Reply to the comment on "Evaluation of X-ray diffraction methods for determining the crystal-growth mechanisms of clay minerals in mudstones, shales and slates" by D.D. Eberl, J. Srodon and V.A. Drits

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Abstract

In their comment on our paper (Warr and Peacor, 2002), Eberl et al. (2004) reemphasize that their XRD techniques represent a precise, accurate and reliable way of determining clay-mineral crystallite-size distributions from which mechanisms of crystal growth can be inferred. We agree on the conditions that must be fulfilled, but describe several key relations which imply that those conditions have yet to be satisfied.

Keywords: Clay minerals, Crystal growth, Crystallite size, Bertaut-Warren-Averbach method.

1. Introduction

Warr and Peacor (2002), hereafter WP, discussed the X-ray diffraction (XRD) approach for evaluating clay mineral crystal-growth mechanisms in naturally occurring, polymineralic rock samples, namely for typical mudstone, shale and slate of the Earth's crust. A number of limitations of Eberl et al.'s modified Bertaut-Warren-Averbach (BWA) technique for determining the X-ray domain (crystallite) thickness distributions of clay minerals were outlined. We further highlighted our concern about using such crystallite data to deduce the crystal-growth mechanisms of clays, as this step involves the assumption that all X-ray scattering domain surfaces of clay mineral separates reflect crystal-growth surfaces. That assumption has not been validated for most clay phases and their mixed-layered structures. Finally, we emphasized the need for caution in using the theoretical modelling approach of Eberl et al. (1998) to determine the crystal-growth mechanisms of clays until such predictions have been verified experimentally.

In their comment on our paper, Eberl, Srodon and Drits (2004, this volume; hereafter ESD) agree on the three important conditions that need to be fulfilled in order to adopt the XRD approach for determining crystal-growth mecha-

nisms. Cases were discussed in which they consider all three criteria to be satisfied to such an extent that the techniques may be used with some confidence in future studies. However, based on our evaluation of the available published work, we do not share this confidence. In fact, many of the studies mentioned appear not to fulfil all three requirements simultaneously, and thus we continue to stress the need for a high degree of caution when applying these XRD techniques for deducing the crystal-growth mechanisms in polymineralic, clay-bearing rocks. In the following reply, we again discuss these basic requirements, but this time focus on the claims of precision, accuracy and power made by ESD in their comment and related papers.

2. Can accurate domain size information be extracted from XRD profiles?

There is little doubt that accurate domain size information can be calculated from simulated NEWMOD XRD profiles representing single mineral phases (Drits et al., 1998). The question at hand, however, is to what degree can accurate clay mineral domain size information be calculated for natural polymineralic assemblages, which are commonly characterized by broad overlapping

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XRD reflections, background effects and the presence of instrumental broadening.

WP highlighted the problem of overlapping reflections and tested the effectiveness of the PeakChopper program. Results on a diagenetic mudstone (SW1) were presented for which (area-weighted) crystallite thickness and defect-free distance data were obtained by transmission electron microscope (TEM) studies (Warr and Nieto, 1998). Small variations were observed during removal of the (001) chlorite reflection by varying the starting angle from 4.8° to 5.8° (ca. 4–8% differences), illustrating how small portions of the background area can influence calculations. The important point of this data set, however, was in demonstrating how the stripping of this reflection produced a result less in agreement with the TEM data, than when using a shorter analytical range that avoided the chlorite reflection during the analysis (6.6° to 9° and not the recommended 4.4° to 9°). This tendency was not just restricted to this sample, but was characteristic of all four pelite samples studied in detail by Warr and Nieto (1998). In more severe cases, stripping of the (001) chlorite peaks resulted in artificial bimodal illite crystallite-size distributions (CTDs), similar to those shown by ESD in Figure 3.

The NEWMOD calculations presented by ESD highlight the problem of removing overlapping reflections (Figs. 2, 3). The peaks calculated in their Figure 2 appear not to overlap in the tail regions, as they do in the samples we studied and in many other natural clay-bearing rocks. However, as soon as the peak intensity was increased above a factor of 0.5 of the reflection of interest, the peaks overlapped and accurate domain-size distributions were no longer obtained. ESD could have also demonstrated this feature by increasing the peak breadth of the reflections involved, or by selecting CTDs which induce more broadening of the tails. Such an exercise, whether demonstrated on calculated or natural samples, highlights the very problem with which we are concerned here. We agree that clay mineral separation, where possible, is probably the only way of removing the effects of such overlapping reflections. However, there is little work showing how such methods as acid digestion or magnetic separation influence the CTDs of individual mineral phases. It has, for example, been demonstrated that separating different particle size fractions of pelitic rocks invariably influences the CTDs measured (e.g. Li et al., 1998; Warr and Nieto, 1998), a point we discussed in detail in our paper.

In published studies of natural polymineralic samples, overlapping reflections appear to us to be a serious obstacle to making accurate domain-size calculations of many individual clay mineral phases. A number of the papers quoted by ESD involve the study of reflections which overlap with others. For example, Dudek et al. (2002) and Dudek and Srodon (2003) studied shale samples containing (001) chlorite reflections that overlap with the broad tails of the (001) illite reflections. Brime and Eberl (2002) also calculated CTDs of illite from complex clay mixtures. Brime et al. (2002) highlighted the complexities of the diagenetic pelites, identifying the presence of overlapping contributions of up to three illite distributions, as well as the occurrence of overlapping reflections of chlorite or chlorite/vermiculite. In the same volume, Brime and Eberl (2002) present a MudMaster analysis of illite-bearing rocks from the same geological units, apparently assuming no overlap of reflections and the presence of just one phase of illite.

In addition to the problems of overlapping clay mineral reflections, we also addressed the role of Lorentz-polarization (Lp) and the layer structure factor (G^2) effects on making accurate X-ray scattering domain size calculations. In testing the degree to which the structure factor influences MudMaster calculations, we selected two mineral phases that are commonly encountered in natural clay-bearing rocks. We showed that for single peak analyses of the (001) illite reflections, varying the K content, but not the inevitable differences in atomic coordinates which occur with changes in composition, did not lead to significant variations in calculated CTDs. ESD also demonstrate that varying the Fe content has little effect on the (001) analysis. These results imply that accurate CTDs can be obtained without accurate compositional knowledge of K or Fe, at least insofar as atom coordinate changes, which occur with solid solution, are taken into account. However, our tests did show that such constraints become necessary for multiple peak analyses, such as those performed by Eberl et al. (1996; example 3) for a K-saturated illite-smectite phase.

Whereas compositional variations cause only minor variation in illite CTDs, our tests on chlorite revealed a different picture. Here, large variations were observed by varying the Fe content in octahedral sites. It is therefore evident that accurate CTDs can only be calculated when the structure and composition of the mineral is well known. Contrary to ESDs claims, we did not state in our paper that the intersection of the shown trends, representing an inappropriate G^2 calculation, represents the correct solution. We labelled the most realistic result using the XRD-determined structural and composition constraints obtained on the monomineralic chlorite sample by a

symbolized star in our Figure 3, and referred to this as the "best result". We agree that a reliable calculation can be made if these constraints are available. However, our concern is focused on applying these methods to polymineralic assemblages where determination of accurate crystal-chemical relations are not routinely possible.

3. Do X-ray Scattering domains (crystallites) provide a direct measure of crystal-growth surfaces?

The most significant question with respect to the application of the BWA method concerns whether or not calculated CTDs of treated clay-mineral separates reflect actual growth surfaces. As was discussed by WP, we here consider several issues, including the effects of cleavage, the nature of "fundamental particles" and deformation-induced modification of growth units.

The tendency of phyllosilicates to cleave along {001} is well known. The now-classic experiments of Nadeau (1985) showed conclusively that collections of smectite- and illite-like layers in illite-smectite readily separated along low-charged smectite-like layers, as verified by direct high-resolution TEM observations of Ahn and Peacor (1986). Li et al. (1998) and Warr and Nieto (1998) also documented various degrees of cleavage occurring both along and across high-charge illite or muscovite layers in mudstones, shales and slates. In these samples, splitting occurred along zones of structural weakness, and was not restricted solely to crystal surfaces as documented for pore-filling hydrothermal clays of the Salton Sea area (Kim and Peacor, 2002). The degree to which sample preparation alters CTDs is therefore seen to be largely a function of both rock texture and crystal size, and therefore poses a problem when dealing with highly anisotropic or crystalline rocks such as bentonites, shales and slates.

ESD acknowledge the separation effects of dry grinding but claim that their gentle treatment does not cause cleavage. But in actual applications, e.g., Eberl and colleagues (Bove et al., 2002) describe methods of wet crushing, ultrasonic treatment and separation with centrifugation and ultracentrifugation. Dudek et al. (2002) described rather harsh physical and chemical treatment, including removal of carbonates, Fe and Mn oxides and organic matter, Na-saturation, dialysis, dispersion in water, and treatment with polyvinylpyrrolidone (PVP), the latter involving suspension in water and further ultrasonic dispersion. More importantly, the effects of separation using mechanical grinding or even immersion in fluids with subsequent ultrasonic treatment can not be tested with a single or even small number of tests, as implied by ESD. The effects of separation are dramatically different for a lithified, coherent mudstone or slate than for a poorly lithified bentonite comprised of illite-smectite with expandable smectite-like layers.

The fundamental particle theory adopted by Eberl and coworkers assumes that, after preparation of clay separates and PVP treatment of illite-smectite, each separated illite packet represent a basic growth unit, with each expandable clay interface constituting a growth surface. This is at best a debatable notion. ESD rely heavily on the studies of Eberl et al. (1998) and Dudek et al. (2002) to show that TEM measures of fundamental particle thicknesses in separates agree with those independently determined by the BWA technique. However, these studies do not show that the CTDs measured on these samples represent the thickness distribution of growth surfaces in unseparated samples, as claimed. We are aware of only one way of validating the physical meaning of X-ray scattering domains in natural clay mineral separates. That is to make direct visual comparisons between original, intact geologic samples and separated and/or treated materials.

At present, the only practical method of observing intact crystals in original geologic samples is by high-resolution TEM. It is critical that such observations be made on samples, which have been prepared so that original textures remain undisturbed. Methods of impregnating specimens accomplishing this are well known (e.g., Kim et al., 1995) and have been applied on a regular basis. TEM images of such samples permit direct observations of the thickness of crystal packets, and in the case of illite-smectite, of direct observations of the sequence of smectite and illite layers within a given packet (e.g., Bauluz et al., 2000). It is our contention that a wealth of TEM studies demonstrate that most illite-smectite occurs in sequences of layers within individual growth units (e.g., Peacor, 1999), the smectite-like low-charge interlayers being integral parts of these growth units (Stixrude and Peacor, 2002).

WP discussed the effects of rock deformation in modifying CTDs by deforming grains and producing subgrain boundaries, which may be subsequently annealed. These effects, which may be significant during low-grade metamorphism, clearly modify surface defects, the resulting array of X-ray scattering domains being unrelated to growth units. Here we refer to the discussion of WP, noting only that ESD do not address these aspects, despite being relevant to some of their publications (e.g. Brime and Eberl, 2002). In such settings,

it is essential that the possibility of such effects be considered, especially as they are generally detected only by direct observation of rock textures and not by XRD.

4. Can crystal-size distributions be used to deduce the crystal-growth mechanisms of clays?

This question has two principal aspects: (1) whether or not the available theoretical models accurately consider all natural growth mechanisms, and (2) whether conditions in natural systems duplicate those of synthetic systems involved in theoretical models. The possible mechanisms of formation of smectite, illite and illite-smectite have been reviewed by Altaner and Ylagan (1997) who showed that this is a complex issue, which has yet to be resolved, one problem being that the modes of formation may vary greatly in different rock types, depending in part on the fluid/rock ratio as implied by the models of Eberl et al. (1998). Whether or not the models of Eberl and co-workers are applicable depends on the specifics of formation mechanisms. Those hydrothermal systems in which crystals directly crystallize from fluids in open pore space are the most likely to fit within the theoretical framework. On the other hand, TEM studies have shown that alteration of volcanic glass to smectite and illite-smectite is a solid-state process, although mitigated by water at the atomic scale (e.g., Masuda et al., 1996). Transformation of smectite to illite may also be by solid-state mechanisms where it occurs layer by layer (e.g., Bauluz et al., 2000). The assumption that the theoretical framework of crystal growth is complete and accurate should, at the least, be questioned.

WP noted that experiments in which crystal-growth mechanisms have been monitored are well constrained in terms of thermodynamic variables which affect the state of a system (P, T, composition), so that only time, and therefore extent of growth, is a significant variable. WP noted, however, that such conditions are rare for large geological systems. For example, burial diagenetic systems are generally viewed as advancing in reaction progress with increasing P and T, whereas hydrothermal systems are produced through fluid flow with diminishing T and changing composition as distance from the fluid source increases (e.g., Kim and Peacor, 2002). It has therefore yet to be shown that crystal-size distributions in such natural systems are a function of single, genetically related crystal-growth sequences through time, rather than a series of separate growth events varying both in time and place, each related to a unique set of P, T and compositional conditions.

Lastly, we reemphasize the problems caused by low-T diagenetic or hydrothermal geologic systems, which are commonly characterized by complex P-T-t histories. Multiple diagenetic-metamorphic events, rather than single-event, time-dependent crystal growth are common, resulting in complex overlap of XRD reflections influenced by crystallite populations of varying origin.

5. Concluding remarks

The methods of ESD do represent advances in the analytical techniques that have been developed and those authors are to be commended for their creativity. ESD also acknowledge that every technique has its limitations and should be used within these limitations. Our main point of contention, however, is that much more testing is necessary, and key questions must be answered, before those methods can be applied to determining the crystal-growth mechanisms of natural systems from XRD data with the confidence expressed by ESD. They claim their techniques to be precise, accurate and powerful tools for routine characterization of the size distributions of clay crystallite in rocks and for studying crystal-growth mechanisms. Such claims are made without statistical analysis concerning the precision of these methods, as has been performed for the Kübler index by Robinson et al. (1989). In fact the empirical nature of XRD peak broadening studies is notorious, and precision and accuracy both within and between laboratories can only be attained by employing calibration methods using laboratory standards (Warr and Rice, 1994). These effects apply equally to the determination of CTDs using XRD methods. Whereas Warr and Rice (1994) and Warr and Nieto (1998) did extend these calibration methods to standardizing mean crystallite thickness, there is at present no routine procedure for calibrating the shapes of CTDs. It would therefore be wise for the moment to treat these XRD methods as empirical techniques, equivalent to all other analytical techniques that do not employ a standardization procedure.

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