# Evaluation of X-ray diffraction methods for determining the crystal growth mechanisms of clay minerals in mudstones, shales and slates

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## Abstract

There has been a recent tendency toward using the X-ray scattering domain (crystallite) sizes of clay minerals for deducing their crystal-growth mechanisms. This approach is based on three requirements: (i) that domain broadening information can be accurately extracted from X-ray diffraction profiles, (ii) the X-ray scattering domains correspond only to crystal-growth surfaces, and (iii) changes in the shape of size-distributions can be linked with established crystal-growth mechanisms. Whereas these methods may be appropriate for monomineralic clay samples, their application to typically polymineralic mudstone, shale and slate lithologies is limited. Firstly, it is difficult to accurately extract domain-size information because of uncertainties with overlapping mineral peaks (particularly within the low-tails of reflections), variations in crystal chemistry and problems with removal of instrumental broadening. Secondly, TEM studies reveal that X-ray scattering domains do not necessarily relate directly to crystal-growth boundaries in all cases but are strongly influenced by other crystal defects, such as those induced by intracrystalline deformation and recovery processes. Crystals are additionally sensitive to sample preparation damage, most notably breakage, kinking and cleavage into smaller domains. Thirdly, we question whether the relationship between crystal-size distributions and the formation mechanisms of clay minerals are well enough studied to allow reliable deductions to be made. It is therefore evident that these methods should only be applied to ideal materials where the outlined requirements can be fulfilled.

*Keywords:* Clay minerals, X-ray scattering domain size, crystal growth mechanisms, mudrocks, shales and slates.

## 1. Introduction

The study of crystal-growth mechanisms constitutes a fundamental aspect of the material and mineral sciences (OHARA and REID, 1973; KIRKPATRICK, 1981; RANDOLPH and LARSON, 1988; TILLER, 1991, 1992). Information concerning kinetically controlled growth processes is important for assessing the physical and chemical conditions of a crystal system in relation to its associated fluid phase (OHARA and REID, 1973). One approach to obtaining information about crystal-growth mechanisms is by considering the shape of resultant crystal-size distributions (CSDs). The foundation of such studies originated in the field of chemical engineering and the use of industrial crystallizers (RANDOLPH and LARSON 1988; EBERL et al., 1998a). In the Earth sciences, CSDs have been successfully applied to investigate the crystallization of igneous rocks from their parent melts (MARSH, 1988; CASHMAN and MARSH, 1988; KILE and EBERL, 1999) and crystallization-recrystallization processes in metamorphic rocks (CASHMAN and FERRY, 1988).

It has been proposed that CSDs can also be used to obtain information concerning the crystal-growth mechanisms of clay minerals (EBERL and SRODON, 1988; EBERL et al., 1990; EBERL et al., 1998; SRODON et al., 2000). Due to their minute size and complex microstructure, measuring the size of clay crystals is not a straightforward procedure (WARR and NIETO, 1998). Two basic approaches to obtaining such data are by direct microscopic imaging (e.g. electron and atomic force microscopy) and by indirect determinations based on diffraction effects (notably X-ray diffraction). Imaging methods have the advantage of allowing direct recognition of the type of struc-

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ture being considered, but are time consuming and expensive in that each crystal in an assemblage must be separately measured. As a result, intensive effort has been invested to resolve crystal size information indirectly from their contribution to broadening of X-ray diffraction (XRD) reflections (KLUG and ALEXANDER, 1974; DRITS et al., 1998 and references within). Indirect methods have advantages of being rapid, low in cost, and average the data for entire assemblages of crystals simultaneously.

Successful study of crystal-growth mechanisms by XRD-based methodology relies on three important requirements. Firstly, the X-ray scattering domain-size distributions need to be accurately calculated. Secondly, the domain boundaries must correspond directly to crystal-growth surfaces, and thirdly, changes in crystal-size distributions (CSDs) for known mechanisms of crystal growth should be constrained. Practical attempts at deducing the crystal-growth mechanisms of naturally occurring clay minerals via the XRD approach (EBERL et al., 1990; EBERL et al., 1998a; BRIME and EBERL, 2002) have been enhanced by the availability of two software programs. MUDMASTER (EBERL et al., 1996) calculates X-ray scattering size distributions of clay minerals using a modification of the Bertaut-Warren-Averbach method (DRITS et al., 1998), and GALOPER (EBERL et al., 1998a) predicts crystal size distributions based on hypothesized crystal-growth models.

The analytical package of MUDMASTER has been tested on idealized, modeled XRD profiles, such as those calculated by REYNOLDS' (1985) NEWMOD program (DRITS et al., 1998). It also produces results in general agreement with mean particle thickness measurements of pure clay separates determined by platinum-shadowing methods (data compiled in EBERL et al., 1998b). However, in the case of consolidated polymineralic rock samples such as mudstones, shales and slates, significant discrepancies exist between the XRD-determined crystallite thicknesses of separates and those imaged directly by TEM studies (ARKAI et al., 1996; JIANG et al., 1997; LI et al., 1998; WARR and NIETO, 1998).

In this contribution, the XRD approach for evaluating clay mineral crystal-growth mechanisms is critically assessed in respect to studying naturally occurring, polymineralic rock samples. We have structured the paper to address the basic requirements and underlying assumptions involved in the order that they are encountered during an analytical study. The results of various analytical tests are presented and discussed along with the growing source of published research on this topic. Based on our combined XRD and TEM studies, we are of the opinion that there are a large number of pitfalls involved in determination of CSDs of clay minerals, which need to be recognized and adequately dealt with before results can be reliably used to deduce crystal-growth processes in natural systems.

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

A number of analytical steps are involved in calculating the thickness distribution of X-ray scattering domains from measured XRD sample profiles. Below we outline the procedure followed by EBERL et al. (1996), which has been applied specifically to clay minerals. After a suitable XRD peak has been selected for analysis (Fig. 1), peak intensities are first corrected for the combined broadening effects of the Lorentz-polarisation (Lp) function and the layer scattering intensity $G^2$ (square of the structure factor). Then, following background subtraction and optional removal of the contribution of $K\alpha_2$ radiation, a Fourier analysis of the interference function is undertaken using the Bertaut-Warren-Averbach method, which calculates the distribution of thicknesses of X-ray scattering domains. The Fourier coefficients and hence the size distributions may also be corrected for instrumental broadening effects and/or the broadening effects of lattice strain. The shape of thickness distributions can be described by two simple parameters: the mean ($\alpha$) and variance ($\beta^2$) of the natural logarithms of sizes (DRITS et al., 1998).

### 2.1. PEAK SELECTION AND THE PROBLEM OF OVERLAPPING REFLECTIONS

The first critical condition for analysis is location or extraction of a suitable XRD peak and adjacent background that contains the broadening effects of a single mineral phase only. Whereas this is straightforward for a simulated XRD pattern calculated using REYNOLDS' (1985) NEWMOD program or a pure, monomineralic clay sample, it generally proves to be a daunting task with polymineralic rock samples typical of geologic studies which invariably have peaks that overlap.

A routine approach in dealing with overlapping reflections is to separate peak contributions by profile fitting (decomposition) procedures (STERN et al., 1991; LANSON and BESSON, 1992). Such procedures rely on assumptions concerning the number of reflections present, and their peak shape, in order to obtain a best-fit solution. Profile
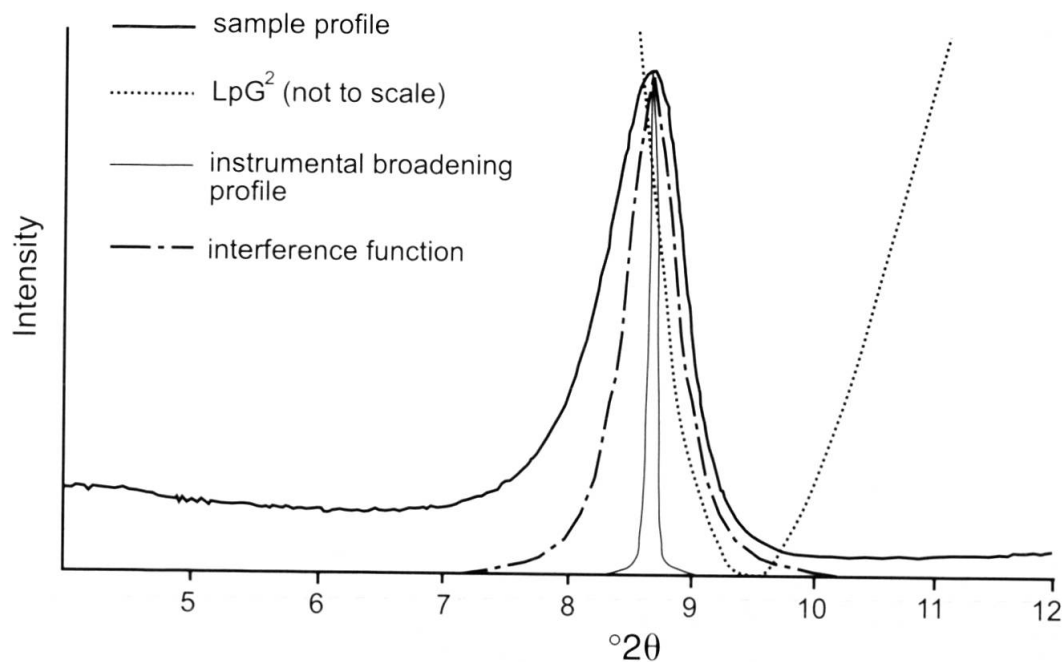
*Fig. 1*   Components of an X-ray diffraction peak (001 illite) used in calculating the X-ray scattering domain size. The sample profile shown is a Paleozoic mudstone from the Cantabrian zone of Spain.

fitting allows overlapping peak contributions to be separated, which can then be used in calculating the X-ray scattering domain sizes of single mineral phases (e.g., SIEMENS, 1991; KRUMM, 1994), but the accuracy of this procedure strongly depends on the effectiveness and reliability of peak fitting.

In order to overcome dependence on peak-fitting models, and avoid any distortion of experimental data, the MUDMASTER program utilizes the raw XRD data. The chance of avoiding overlapping reflections is enhanced by performing analyses on half-peak reflections, from which the symmetrical interference function can be calculated. This procedure is mathematically favorable, but it does assume that overlapping reflections can be successfully avoided. This requirement is worsened by the need for large areas of background to be included in computations, so as to involve the effects of very small scattering domains, and to improve calculation of background. Adjacent reflections that do not strongly overlap, but occur within the required range of analysis, may be removed using a PEAKCHOPPER tool, which is supplied together with the MUDMASTER program.

An example of some of the problems encountered when dealing with overlapping peak reflections is illustrated on the XRD pattern of a diagenetic mudstone (Fig. 2a), for which TEM-measured (area-weighted) crystallite thickness and defect free distance data are available (Sample SW1 of WARR and NIETO, 1998). Analysis of the 10-Å

illite (001) reflection using the recommended range of analysis (4.4 to 9°) given in MUDMASTER is clearly hindered by the presence of the small chlorite (001) reflection at ~14-Å. In the case of relatively sharp reflections WARR and NIETO (1998) used a shortened analytical range to avoid the contribution of the chlorite peak (e.g. 6.6–9 °2θ). However, according to EBERL (pers. comm.) this may lead to the exclusion of the effects of small, diffusely scattering crystallites that cause broadening at angles less than 6.6 °2θ. Analysis of the PVP illite using the shortened range yields shape parameter values ($\alpha = 2.01$, $\beta^2 = 0.45$) that do not accurately match the size of crystallites ($T_L$) measured by TEM, but do approximate to the defect-free distances ($T_\delta$) measured (Fig. 2c).

Attempts at peak chopping the chlorite reflection and using the full analytical range (4.4–9°) were also tested (Fig. 2b,c). As expected, the mean X-ray scattering thickness values are smaller (smaller value of $\alpha$) and the variance parameter ($\beta^2$) is larger. However, these shape parameters show less resemblance to the results obtained by TEM methods which were obtained on the clay separates as well as the intact rock (WARR and NIETO, 1998). It is also apparent that differences in the chopping range selected lead to variation in the shape of measured distributions (Fig. 2c). As PEAKCHOPPER removes reflections by subtracting the peak that lies above a linearly extrapolated background, drawn through the angular (2θ) range selected, it is evident that effective chopping can only be achieved when peak broad-

ening related to a given mineral does not overlap with an adjacent reflection. If diffusely scattering domains of both illite and chlorite overlap in their broad tails, as in Fig. 2, such interference cannot be accurately separated either by peak chopping or profile fitting procedures.

## 2.2. LPG² CORRECTIONS AND COMPOSITIONAL VARIATIONS

Once the analyst is confident that the area selected for study contains the broadening information of a single mineral phase, peak intensities can be
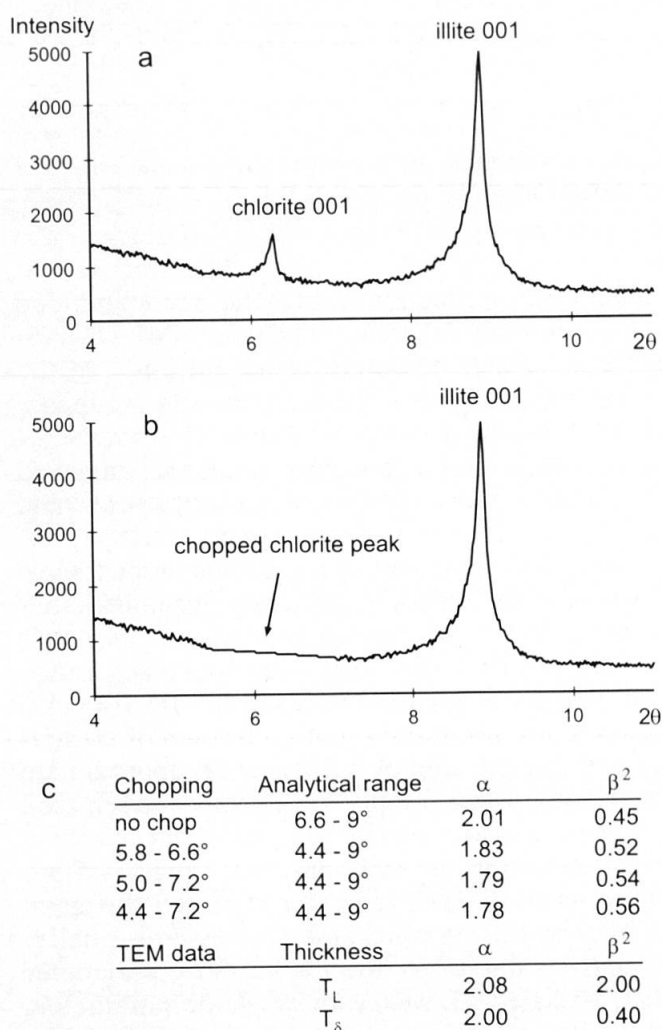
corrected for LpG² effects. The Lp factor is dependent on the volume of crystal that is exposed to irradiation and the number of crystals that are oriented for diffraction (REYNOLDS, 1986). For this reason, samples of varying density and particle orientation, such as textured clay separates, single crystals and random powders produce different Lp profiles. In contrast, G² is dependent on the structure and composition of the mineral in question. For minerals with only minor compositional variations, such as kaolinite, LpG² factors do not vary greatly. However, structure factor magnitudes are primarily a function of both scattering factors and atomic coordinates. Solid solution of atoms with electron densities as different as Mg and Fe results in major changes in scattering factors. More important, however, are the changes in atomic coordinates that accompany solid solution. Thus, modeling Mg- and Fe-rich smectites with the same atomic coordinates fails to include such factors. Worse, the crystal structures of only a few clay minerals, which occur in crystals large and perfect enough for structure analysis (e.g., kaolinite), have been fully deter-



| c | Chopping | Analytical range | α | β² |
|---|---|---|---|---|
| | no chop | 6.6 - 9° | 2.01 | 0.45 |
| | 5.8 - 6.6° | 4.4 - 9° | 1.83 | 0.52 |
| | 5.0 - 7.2° | 4.4 - 9° | 1.79 | 0.54 |
| | 4.4 - 7.2° | 4.4 - 9° | 1.78 | 0.56 |
| TEM data | | Thickness | α | β² |
| | | $T_L$ | 2.08 | 2.00 |
| | | $T_\delta$ | 2.00 | 0.40 |

*Fig. 2* Low-angle X-ray diffraction pattern (4–12 °2θ) of a diagenetic pelite (SW1) containing both illite and chlorite peaks. This particular sample was prepared using the PVP method described by EBERL et al. (1998b). (a) Sample profile before removal of the 14-Å chlorite (001) reflection, (b) Sample profile after removal of the 14-Å chlorite (001) reflection. (c) Shape parameters calculated using various chopping and analytical ranges. TEM determined shape parameters (area-weighted) for crystallite size ($T_L$) and the defect free distances ($T_\delta$) are also given (WARR and NIETO, 1998).

*Fig. 3* α–β² graph showing the theoretical paths of growing crystal size distributions as modeled by EBERL et al. (1998a). The X-ray scattering thickness distributions calculated for the Fe-chlorite sample (CCa-2) are plotted (data in Table 1) based on varying the amount of Fe in silicate and hydroxide layers. Three types of sample preparation were tested, random powder, thick textured and thin film slides. The most realistic calculation is also shown (symbolized star), based on XRD estimates of the total Fe content and symmetry within octahedral sites (random powder measurement).

*Table 1*  $\alpha–\beta^2$ shape parameters for X-ray scattering domain size distributions of the chlorite sample (CCa-2) based on various assumptions of octahedrally positioned Fe within silicate (sil) and hydroxide (hyd) layers. $LpG^2$ corrections were calculated for random powder, thin film and sedimented texture preparation, accordingly.

| Fe(sil) | Fe(hyd) | POWDER | | FILM | | TEXTURE | |
|---|---|---|---|---|---|---|---|
| | | $\alpha$ | $\beta^2$ | $\alpha$ | $\beta^2$ | $\alpha$ | $\beta^2$ |
| 0.0 | 1.0 | 3.30 | 0.34 | 3.40 | 0.40 | 3.30 | 0.34 |
| 0.5 | 1.0 | 3.04 | 0.45 | 3.20 | 0.37 | 3.04 | 0.45 |
| 1.0 | 1.0 | 2.74 | 0.41 | 2.74 | 0.41 | 2.74 | 0.41 |
| 1.5 | 1.0 | 2.63 | 0.44 | 2.63 | 0.44 | 2.63 | 0.44 |
| 2.0 | 1.0 | 2.54 | 0.46 | 2.54 | 0.46 | 2.54 | 0.46 |
| 2.5 | 1.0 | 2.48 | 0.48 | 2.48 | 0.48 | 2.48 | 0.48 |
| 3.0 | 1.0 | 2.44 | 0.48 | 2.44 | 0.48 | 2.44 | 0.48 |
| 1.0 | 0.0 | 2.53 | 0.47 | 2.53 | 0.47 | 2.53 | 0.47 |
| 1.0 | 0.5 | 2.62 | 0.44 | 2.62 | 0.44 | 2.62 | 0.44 |
| 1.0 | 1.0 | 2.74 | 0.41 | 2.74 | 0.41 | 2.74 | 0.41 |
| 1.0 | 1.5 | 3.05 | 0.44 | 3.05 | 0.44 | 3.05 | 0.44 |
| 1.0 | 2.0 | 3.32 | 0.33 | 3.32 | 0.33 | 3.32 | 0.33 |
| 1.0 | 2.5 | 4.15 | – | 4.15 | – | 4.15 | – |
| 1.0 | 3.0 | – | – | – | – | – | – |
| 1.2 | 0.5 | 2.58 | 0.45 | – | – | – | – |

mined. Structure coordinates must therefore be approximated for minerals such as smectite, corrensite and illite by those obtained from refinements of structures of minerals such as micas or chlorite, which form as crystals large enough and sufficiently defect-free to serve for structure refinement. When dealing with most clay minerals, the accuracy of the X-ray scattering size distributions will clearly be affected, to some degree, by these factors.

To test the variability in the X-ray scattering domain sizes calculated in relationship to $LpG^2$ effects, a pure Fe-bearing chlorite sample was studied (CCa-2 from the Clay Mineral Society source clay collection). The sample was prepared in three states: A random powder, a sedimented textured preparation (5 mg/cm$^{-2}$) and a highly orientated thin film (0.25 mg/cm$^{-2}$). The profiles were analyzed using MUDMASTER assuming we knew that the sample is trioctahedral Fe-bearing chlorite (from XRD study), but with no precise compositional data. A range of $LpG^2$ curves were calculated for varying Fe content and degrees of symmetry using the spreadsheet CALC-LpG2 program of EBERL et al. (1996). The calculated compositions and the resultant shape parameters ($\alpha$ and $\beta^2$) are shown in Table 1 and the $\alpha–\beta^2$ results plotted graphically in Fig. 3.

The sensitivity of the X-ray scattering domain size calculated in respect to sample preparation is apparent. Probably the most realistic results are those for the powder preparation; they fulfill requirements of homogeneity and infinite specimen thickness. The data for thin-film preparations come close to those of the random powder, suggesting a high degree of particle orientation and homogeneity. However, notably different results are obtained from the thicker, graded and thus inhomogeneous, textured specimens, reflecting the inadequacy of this preparation technique.

Differences in the quantity and site occupancy of Fe (distribution between silicate and hydroxide octahedral sites) also result in major variations in the shape of calculated size distributions. These variations follow similar trends in $\alpha–\beta^2$ space as those predicted for Ostwald ripening-controlled crystal growth (Fig. 3). All three trends measured on random powder, thin film and thicker textured preparation show convergence toward values $\alpha \sim$ 3.3 and $\beta^2 \sim 0.33$.

The structure and composition of this chlorite was approximated using the XRD-determined analytical parameters D and Y (BROWN and BRINDLEY, 1980; MOORE and REYNOLDS, 1997). A D-value of 0.7 was calculated using the I(003)/I(005) relationship, and Y was estimated to be ~1.7, based on I(002)+I(004)/I(003). Before calculating Y, the intensity of (003) was first corrected for asymmetry. Using these parameters, $LpG^2$ corrections were calculated assuming 1.2 Fe in the silicate layer and 0.5 Fe in the hydroxide sheet (equivalent to D = 0.7, Y = 1.7). The X-ray scattering domain sizes calculated using these estimates of composition and structure produced shape parameters ($\alpha = 2.58 – \beta^2 = 0.45$; Table 1) that do not correspond with the point of convergence observed in Fig. 3, having significantly smaller sizes and a higher degree of variance.

It is evident from these analyses that calculating accurate X-ray scattering domain sizes is

strongly dependent on accurate compositional and structural constraints. When such information is absent or poorly known, which is often the case in polymineralic assemblages, size distributions cannot be accurately calculated. The large variation in shape parameters calculated for the Fe-chlorite (CCa-2) is a clear example of the degree of sensitivity that may exist. As this is only one of many heavy metal substitutions described in chlorite-family minerals (combined tetrahedral-octahedral substitutions also occur), calculation of "true" X-ray scattering domain size distributions of such minerals is problematic.

When calculating the X-ray scattering domain size of a compositionally unconstrained Paleozoic illite, based on analysis of the 001 reflection (shown in Fig. 1), similar results are obtained assuming a K content varying in the range of 0.85 to 1 (Table 2). Lower K contents failed to produce realistic size distributions. However, when the 002 reflection was incorporated into the procedure, and the Fourier transforms corrected for the presence of lattice strain, small variations in K content

*Table 2* $\alpha$–$\beta^2$ shape parameters for X-ray scattering domain size distributions of a Paleozoic illite sample (Cantabrian zone of Spain) based on various assumptions of the amount K in interlayer sites. The shape of distributions based on multiple analyses (001 and 002 reflections) are presented and corrected for the presence of lattice distortion (strain effects). RMS = root mean square of strain (Å). The distribution data for 002 reflections are strain corrected.

| K content | 001 PEAK | | 002 PEAK | | |
|---|---|---|---|---|---|
| | $\alpha$ | $\beta^2$ | $\alpha$ | $\beta^2$ | RMS |
| 0.75 | 2.21 | 0.23 | 3.74 | 0.04 | 0.36 |
| 0.80 | 2.23 | 0.23 | 3.64 | 0.05 | 0.37 |
| 0.85 | 2.24 | 0.23 | 2.31 | 0.21 | 0.38 |
| 0.89 | 2.25 | 0.23 | 2.33 | 0.22 | 0.40 |
| 0.90 | 2.25 | 0.23 | 2.33 | 0.21 | 0.39 |
| 0.95 | 2.27 | 0.23 | 2.35 | 0.22 | 0.40 |
| 1.00 | 2.29 | 0.23 | 2.39 | 0.24 | 0.41 |

Another example of compositional variation is the amount of K in the interlayer sites of illite. According to SRODON et al. (1992), illite has a fixed K content of 0.89 ions per half unit cell. However, DRITS et al. (1997) described illite interlayers from the Upper Jurassic shales of Denmark with ~ 0.75 K per $O_{10}(OH)_2$. In the presence of $NH_4$, illite may even contain as little as 0.55 K per $O_{10}(OH)_2$ (LINDGREEN et al., 2000). During prograde metamorphism illite also undergoes restructuring to form muscovite, with a resulting fixed K content approaching 1 (HUNZIKER et al., 1987).

produced notable variations in $\alpha$–$\beta^2$ values and in the amount of strain measured. It therefore appears that even minor errors in mineral composition may cause variations when undertaking multiple reflection analysis. This probably reflects the increasing impact of erroneous $LpG^2$ corrections with increasing two-$\theta$ angle (REYNOLDS, 1986).

### 2.3. THE PROBLEM OF INSTRUMENTAL BROADENING

A final problem when dealing with relatively sharp reflections is the effective removal of instrumental broadening (LANSON and KUBLER, 1994; ARKAI et al., 1996), the significance of which becomes larger on a relative basis as crystallite sizes increase and the degree of natural broadening decreases. For X-ray scattering sizes that are larger than 30 nm, where instrumental broadening effects are relatively significant, a satisfactory procedure for removing them has not yet been perfected. According to KOTARBA and SRODON (2000), the upper size limit for accurate calculations is as small as 20 nm.

There are a number of problems that are involved in preparing suitable material for measuring the instrumental broadening contribution. Firstly, the standard needs to be free of any microstructural broadening effects (domain or lattice-strain effects), and secondly, the standard should ideally be in particulate form (not a single crystal), to match the varying degree of particle orientations occurring in a clay sample.

Attempts at preparing an instrumental standard were made using the muscovite flake (MF1c) of WARR and RICE (1994). The flake was first cut into small fragments using sharp scissors and then ultrasonically treated in a bath for several hours. The coarse fraction (> 100 μm) was separated by gravity settling and then the sample repeatedly washed in order to remove all fines. Effective removal of the small fragments and damaged edges of crystals is critical for avoidance of domain-size broadening effects. A $LpG^2$ correction based on K = 1 and a Fe content of 0.14 per half unit cell (based on chemical analysis) were used to calculate the "apparent size distribution" caused by instrumental effects. The distribution was lognormal, with $\alpha$–$\beta^2$ values of 4.02 and 0.31, respectively (Fig. 4).

Attempts at correcting the natural size distribution using this instrumental broadening data in MUDMASTER proved unsatisfactory. Unrealistic distortion of size distributions occurred. As the degree of distortion was observed to increase when analyzing sharper reflections, it appear

## Instrumental standard
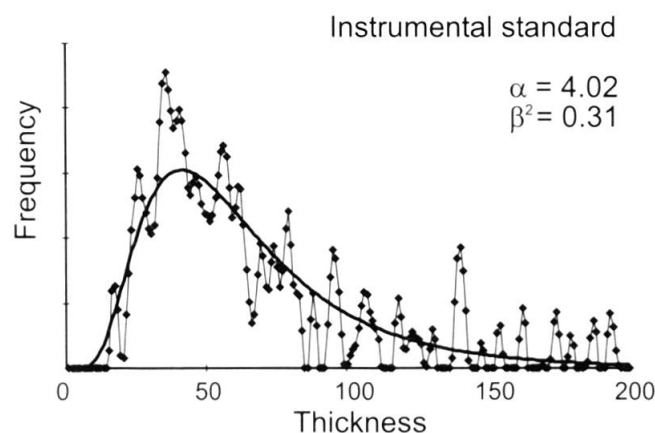


$\alpha = 4.02$
$\beta^2 = 0.31$

*Fig. 4* X-ray scattering domain size distribution produced by instrumental broadening (muscovite flake, MF1 of WARR and RICE, 1994). The solid line shows the theoretical lognormal distribution calculated for the shape parameters given.

that the measured data are of insufficient accuracy and precision to allow reliable correction of Fourier coefficients. Clearly the best approach to resolving the instrumental broadening problem is to limit its contribution in the first place by selecting the finest slit geometries possible and using appropriate step sizes and longer counting times. Therefore any advancement in modern XRD diffractometers that allow for improved optics and measured intensities (such as rotating anodes) is a step in the right direction.

## 3. X-ray scattering domains and crystal growth surfaces

Upon completion of the XRD profile analyses and assuming that all calculations have been realistically and accurately performed, the second group of assumptions can be addressed, namely the crystal-chemical meaning of X-ray scattering domains in clay minerals.

### 3.1. THE NATURE OF X-RAY SCATTERING DOMAINS

The Bertaut-Warren-Averbach method calculates the thickness of X-ray scattering domains, in this case parallel to the crystallographic c*-direction, weighted in relation to the area of diffracting domains in the crystallographic a*-b* plane (DRITS et al., 1998; WARR and NIETO, 1998). This measure is not equivalent to the dimensions used in most CSD studies, which are absolute measurements weighted in respect to the number of crystals (e.g., CASHMAN and FERRY, 1988). Area-

weighted thickness distributions have the disadvantage of being dependent on the shape of domains that are measured (KLUG and ALEXANDER, 1974). This influence is not a significant problem when domain shape is known and does not vary (e.g., hexagonal morphologies). In such cases, size populations can be easily converted among N-weighted, area-weighted or volume-weighted data (e.g., JIANG et al. 1997; WARR and NIETO, 1998). However, where domain shape varies within a given population, distributions may no longer be solely a function of the mechanism of growth, but be complicated by crystal morphology and preferred directions of crystal growth. Such a case was recognized in the experimental study of BAUER et al. (2000). Using kaolinite as starting material, treated with KOH solution (molarity between 1–4) at temperatures between 35–80 °C, simultaneous growth of both fibrous laths and blocky hexagonal crystals of mica-illites were described. Similarly, coexisting fibrous and blocky illite are also known to occur in natural samples (e.g., LANSON and CHAMPION, 1991).

### 3.2. DEFORMATION AND ANNEALING-INDUCED MODIFICATIONS OF CSDS

Where crystals form in environments that are relatively stress-free, and the growth surfaces can be unambiguously recognized, the CSDs can be related to some specific growth process. However, in those rocks affected by regional metamorphism, or by local high-stress environments associated with faulting, high concentrations of defects may occur, modifying CSDs. Strain can cause subgrain boundaries within what otherwise would be individual crystals. The formation of dislocation arrays or sub-grain boundaries induced by the migration and annealing of defects within crystals is a process generally referred to as recovery (KLUG and ALEXANDER, 1974; BONS, 1988; MERRIMAN et al., 1985). An example of crystal recovery is shown in hydrothermal chlorite from the Alpine Fault of New Zealand (Fig. 5). This chlorite formed as an alteration product of an exhumed pseudotachylyte (glass-bearing) fault rock, as hydrous fluids of meteoric origin circulated deep into the fault zone (WARR and COX, 2001). Following formation, the chlorite grain was kinked during deformation and subsequently annealed. During the recovery process the intracrystalline defects migrated and merged, to form energetically more stable domain (sub-grain) boundaries. Whereas this process is common in metamorphic rocks, it is also recognized that annealing of phyllosilicate minerals occurs at sig-

nificantly lower temperatures than minerals such as quartz or feldspar (SHEA and KRONENBERG, 1992). Annealing of chlorite may occur at temperatures as low as 250–300 °C (BONS, 1988). In fact, very little is known concerning the annealing temperatures of clay minerals, but based on their small size and high concentrations of defects, clays can be expected to anneal at significantly lower temperatures than their parent metamorphic phyllosilicates.

The extreme effect of deformation is illustrated in the studies of MERRIMAN and PEACOR (1999) and GIORGETTI et al. (2000). They described prograde sequences in which the KUBLER index, which is a measure of effective illite domain size, is significantly larger (i.e. broader reflections) than that predicted by other indicators of low temperature metamorphism. Strain-induced subgrain boundaries actually caused a decrease in the domain size within metamorphic rocks, thus modifying the CSDs produced by growth.
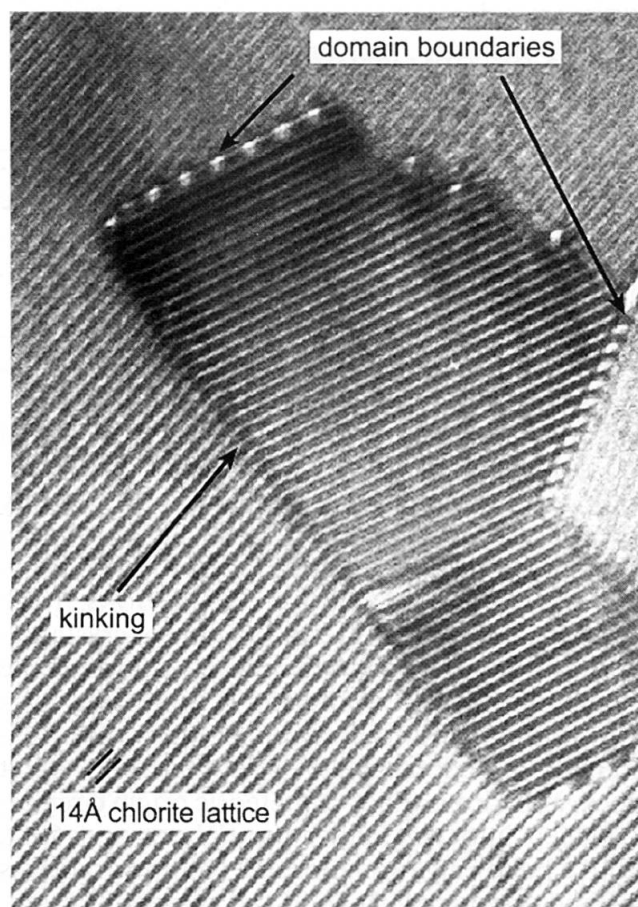


*Fig. 5* Formation of subgrains in a kinked chlorite crystal within a hydrothermally altered pseudotachylyte formed along the Alpine Fault, New Zealand. The domain structure does not relate to crystal growth processes, but is a result of recovery mechanisms. Annealing has also removed fields of lattice strain.

Stress-modified CSDs may be further altered by dissolution and crystallization processes. It is the smallest and highly strained crystallites that are relatively unstable and most susceptible to dissolution. During slaty cleavage formation, for example, deformed mica crystals within microlithons undergo dissolution, with neocrystallization in cleavage lamellae (KNIPE, 1981; MERRIMAN et al., 1995). The crystal-growth process in a high-stress, low-grade metamorphic environment can thus be one in which formation of defects and subgrain boundaries, which decrease the size of scattering domains, competes with dissolution and crystallization causing an increase. CSDs resulting from such processes have yet to be theoretically treated, but as noted in the references above, may be determining factors in some cases.

### 3.3. MODIFICATIONS DUE TO SAMPLE PREPARATION

Clastic mudstones, shales and slates typically consist of complex mixtures of mineral phases formed at various stages during the geological history of the rock. The coarse fractions usually contain more detrital material and the fine, reactive fractions, more of the newly formed authigenic components of the assemblage. For crystal-growth studies by XRD, grain-size separation procedures are often necessary in order to concentrate the fine authigenic or metamorphic portion of a sample, and to exclude portions of the rock that do not relate to the same generation. It is also critical that the surface boundaries correspond to crystal boundaries if XRD measurements are to have any meaning with respect to growth mechanisms.

The approach of separating the <2-μm fraction used by the majority of clay mineralogists is viewed as a practical but crude method for differentiating between authigenic/metamorphic and detrital phases. Electron microscope investigations and radiogenic isotope studies show clear evidence that detrital material may be present in the clay-sized fraction (REUTER et al., 1987). PEVEAR (pers. comm.) noted that extrapolation of K/Ar isotope data for a series of size fractions obtained from the same sediment with authigenic and detrital components showed that a detrital component remains even in the very finest size fraction.

To further concentrate the authigenic clay minerals, some workers prefer to isolate the <0.2-μm or even <0.1-μm fraction for studying clay mineral particle sizes (e.g., SRODON et al., 2000; NADEAU et al., 1984). This approach appears to work for clay samples dominated by extremely

small particles sizes, such as bentonites (MYSTKOWSKI et al., 2000). However, application of these procedures to clay-bearing pelites and metapelites is questionable. The strong dependence between grain size and the Full-Width-at-
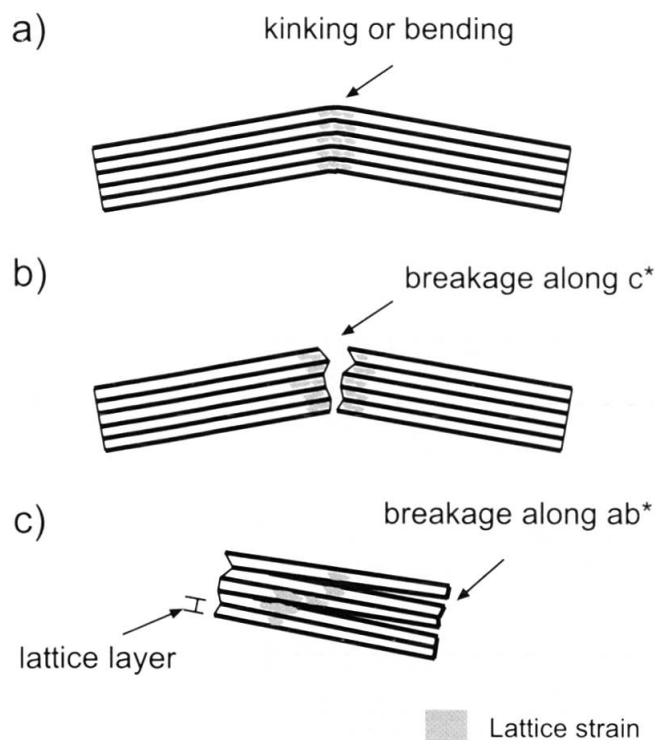
a) **kinking or bending**

b) **breakage along c\***

c) **breakage along ab\***

lattice layer

Lattice strain

*Fig. 6*  Schematic diagram showing the various types of sample preparation damage caused by rock disaggregation (a) kinking or bending of crystals, (b) breakage roughly parallel to c\*, (c) breakage (splitting) along ab\*. Associated fields of lattice distortion (strained crystal) are also indicated.

Half-Maximum (FWHM) parameter of XRD reflections, which is well known in clay-mineral crystallinity studies of pelites, is seen as a reflection of rock sample heterogeneity (KRUMM and BUGGISCH, 1991). In these cases, any separation of a range of grain sizes which are smaller that the true population of sizes can cause an increase in the degree of log-normality measured in a size distribution, as described by LI et al. (1998) and WARR and NIETO (1998). As a result, investigations of clay mineral CSDs based on any form of grain size separation is in danger of excluding parts of the true distribution of crystal sizes.

Perhaps the most significant factor affecting the relation between CSDs as they occur in rocks and those determined by powder XRD is that of modification of sizes by cleavage and by the introduction of defects. When dealing with well-crystallized material, with interlocking mineral textures, it appears virtually impossible to disaggregate and disperse individual minerals without incurring some form of damage or modification. Figure 6 summarizes the type of crystal damage that can occur, involving kinking or bending of grains, and breakage along c\* or a\*-b\* directions caused by both mechanical grinding and ultrasonic disaggregation (JIANG et al., 1997; LI et al., 1998; WARR and NIETO, 1998). An example of the more brutal effects of dry grinding is shown in Fig. 7. A thick crystal of chlorite within a metapelite sample of the Otago Schist from New Zealand shows an irregular zone of kink damage, associated with detachment of a crystal fragment. In this case, splitting of the crystal has occurred both along the
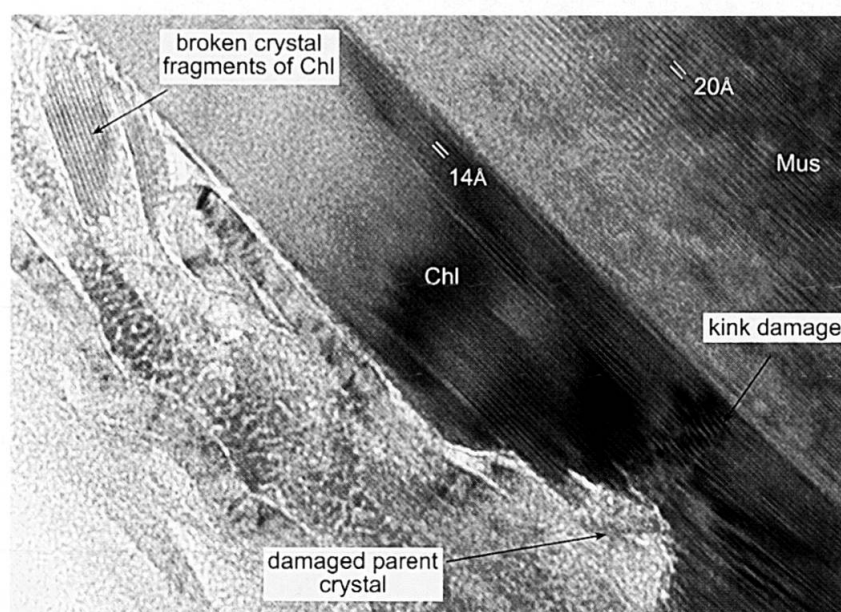


*Fig. 7*  Mechanical damage of a chlorite crystal in Otago Schist from New Zealand (Pumpellyite-actinolite facies) induced by initial dry grinding. Disaggregation damage occurs in the form of kink damage and broken fragments of chlorite that have been ripped-out of their parent chlorite crystals.
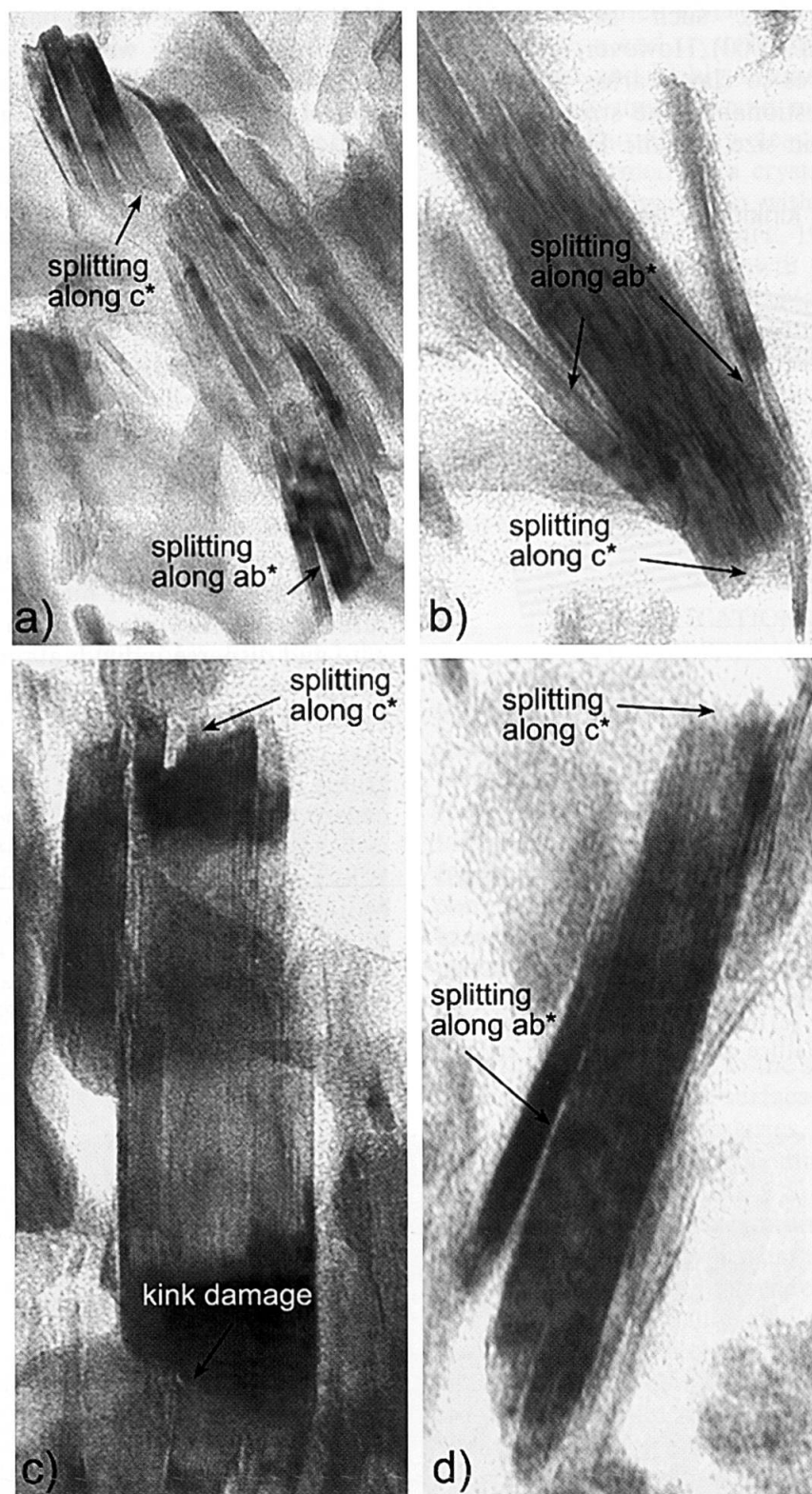
*Fig. 8*  Disaggregation damage of illite grains in pelites from SW England (SW samples documented in WARR and NIETO, 1998). Splitting of grains occurs along c* and ab*. (a) Diagenetic mudstones (SW1), (b) anchizonal slate, (c) anchizonal slate, (d) epizonal schist.

c* and a*-b*-directions, and a number of crystal "split-ends" are produced. Similar types of microstructural damage have been described in clay separates following ultrasonic disaggregation. Examples of kink damage and splitting in various crystallographic directions are shown in Fig. 8. As noted by a number of authors, the degree of damage appears to significantly increase with the degree of metamorphic grade and average crystal size (LI et al., 1998; WARR and NIETO, 1998).
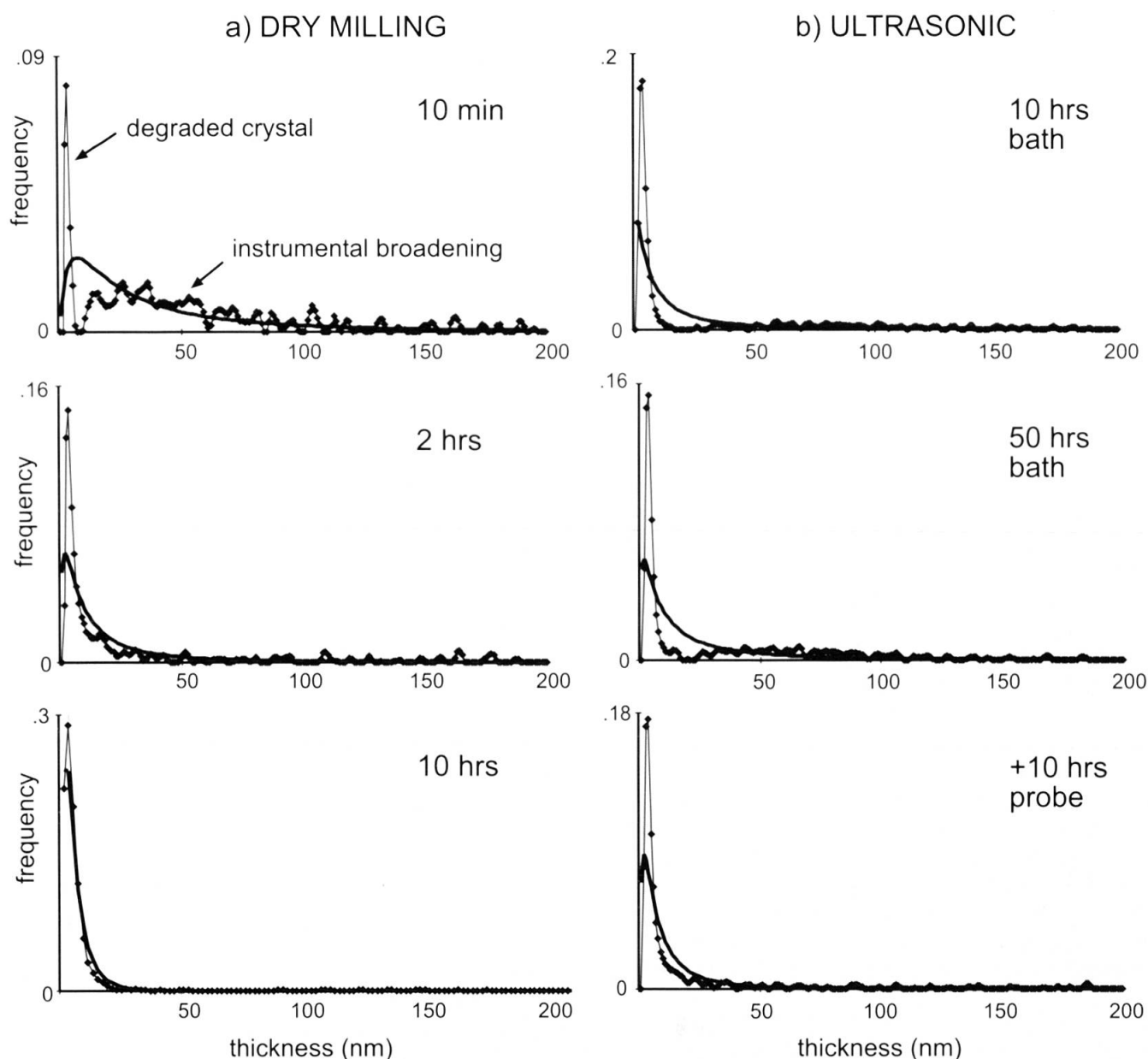
## a) DRY MILLING

## b) ULTRASONIC



*Fig. 9* X-ray scattering domain size distributions of the degraded muscovite flake (MF1c). (a) Dry milled samples are shown after 10 minutes, 2 hours and 10 hours grinding. (b) Ultrasonic treated samples in a bath are shown after 10 hours and 50 hours treatment, and finally, after an additional 10 hours probe.

Whereas there is general agreement that damage occurs when disaggregating crystalline rocks, the exact way in which damage modifies size distributions is not so clear. Complex modifications of particle size distributions were documented by UHLIK et al. (2000) by progressive dry grinding of a pyrophyllite sample. In order to test the effects of mechanical grinding and ultrasonic disaggregation methods, the muscovite flake (MF1c) that was used to measure the degree of instrumental broadening was selected. Although this crystal flake is a poor example of the effects that may occur when disaggregating rocks of various initial grain sizes, degradation of a muscovite crystal does provide some useful constraints. Firstly, we

can assume that the material contains initially no X-ray scattering domains, and secondly, the scattering domains produced during progressive treatment must result only from the effects of crystal damage.

The distribution of X-ray scattering domain sizes were calculated based on analysis of the muscovite (001) reflection, adopting the same constraints used for calculating the instrumental broadening. Both forms of degradation (dry milling and wet ultrasonic treatment) initially produced apparent bimodel size distributions (Fig. 9). These distributions contain a population of grinding-induced domains less than 10 μm in thickness, together with a population of thicker domains

which is in fact an artifact caused by the instrumental broadening. Progressive treatment by both methods increased the abundance of smaller domains. All shape distributions are non-lognormal and show strong asymmetry toward smaller sizes. After 10 hours of mechanical grinding by milling, the muscovite no longer contained a distinct 001 reflection, and the broadened background of the near-amorphous material produced an "asymptotic-like" distribution, with a continuous increase in the abundance of small diffraction domains.

The $\alpha$–$\beta^2$ shape parameters for these complex distributions are presented in Fig. 10. Despite the range of $\alpha$–$\beta^2$ values measured, which are complicated by the presence of instrumental broadening that could not be effectively removed, trends can be recognized in the data. All size distributions of dry-milled and wet ultrasonically treated material show significantly different shape parameters, which follow different trends depending on the method of breakup. The least damage was incurred by ultrasonic treatment in a bath, whereas more significant reductions in size and variance where induced by dry grinding and intense ultrasonic probe treatment. Such processes will lead to an overestimation of small domain size than are present in the natural rock sample.

The degree to which separation affects particle sizes has been found to depend on rock texture. Li et al. (1998) observed that, as metamorphic grade increased, the mean thickness of separates tended to be relatively smaller than that for original rocks as observed by TEM observations
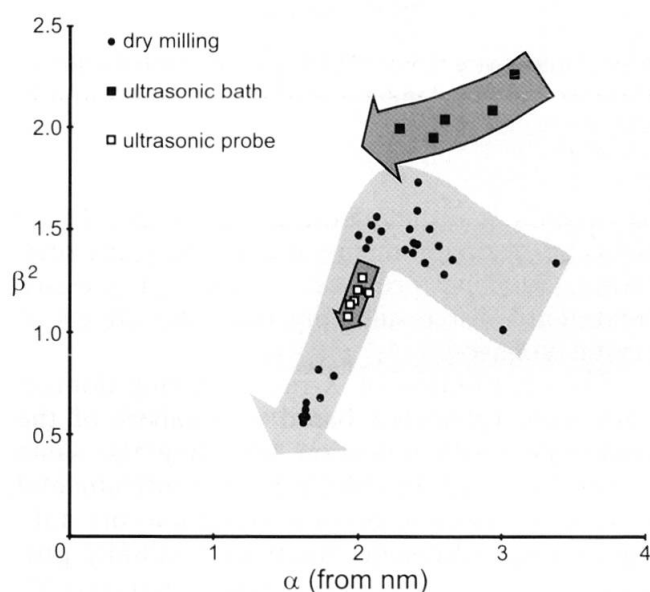
of ion-milled samples. This was attributed to the breakage of interlocking grains typical of metamorphic rocks. On the other hand, where individual euhedral crystals form in pore spaces, as in some hydrothermal environments, separates may represent unmodified crystals. Such was the case for CSDs measured on both separates and ion-milled samples for the Salton Sea hydrothermal system (KIM and PEACOR, 2002). In clay-dominated rocks such as bentonites and some mudstones, smectite and I/S may form arrays which, based on TEM observations, appear to be continuous stacks with high concentrations of defects (MASUDA et al., 2001). Definition of crystal growth surfaces in such rocks appears to be a difficult and controversial exercise. The meaning of "fundamental particles" separated by intense physical and chemical treatment of such arrays, are considered either as the basic growth units (NADEAU et al., 1984; EBERL et al., 1998b) or alternatively, as a simple consequence of sample preparation damage (PEACOR, 1998; KASAMA et al., 2001). The latter viewpoint considers CSDs of clay separates as been dependent both on the specific texture of a given rock and the severity of the separation technique. Until those relations are defined, caution should be used in treating CSDs of separates as unmodified growth CSDs.

## 4. Crystal-growth models and their relevance to clay minerals

Assuming that the X-ray scattering domain size distribution has been accurately calculated and verification obtained that the domain size data provides a direct measure of crystal growth surfaces, the final step in the procedure is to evaluate the validity and reliability of crystal growth models.

### 4.1. THE NATURE OF CRYSTAL GROWTH MODELS AND THEIR CSDS

The growth of crystals from a nutrient-rich fluid phase is a complex process, governed by the laws of fluid-crystal kinetics. The several distinct and different shapes of CSDs observed in natural and synthetic samples are considered to reflect the varying mechanisms of crystal growth (BARONNET, 1982; EBERL et al., 1998a; KILE and EBERL, 1999). The theoretical approach of EBERL et al. (1998a) uses the empirical Law of Proportionate Effect (responsible for producing lognormal distributions), in combination with equations for Ostwald ripening and mass transfer, to predict



*Fig. 10*   $\alpha$–$\beta^2$ graph shown the changes in shape parameters during dry milling, ultrasonic bath treatment and ultrasonic probe treatment.

CSDs for five crystal-growth mechanisms. This modeling approach, covering continuous nucleation and growth, surface and supply-controlled growth, as well as Ostwald ripening and random ripening, produces distinctive CSD shapes and $\alpha$–$\beta^2$ trends. Comparison with synthetic and natural mineral data, reflecting crystallization over a wide range of physical and chemical conditions and presumably by different crystal growth mechanisms, show some correspondence with modeled predictions (Fig. 14 of EBERL et al., 1998a). Such consistency is necessary for verification of a given modeled crystal-growth mechanism, but does not constitute proof of its validity. Tests of the models are valid only where the crystal-growth mechanism is known, and where the CSDs are unambiguously recognized to be measures of true growth surfaces.

There are a number of aspects concerning these models that need to be addressed before they can be applied in evaluating clay mineral growth mechanisms. Firstly, predicted CSDs and their $\alpha$–$\beta^2$ trends represent crystal growth within a single system as a function of time (KIM and PEACOR, 2002). Secondly, such crystal growth systems need to be fixed in terms of pressure, temperature and closure with respect to components (closure defined in the thermodynamic sense); Ostwald ripening, for example, is defined for closed systems at constant P, T. If samples owe their states to evolving P–T conditions, volumes of fluid or proportions of solutes in an open system, resultant CSDs may be interpreted to be caused by variation in such variables – rather than reflecting theoretically derived crystal-growth mechanisms. The crystal-growth models therefore represent time-dependent crystal size changes, assuming fixed P–T-fluid conditions, which differ by changing crystal growth parameters such as surface areas, supply of nutrients and interfacial energies.

Crystal-growth models, such as those theorized by EBERL et al. (1998a), are in fact best reproduced and tested by the synthesis of crystals in the laboratory. As crystal growth usually occurs directly from a nutrient rich fluid phase, at constant P–T–X conditions, they present the equivalent conditions as involved in the crystal-growth models. Problems, however, arise when applying these models to natural crystal-growth systems in geological environments, for which constant P–T–X conditions are considered to be rare. For example, KIM and PEACOR (2002) obtained clay mineral CSDs of the Salton Sea hydrothermal system, for which growth mechanisms and conditions are well known. The lognormal shape of CSDs and their apparent steady state evolution within the

profile fit the theoretical criteria for initial growth of a log-normal distribution in an open system, followed by modification either by supply-controlled growth or by random ripening, as defined by EBERL et al. (1998a). The necessary conditions for that model were therefore fulfilled. Whereas it is clear that these clays grew within an open system, however, there is no indication that any modification of the crystal population has occurred. On the contrary, the clays appear to have crystallized directly as a single generation of subsequently unmodified crystals. Moreover, the differences in CSDs occurring as a function of depth are distributed over a range of directly measured depth-related temperatures, for which changes in composition of fluids being convected through the sediment pile are well documented. The apparent steady state sequence therefore does not represent a progressive time sequence, governed by progressive burial, but represents simultaneous growth under varying P–T–X conditions, at different depths within the borehole sequence. Indeed, such ideas have been at the core of our understanding of the causes of changes in clay minerals as a function of depth, in part as originally rationalized by HOWER et al. (1976) for Gulf Coast clays, generally being interpreted as temperature dependent. Temperature is a key parameter in controlling reaction kinetics, for example, and changes in reaction rates have a primary influence on the states of metastable systems undergoing reaction. KIM and PEACOR (2002) suggested that changes in geologic systems are primarily caused by changes in P, T and composition in closed systems, or by changes in fluid activity and solutes in open systems. These relations imply that it is difficult to properly test models of crystal-growth mechanisms in natural systems, because differences in CSDs may ubiquitously be due to changes in such variables, rather than by the constraints of crystal-growth models. Synthetic systems are easily tested. We do not mean to imply that conditions consistent with growth models do not exist in natural systems. Indeed, even where conditions of formation change for sediments as a function of depth, or for low-grade metamorphic rocks as a function of grade, it may be possible to show that variables such as temperature have a minimum effect, and that constraints of crystal-growth models are valid. We do maintain, however, that it is necessary to provide evidence of the significance of changes in variables such as temperature before tests of crystal-growth models in natural systems can be accepted as valid.

## 4.2. THE COMPLEXITIES OF CLAY MINERAL FORMATION IN GEOLOGICAL ENVIRONMENTS

The Salton Sea hydrothermal system was chosen for study of CSDs by KIM and PEACOR (2002) because it is a relatively simple case characterized by the growth of clays directly from a nutrient-rich fluid phase in an open system. Here, clay minerals have formed during a single, constrained event, with variations occurring simply as a function of depth. Such simple systems are the exception, however, especially when compared with rocks in the zone of diagenesis and anchizone. Because sediments affected by low temperatures are generally in a state of metastable equilibrium, more than one mode of clay mineral may coexist metastably with another, in contrast to the more stable and homogeneous muscovite and chlorite assemblages of greenschist-facies pelites. It is not uncommon to find at least three members of the I/S-illite-illite/muscovite sequence in the same sample, each derived by different processes (e.g., authigenic, low-grade metamorphic, detrital high-grade) and each with their own CSD (PEACOR, 1992). In shallow Gulf Coast sediments, for example, detrital illite/muscovite coexists with smectite. In transitional sediments, smectite, I/S and detrital mica coexist, the smectite being a remnant of lower-temperature relations. Anchizonal pelites may have detrital mica, bedding-parallel $1M_d$ illite, and higher-grade bedding-parallel 2M muscovite, whereas rocks transitional to those with slaty cleavage have separate populations of authigenic, bedding-parallel illite or mica, coexisting with cleavage-parallel muscovite. Such occurrences represent incomplete modification of preexisting metastable phases through incomplete reactions, which largely involve processes of dissolution and crystallization. Incomplete reactions are in large part the result of the low temperatures typical of diagenetic and low-grade metamorphic environments. The occurrence of multiple modes of formation of, say, dioctahedral clay minerals, results in complex overlapping peaks, and thus to additional errors even where such peaks can be analyzed in terms of their components. In addition, even where peaks do not entirely overlap, they affect background, with resulting inaccuracy in CSDs.

## 4.3. THE PROBLEM OF MIXED-LAYERED CLAY MINERALS

Mixed-layered clay minerals present a particularly complex problem, which has been the center of continuous controversy (see MOORE and REY-NOLDS, 1997 for summary). A vast number of crystal-chemical models have been presented for mixed-layered minerals, in particular for interstratified illite-smectite, but these can be approximated by two models. In one, that of MacEwan crystallites, a given sequence of illite-like and smectite-like layers is considered to be a "crystal" with boundaries that are crystal-growth surfaces. This model is consistent with a plethora of families of mixed-layered inorganic phases in the mineral and materials sciences; e.g., the hexagonal ferrites and bastnaesite-family minerals. In those and related cases, the entire sequences of layers are universally regarded to be growth units. That is more evident in those cases than in I/S because there are no interlayers across which bonding is so weak as to give rise to incoherent interfaces. The more recent and now popularized viewpoint of the fundamental particle model, in contrast, treats each smectite-like interlayer, postulated to be universally incoherent, as a growth-surface boundary. The thicknesses of so-called "fundamental particles" are therefore theorized to be equivalent to crystal thicknesses (NADEAU, 1984). A sample-preparation method for separating fundamental particles (causing separation of 2:1 layers at all smectite interlayers) using PVP was described by EBERL et al. (1998b) and the crystal-growth mechanisms of illite fundamental particles discussed.

The validity of the "fundamental particle approach" depends on the opinion that the CSDs of such separates represent crystal growth units. Alternative viewpoints consider fundamental particles as an artifact of the separation process, and that most smectite interlayers in interstratified I/S do not represent growth surfaces (PEACOR, 1998; KASAMA et al., 2001). If so, conclusions regarding growth mechanisms based on CSDs for separates (e.g., "illite" fundamental particles produced by PVP treatment) have no relation to recognized crystal-growth models. But we also recognize that others may conclude that the fundamental particle model is valid insofar as crystal-growth surfaces are concerned. Given the differences in conclusions, we suggest that deductions regarding growth mechanisms, which are based on the fundamental particle model, are at least problematic and are dependent on factors that are yet to be satisfactorily resolved.

## 5. Conclusions

(1) Three basic requirements are needed in order to deduce clay mineral crystal growth mechanisms from their size distributions of X-ray scat-

tering domains. (a) that domain broadening information can be accurately extracted from X-ray diffraction profiles, (b) the X-ray scattering domains correspond only to crystal growth surfaces, and (c) changes in the shape of size-distributions can be linked with established crystal growth mechanisms.

(2) As a result of the large number of variables that need to be accurately known for calculating the distribution of X-ray scattering domains using the Bertaut-Warren-Averbach method, such as particle orientation and composition constraints, calculations should be viewed as a modeling procedure, rather than a routine calculation of known quantities.

(3) X-ray scattering domains do not necessarily correspond directly to the growth surfaces of a single generation of crystal formation. Scattering domains are often modified by sample preparation effects, grain size dependent factors and disaggregation damage, as well as by natural recovery processes in defect-rich minerals.

(4) Validation of crystal growth models for clay minerals are required before empirical growth models can be effectively used to determine crystal growth mechanisms. Until such constraints are available, such models remain predictive rather than indicative in nature.

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