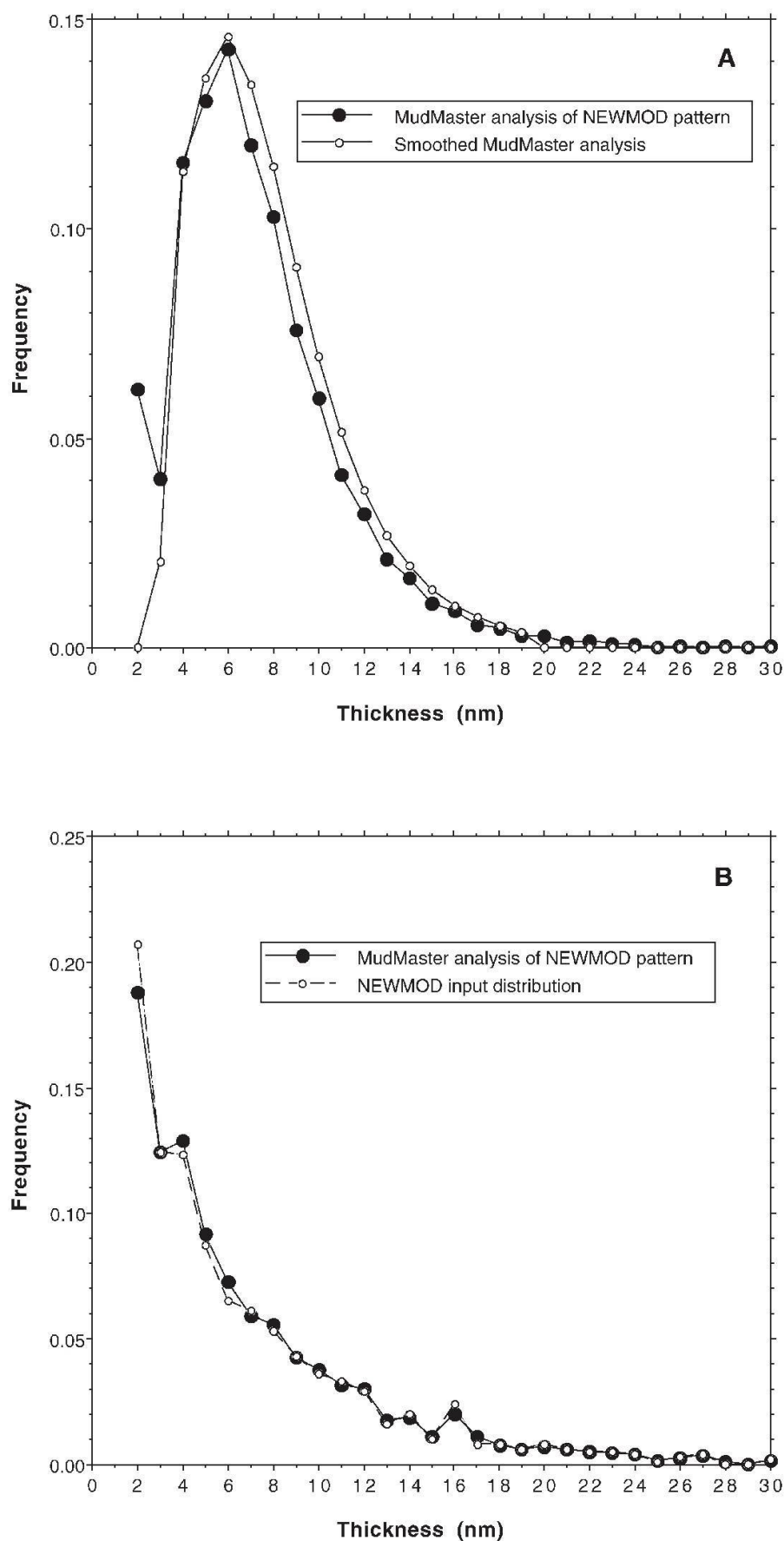


Fig. 1 (A) MudMaster analyses of a NEWMOD-calculated XRD pattern having a lognormal CTD with a mean thickness of 7 nm. An artifact appears at 2 nm for the non-smoothed CTD. (B) MudMaster analyzed CTD compared with CTD used as NEWMOD input. An artifact for the asymptotic CTD is not apparent at 2 nm.

2. Extracting accurate domain size information from X-ray diffraction profiles

Information concerning the crystallite size distribution, which is found using the BWA technique, is contained in the interference function Φ , which is extracted from the measured diffraction intensity (I) by subtracting the background (bg), and by dividing by the Lorenz-polarization function (Lp) and by the structure factor (G^2):

$$I = LpG^2\Phi + bg.$$

Thus,

$$\Phi = (I - bg)/LpG^2.$$

Only I is measured for a given sample. The remaining factors have to be approximated in order to extract Φ , and the quality of the analysis depends on these approximations. MudMaster analysis of Φ is very precise, as has been demonstrated previously (Drits et al., 1998; Eberl, 2002) using NEWMOD-generated XRD patterns (Reynolds, 1985), where all of the parameters that went into the intensity calculation are known. However, sometimes an artifact does appear when analyzing calculated patterns that have used lognormal-type CTDs in the calculation. Occasionally, a spike appears in the first (2 nm for illite) thickness category. This spike can be removed by using a smoothing power of 1 in the MudMaster program (Fig. 1A; see also Figs. 1d–e in Brime and Eberl, 2002). The artifact is related to the method used to make the hook correction in the BWA technique (Drits et al., 1998). The hook correction to the Fourier coefficients is necessary because background cannot be removed perfectly from I . The artifact is not apparent for asymptotically-shaped CTDs (Fig. 1B), which is the other common CTD shape for illite, and, therefore, these CTDs do not require smoothing.

There are three additional major factors, which complicate the BWA measurement:

(1) instrumental broadening, which theoretically should be deconvolved from the measured intensities to obtain I ; (2) $K\alpha_1 - \alpha_2$ splitting, which deforms the peak profile (theoretically $K\alpha_2$ should be removed); and (3) so called “strain broadening,” which results from fluctuations in layer spacing, and which also should be taken into account by the analysis of at least two $00l$ reflections. MudMaster contains routines for making these corrections, but, in practice, minimizing their effects is the best strategy. Factors 2 and 3 are strongly dependent on the diffraction angle, and their effects are negligible if low-angle reflections are used (e.g., 001 of illite). Instrumental broadening depends on the slit arrangement and

the overall quality of the diffractometer. According to our experience, using narrow slits and a modern diffractometer allows one to ignore instrumental broadening to a mean thickness of at about 25 to 30 nm for illite, as will be discussed below. Extension of the technique beyond this limit will require better diffractometers or a method for removing the instrumental effect precisely enough so as not to disturb the interference function. Attempts are under way to use synchrotron diffraction patterns (which are mostly free from instrumental broadening) to extract precisely the shape of the instrumental broadening intensity function.

When following the outlined strategy, we still have to approximate the background, the shape of the Lp factor (using a particle orientation coefficient) and G^2 (in practice, the proportion of Fe, K and illite edges may influence G^2). These approximations are never perfect, and their overall quality can be judged by the size of an artifact which distorts the shape of the recovered Φ (see Fig. 4 in Kotarba and Środoń, 2000). There is room for improvement, and the technique has to be adapted and evaluated for each mineral. Our experience indicates that for illite the analysis is robust, reproducible and very consistent with independent measurements of mean crystal thickness by a modified Scherrer technique (Drits et al., 1998), by transmission electron microscopy (TEM; Eberl et al., 1998b), by calculation from fixed cation content (Drits et al., 1998; Eberl et al., 1998b), by atomic force microscopy (AFM; Blum and Eberl, 1992), by reaction path modeling (Bove et al., 2002), and by SAXS (Shang et al., 2003). Furthermore, Dudek et al. (2002) demonstrated that for pure illite-smectite, MudMaster analysis is consistent with HRTEM measurements. For shale samples (having a complex mineralogy), MudMaster analysis is much closer to reality than is HRTEM, as was demonstrated by back-calculation of illite diffraction patterns using the crystal thickness distributions resulting from the two techniques (Dudek et al., 2002). This back-calculation also demonstrated that a peak flip operation, used in MudMaster to remove an artifact from Φ , does not introduce distortion to the interference function.

Undoubtedly, the accuracy of MudMaster in evaluating the variance (β^2) of a CTD is less than that for evaluating the mean size, because β^2 is very sensitive to crystallites found in the tails of the distribution. Caution in applying β^2 for petrological interpretation should be exercised. Only the reproducibility of the β^2 measurement can be evaluated, because more reliable techniques to measure β^2 are lacking, but reproducibility is ex-

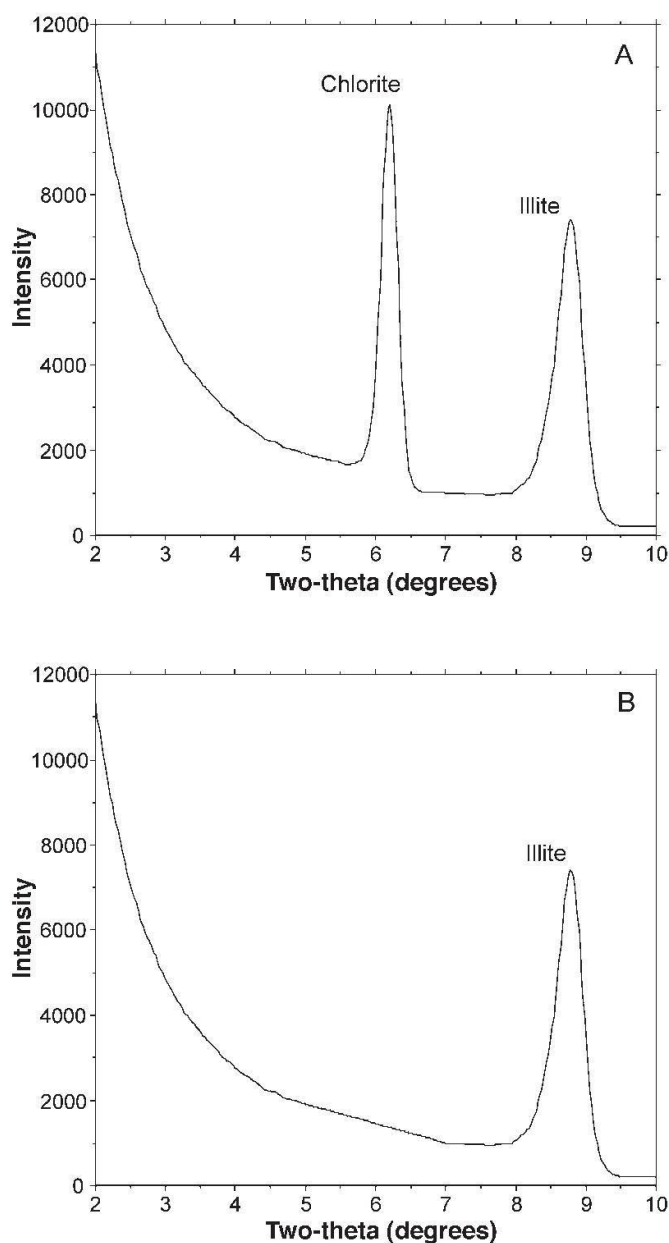


Fig. 2 (A) NEWMOD (Reynolds, 1985) calculated diffraction profiles for chlorite and illite mixed in the ratio 1:1. (B) Same pattern as in A, but the chlorite peak has been removed using PeakChopper.

cellent. Again, our expertise with illite indicates that new and valuable information can be extracted using β^2 measured by MudMaster (Bove et al., 2002).

The next question is whether the program can perform as well with a mixture of clay minerals. Chlorite and illite NEWMOD-calculated patterns were mixed together in various proportions to check the effectiveness of the PeakChopper program in removing unwanted peaks from the tails of peaks to be analyzed. A Mg-chlorite pattern was used to maximize the interference of the chlorite (001) on the illite (001) peaks. The chlorite peaks in the original, calculated, mixed XRD patterns (e.g., Fig. 2A) were removed using the

PeakChopper program (e.g., Fig. 2B), which removes the peak simply by drawing a line along the background through the base of the peak. The MudMaster calculated CTDs demonstrate that the effect of a neighboring chlorite peak on illite (Fig. 3A), or that of an adjacent illite peak on chlorite (Fig. 3B), is insignificant as long as the accessory phase is present in a proportion that is less than approximately 0.5. In the example given by WP in their Figure 2a, the small adjacent chlorite peak, if removed by PeakChopper, would have little or no effect on the illite measurement. Analogous results were found for illite-kaolinite interferences. If the ratio of interfering phase to the one to be measured is greater than 0.5, then separation techniques may be applied to decrease this ratio (e.g., acid treatment, magnetics, particle size separation).

WP give results for mean thickness measurements on illite when an adjacent chlorite peak is removed from the XRD pattern with the PeakChopper program (their Fig. 2c), starting at various two-theta angles. They list the logarithmic means (α) and variances (β^2) for this exercise. Mean thicknesses can be calculated from these parameters for lognormal-like CTDs using the formula: mean thickness = $\exp(\alpha + \beta^2/2)$. This calculation using WP's data shows that varying the starting angle from 4.4° to 5.8° varies the measured mean thickness by only 3 Å, from 7.8 nm to 8.1 nm, a range of values that is well within the experimental error. Similarly, β^2 varies by only 0.04. The use of a two-theta range that is narrower than that recommended for peak analysis (i.e., it is recommended to start half-way between adjacent reflection orders) may yield an accurate mean size, but should be avoided if determination of the shape of the CTD is important.

WP indicate that compositional differences or shifts in atomic positions in clays make calculation of the structure factor (G^2) inexact, thereby severely limiting the accuracy of the MudMaster calculations, because G^2 must be removed from the XRD peak by division before the crystallite thickness determination can be made. Figure 4 plots CTDs for sample RM30, an illite that contains no Fe (Eberl et al., 1987), determined with G^2 's calculated using various Fe contents, and with a shift in the position of the octahedral cations by +0.2 Å. The CTDs are nearly identical, and therefore it is unlikely that WP's objection is valid for illite. WP present the effect of changing illite's interlayer K content on the calculation in their Table 2. Changing the fixed K content between the reasonable values of 0.75 to 1.0 equivalents per half unit cell in the G^2 calculation changes the calculated mean thickness by only 8 Å,

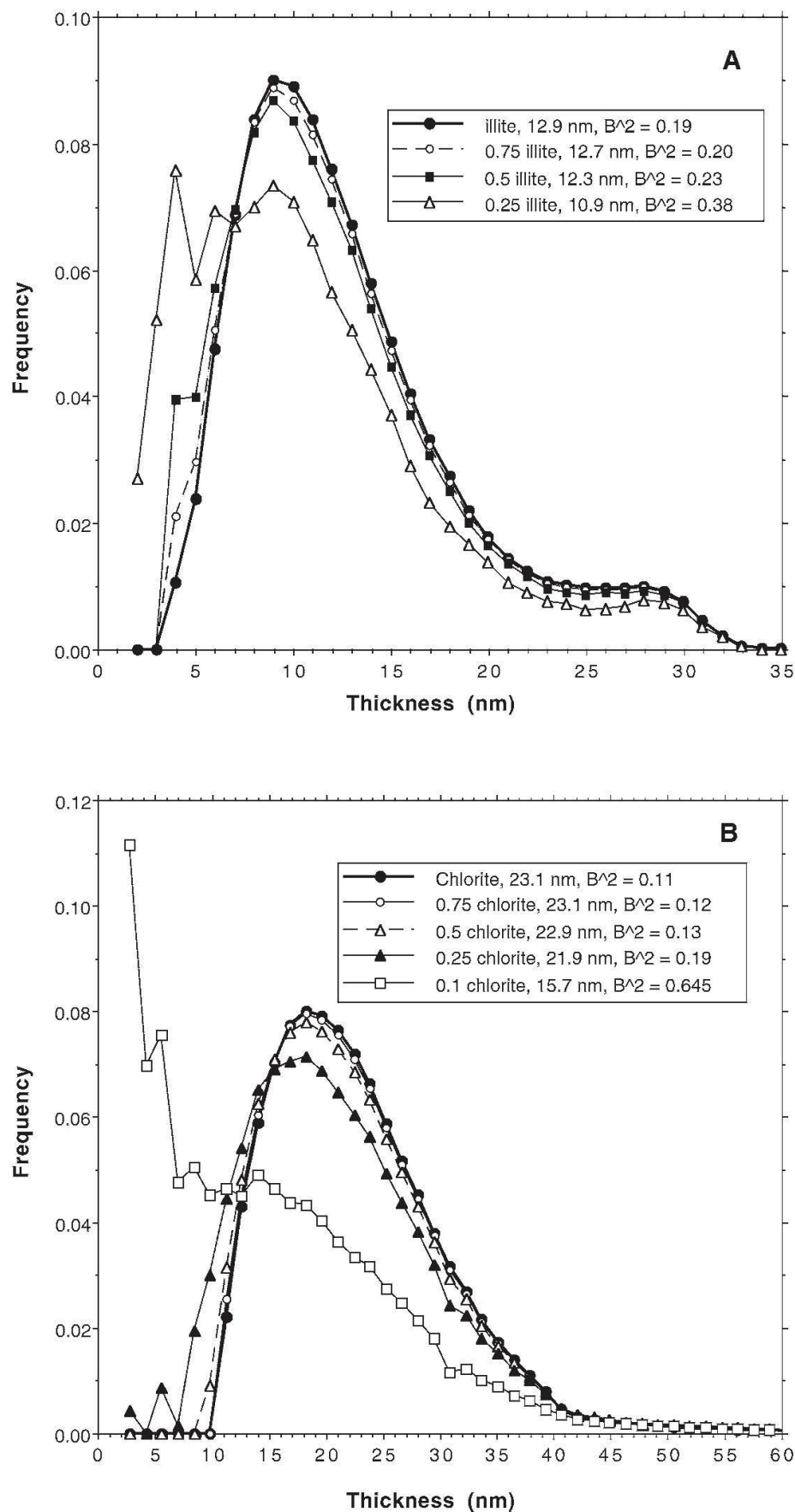


Fig. 3 (A) MudMaster analyses of illite diffraction patterns similar to that shown in Fig. 2B, in which chlorite peak has been removed using PeakChopper. (B) MudMaster analysis of chlorite diffraction patterns after illite peak has been removed.

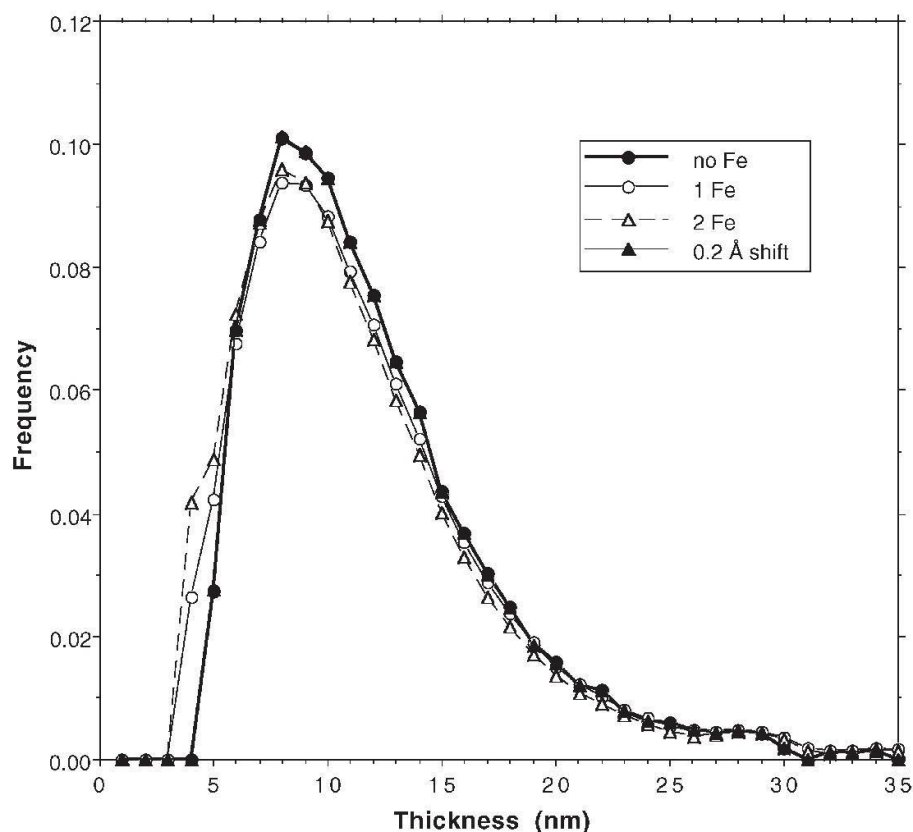


Fig. 4 Effect of various Fe contents and atomic positions used in calculation of the structure factor for crystallite size analysis of illite RM30 by MudMaster.

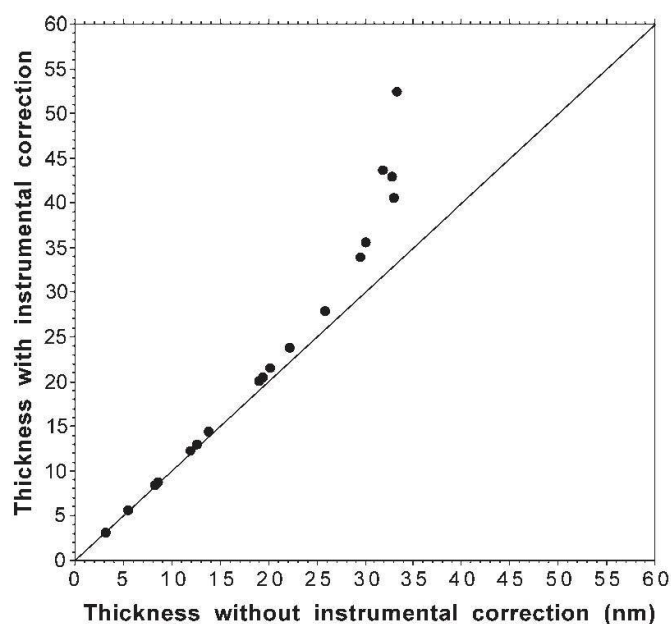


Fig. 5 Effect of instrumental broadening correction as a function of crystallite size for illites from the Glarus Alps (samples from Hunziker et al., 1986).

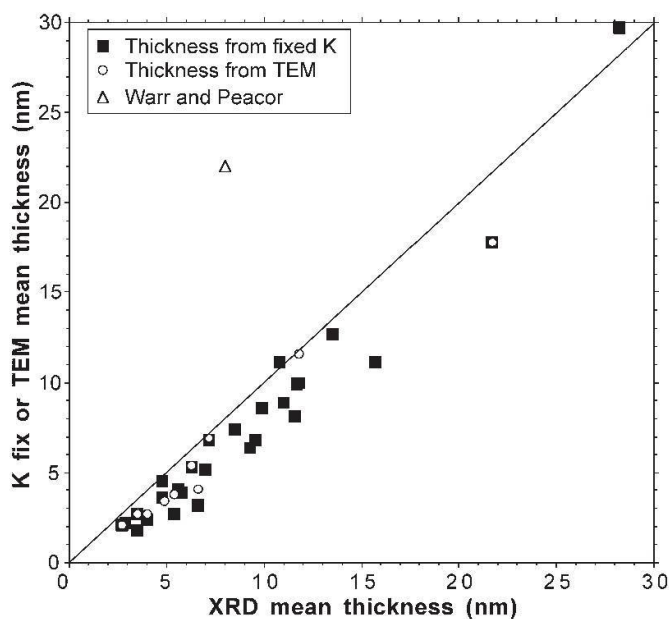


Fig. 6 Comparison of TEM and fixed K measurements of illite crystal thickness with MudMaster determinations of illite crystallite thickness (Eberl et al., 1998b). Also plotted is the sample measured by Warr and Peacor (2002).

from 10.2 to 11.0 nm for their Paleozoic illite from Spain, when the recommended (001) reflection is used for the analysis. The variance remains constant at 0.23.

WP indicate in their Figure 3 that a large range of thickness parameters can be obtained for chlorite, depending on the Fe-content chosen for the structure factor. However, they also state that Fe

content can be obtained from the XRD pattern. When the calculation of G^2 is done correctly, with the correct content and distribution of Fe over the chlorite octahedral sheets, the correct answer should be obtained. There is no reason to suppose that the correct answer should be obtained by the intersection of trends found using the wrong G^2 . WP used three types of sample preparation for

these measurements. We favor the thin film method, because the X-ray beam is not subject to defocusing by sample transparency effects. The data of WP demonstrate that in case of chlorite, introducing correct Fe content is essential for the analysis. Total Fe can be evaluated from $d_{(001)}$ and $d_{(060)}$ (Wiewióra et al., 1996, 1998), and Fe distribution between the octahedral sheets can be ascertained by measuring the relative intensities of the (00 l) series (Moore and Reynolds, 1997).

WP had trouble finding a good instrumental standard. We currently are using the >20 μm size fraction of NBS 675, a synthetic fluorophlogopite (Eberl et al., 1996). It is not ideal, because, although it may yield an accurate mean thickness, it may distort the shape of the distribution. We currently are developing a better standard, which is crucial for analyzing clays from higher metamorphic grades. However, MudMaster calculations that are run with and without the NBS standard demonstrate that an instrumental standard may be unnecessary (at least for our experimental set-up using 1° slits and a monochromator) for illites having mean thicknesses less than approximately 25 to 30 nm (Fig. 5).

3. Relationships between data obtained by XRD, TEM and other techniques

In WP's Figure 2c, the parameters determined for a single sample by TEM are very different from XRD-determined values. The mean thickness for sample SW1 is 19.1 nm by TEM (using the value given in Warr and Nieto, 1998) versus about 8 nm by XRD, but the XRD mean is similar to that measured for defect-free distances by TEM (9.0 nm). MudMaster could well be giving mean defect-free distance rather than crystal thickness (i.e., crystallite thickness rather than crystal thickness) for this sample. This possibility points to a limitation of the BWA technique, a limitation that is found in all XRD techniques, which is why the method needs to be checked by other techniques (e.g., surface area, fixed K content, TEM, HR-TEM, AFM, reaction path modeling, SAXS). However, crystallite thickness and crystal thickness are almost identical for illite crystals that we have measured (Fig. 6). In this figure, measurements made by the BWA method are on average one nm larger than those made by the other techniques, a difference that is opposite in sign to that expected if crystallite size does not equal crystal size. The conclusion that crystallite size commonly equals crystal size for illite is reinforced by the recent study by Dudek et al. (2002), which carefully compared the thickness-

es of illite crystals from shales and bentonites using TEM, HRTEM and XRD.

As was discussed by WP, TEM normally gives number-weighted frequencies, whereas XRD gives area-weighted frequencies. The TEM measured frequencies in Fig. 6 were corrected for area by measuring crystal basal areas as well as crystal thicknesses. Area-weighted measurements are more useful than number-weighted ones because they are directly related to chemistry and they can readily be converted into volume-weighted frequencies (Eberl et al., 1998b). Particles of unequal size, but of equal thickness, are equally weighted in the frequency distribution calculated by the number-weighting method in which, for example, a crystal having a volume of 1 mm^3 would be counted the same as one having a volume of 1 μm^3 .

WP suggest that sample preparation may change measured CTDs in unpredictable ways, and show results that demonstrate this effect for dry milling of muscovite for times ranging from 10 minutes to 10 hours, and for ultrasonic treatments ranging up to 50 hours. We do not treat our samples so harshly. It is common knowledge that prolonged dry grinding should be avoided in mineralogical studies (unless it is the subject studied), because it leads to delamination and to the formation of amorphous material (e.g., O'Connor and Chang, 1986). In general, wet grinding is the method of choice. We grind our samples gently by hand, and treat them at most for 1 minute with an ultrasonic probe. Results of ultrasonic probe treatment for shorter times than those explored by WP (Fig. 7) indicate that only the chlorite sample may have been altered significantly by such treatment (Fig. 7C).

4. Correlation of CTDs to crystal growth mechanisms

If crystallite size distributions have been measured accurately (and evidence points to their accurate measurement by the MudMaster technique), and if these crystallite sizes correspond to crystal sizes and not simply to X-ray scattering domain sizes (which our data indicates is true for many illites, but which always needs to be checked), then CTD shapes can be used to determine aspects of crystal growth history (Eberl et al., 2000). Contrary to the arguments of WP, our approach to crystal growth (Eberl et al., 1998a, 2002) is unrelated to pressure, temperature and time conditions. Rather, the approach describes mathematically how CTDs may develop and change shape based on the dominant crystal

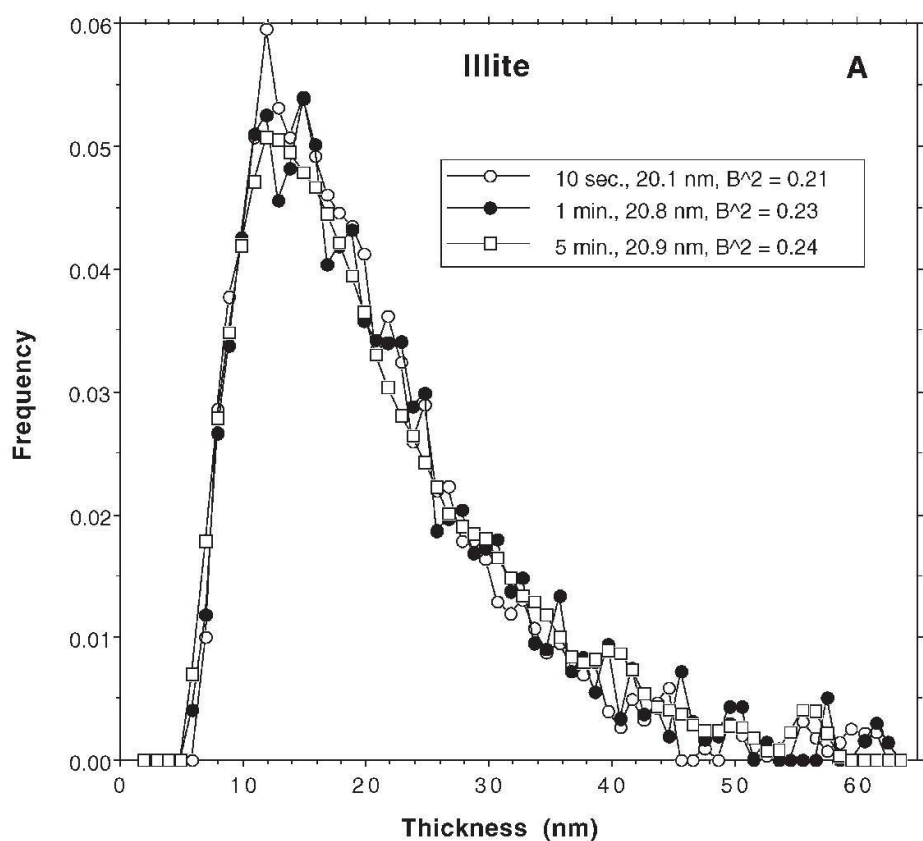
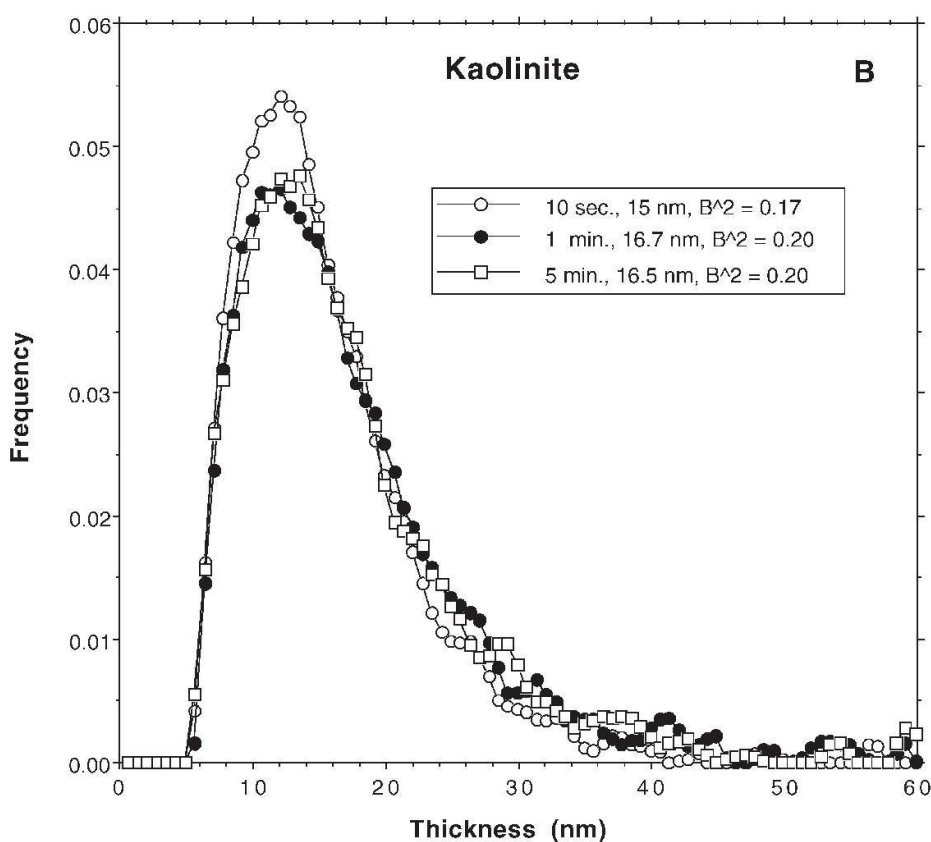


Fig. 7 Effect of ultrasonic probe treatment for various lengths of time on MudMaster-determined CTDs for (A) illite; (B) kaolinite; and (C) chlorite.



growth mechanisms, which operated under unspecified conditions.

The approach for simulating crystal size distributions (CSDs) has been tested experimentally with calcite growth experiments (Kile et al., 2000; Kile and Eberl, 2003), rather than with clays, be-

cause calcite is easier to crystallize. These experiments showed that the postulated three basic shapes for CSDs, asymptotic, lognormal and Ostwald, are related to three fundamental crystal growth mechanisms for calcite: simultaneous nucleation and size-dependent growth, size-depend-

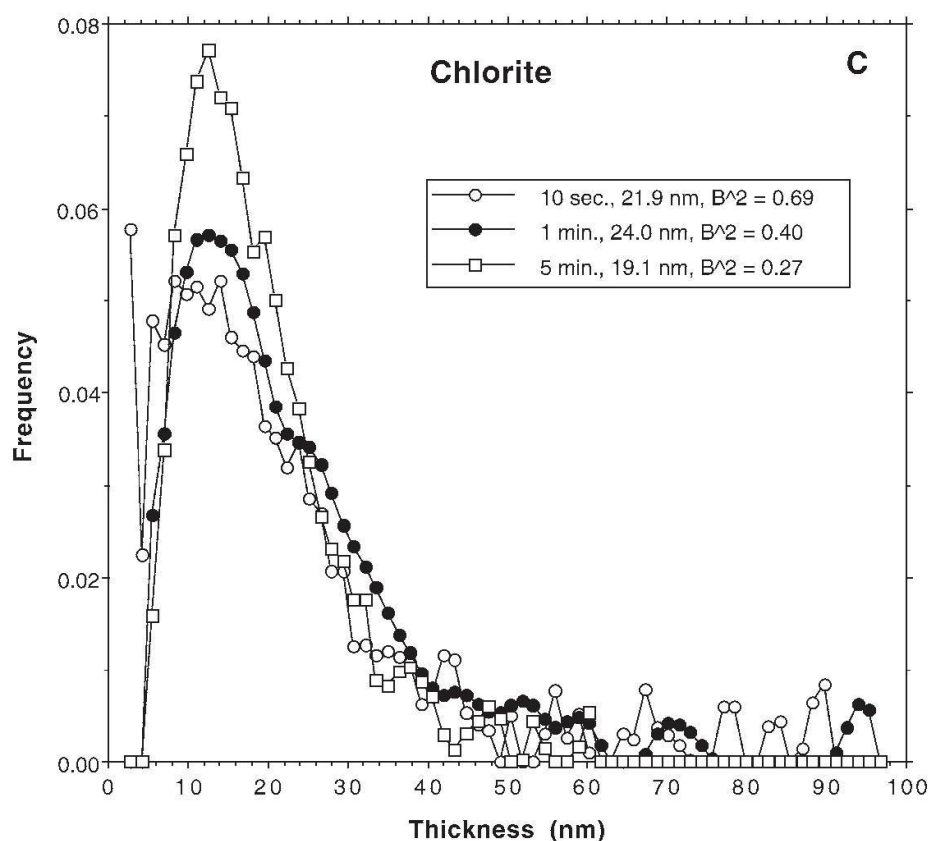


Fig. 7C

ent growth without simultaneous nucleation, and Ostwald ripening, respectively. The Ostwald shape has not been observed for clays, but the two other shapes develop in predictable ways for illites formed in nature (Środoń et al., 2000; Bove et al., 2002).

We agree with WP that our approach to crystal growth needs further testing. However, as with any scientific theory or modeling exercise, this approach can never be proven correct; it can only be proven incorrect or incomplete (Popper, 2002). One would have to perform every experiment to prove the approach, but just one experiment may disprove it. Thus far, however, it is the only approach that can simulate the shapes of naturally and experimentally produced CSDs with statistical significance.

For clays, there is still an ongoing controversy as to whether MacEwan crystallites or fundamental illite particles are the thermodynamically significant unit (Peacor, 1998). With MudMaster one can measure both types of crystals (Drits et al., 1998; Eberl et al., 1998b), and, therefore, through these types of studies the problem may be resolved.

5. Conclusion

The BWA technique, as exemplified in the MudMaster computer program, is a rapid, precise, accurate, and therefore powerful technique for characterizing mean crystallite thicknesses and

crystallite thickness distributions for clay minerals having a periodic structure along the *c* axis. The BWA method has several advantages over microscope methods, including the broad availability of X-ray diffractometers, the relative speed and ease of use for the technique, and the fact that the X-ray pattern averages diffraction effects for billions of crystals in a sample, thereby giving statistically significant CTD shapes. The problem inherent to the X-ray method is that crystallite size must be shown to equal crystal size using supplemental techniques. For illites this connection has been made by comparing MudMaster determined thicknesses to TEM, HRTEM, AFM, SAXS, fixed K content, and surface area measurements. Now that this connection has been established for many types of illite, the shapes of CTDs determined by MudMaster can be used to study the evolution of illite in geological systems (e.g., Bove et al., 2002). WP's data have pointed to possible problems in applying the method to chlorite, unless care is taken to use the correct G^2 and sample preparation techniques.

Acknowledgements

We thank D. Bove, C. Brime, D. Kile, S. Krumm and R. Merriman for reviewing the original manuscript.

References

- Bove, D.J., Eberl, D.D., McCarty, D.K. and Meeker, G.P. (2002): Characterization and modeling of illite crystal particles and growth mechanisms in a zoned hydrothermal deposit, Lake City, Colorado. *Am. Mineral.* **87**, 1546–1556.
- Blum, A.E. and Eberl, D.D. (1992): Determination of clay particle thickness and morphology using Scanning Force Microscopy. In: Kharaka, Y.K. and Maest, A.S. (eds.): *Low Temperature Environments. Water-Rock Interaction Vol. 1*, A.A. Balkema, Amsterdam, p. 133–136.
- Brime, C. and Eberl, D.D. (2002): Growth mechanisms of low-grade illites based on the shapes of crystal thickness distributions. *Schweiz. Mineral. Petrogr. Mitt.* **82**, 203–209.
- Drits, V.A., Eberl, D.D. and Środoń, J. (1998): XRD measurement of mean thickness, thickness distribution and strain for illite and illite-smectite crystallites by the Bertaut-Warren-Averbach technique. *Clay Clay Min.* **46**, 38–50.
- Dudek, T., Środoń, J., Eberl, D.D., Elsass, F. and Uhlik, P. (2002): Thickness distribution of illite crystals in shales. 1: X-ray diffraction vs. high-resolution transmission electron microscopy measurements. *Clay Clay Min.* **50**, 562–577.
- Dudek, T. and Środoń, J. (2003): Thickness distribution of illite crystals in shales. II: Origin of the distribution and the mechanism of smectite illitization in shales. *Clay Clay Min.* **51**, 529–542.
- Eberl, D.D. (2002): 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. In: Rule, A.C. and Guggenheim, S. (eds.): *Teaching Clay Science, CMS Workshop Lectures, Vol. 11*, p. 131–142.
- Eberl, D.D., Drits, V.A., Środoń, J. and Nüesch, R. (1996): MudMaster: A computer program for calculating crystallite size distributions and strain from the shapes of X-ray diffraction peaks. *U.S. Geological Survey Open File Report 96-171*, 44 pp.
- Eberl, D.D., Drits, V.A. and Środoń, J. (1998a): Deducing crystal growth mechanisms for minerals from the shapes of crystal size distributions. *Am. J. Sci.* **298**, 499–533.
- Eberl, D.D., Nüesch, R., Šucha, V. and Tsipursky, S. (1998b): Measurement of fundamental illite particle thickness by X-ray diffraction using PVP-10 intercalation. *Clay Clay Min.* **46**, 89–97.
- Eberl, D.D., Środoń, J., Lee, M., Nadeau, P.H. and Northrup, H.R. (1987): Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin, and particle thickness. *Am. Mineral.* **72**, 914–934.
- Eberl, D.D., Drits, V.A. and Środoń, J. (2000): User's guide to GALOPER – a program for simulating the shapes of crystal size distributions – and associated programs. *U.S. Geological Survey Open File Report 00-505*, 44 pp.
- Eberl, D.D., Kile, D.E. and Drits, V.A. (2002): On geological interpretations of crystal size distributions: Constant vs. proportionate growth. *Am. Mineral.* **87**, 1235–1241.
- Hunziker, J.C., Frey, M., Clauer, N., Dallmeyer, R.D., Friedrichsen, H., Flehmig, W., Hochstrasser, K., Roggwiler, P. and Schwander, H. (1986): The evolution of illite to muscovite: mineralogical and isotopic data from the Glarus Alps, Switzerland. *Contrib. Mineral. Petrol.* **92**, 157–180.
- Kile, D.E. and Eberl, D.D. (2003): On the origin of size-dependent and size-independent crystal growth: Influence of advection and diffusion. *Am. Mineral.* **88**, 1514–1521.
- Kile, D.E., Eberl, D.D., Hoch, A.R. and Reddy, M.M. (2000): An assessment of calcite crystal growth mechanisms based on crystal size distributions. *Geochim. Cosmochim. Acta* **64**, 2937–2950.
- Kotarba, M. and Środoń, J. (2000): Diagenetic evolution of crystallite thickness distribution of illitic material in Carpathian flysch shales studied by Bertaut-Warren-Averbach XRD method (MudMaster computer program). *Clay Min.* **35**, 387–395.
- Moore, D.M. and Reynolds, R.C., Jr. (1997): *X-ray diffraction and the identification and analysis of clay minerals*. 2nd edn. Oxford University Press, New York, 378 pp.
- Mystkowski, K. and Środoń, J. (2000): Mean thickness and thickness distribution of smectite crystallites. *Clay Min.* **35**, 545–557.
- O'Connor, B.H. and Chang, W.J. (1986): The amorphous character and particle size distribution of powders produced with the micronizing mill for quantitative X-ray powder diffractometry. *X-ray Spectrometry* **15**, 267–270.
- Peacor, D.R. (1998): Implications of TEM data for the concept of fundamental particles. *Can. Mineral.* **36**, 1397–1408.
- Popper, K. (2002): *The logic of scientific discovery*. 15th edn. Routledge, London, 544 pp.
- Reynolds, R.C., Jr. (1985): NEWMOD, a computer program for the calculation of one-dimensional diffraction patterns of mixed-layered clays. R. C. Reynolds, Jr., 8 Brook Dr., Hanover, NH 03755, U.S.A.
- Shang, C., Rice, J.A., Eberl, D.D. and Lin, J.-S. (2003): Measurement of illite particle thickness using a direct Fourier transform of small-angle X-ray scattering data. *Clay Clay Min.* **51**, 293–300.
- Środoń, J., Eberl, D.D. and Drits, V.A. (2000): Evolution of fundamental-particle size during illitization of smectite and implications for reaction mechanism. *Clay Clay Min.* **48**, 446–458.
- Środoń, J., Clauer, N. and Eberl, D.D. (2002): Interpretation of K–Ar dates of illitic clays from sedimentary rocks aided by modelling. *Am. Mineral.* **87**, 1428–1535.
- Šucha, V., Kraus, I., Šamajová, E. and Puskelova, L. (1999): Crystallite size distribution of kaolin minerals. *Periodico di Mineralogia* **68**, 81–92.
- Šucha, V., Środoń, J., Clauer, N., Elsass, F., Eberl, D.D., Kraus, I. and Madejová, J. (2001): Weathering of smectite and illite-smectite in Central-European climatic conditions. *Clay Min.* **36**, 403–419.
- Uhlik, P., Šucha, V., Eberl, D.D., Puskelova, L. and Čaplovičová, M. (2000): Evolution of pyrophyllite particle sizes during dry grinding. *Clay Min.* **35**, 423–432.
- Warr, L.N. and Peacor, D.R. (2002): Evaluation of X-ray diffraction methods for determining the crystal growth mechanisms of clay minerals in mudstones, shales and slates. *Schweiz. Mineral. Petrogr. Mitt.* **82**, 187–202.
- Wiewióra, A. and Wilamowski, A. (1996): The relationship between composition and *b* for chlorite. *Geologica Carpathica—Series Clays* **5**, 79–87.
- Wiewióra, A., Wilamowski, A., Łacka, B., Kuźniarski, M. and Grabska, D. (1998): Chamosite from oolitic ironstones: the necessity of a combined XRD-EDX approach. *Can. Mineral.* **36**, 1547–1557.

Received 6 June 2003

Accepted in revised form 8 October 2003

Editorial handling: R. Gieré