

BEYOND THE KUBLER INDEX

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(Received 14 February 1989; revised 9 May 1989)

ABSTRACT: The value of peak width at half-height for the illite 001 XRD reflection is known as the Kubler index or the illite 'crystallinity' index. This measurement, which has been related to the degree of metamorphism of very low-grade, pelitic rocks, is a function of at least two crystal-chemical factors: (1) illite X-ray scattering domain size; and (2) illite structural distortions (especially swelling). Reynolds' NEWMOD computer program is used to construct a grid with which these two contributions to illite peak width can be determined independently from measurements of the 001 peak width at half-height and the Šrodoň intensity ratio. This method yields more information about changes undergone by illite during metamorphism than application of the Kubler index method alone.

The Kubler index (also known as the illite 'crystallinity' index) has proved to be useful for determining the degree of metamorphism in very low-grade, pelitic rocks (Kubler, 1964, 1967, 1968). This index, which is the width, at half-height, of the illite 001 X-ray diffraction (XRD) reflection obtained from oriented clay specimens, has been applied successfully by more than 100 authors (Frey, 1987; Kisch, 1983). However, there are difficulties in applying the 'crystallinity' index. Because the index is strictly empirical, there has not been a clear understanding of the underlying causes for the measured differences in peak width (Blenkinsop, 1988). Some of these difficulties include problems in comparing measurements from various laboratories because of differences in sample preparation techniques (Kisch, 1983; Kisch & Frey, 1987) and problems in relating metamorphic grade to the 'crystallinity' index for rocks from different regions (Eberl *et al.*, 1987; Kisch, 1987).

According to Klug & Alexander (1974), the profile of an XRD peak produced by a crystalline powder is mainly a function of four factors: (1) machine effects; (2) dispersion of the incident X-ray radiation; (3) crystallite-size distribution; and (4) nature and magnitude of structural distortions. In comparing Kubler indices measured in various laboratories, factors 1 and 2 can be minimized by using standardized machine conditions and appropriate interlaboratory standards. In the present study, factors 1 and 2 have been ignored, because we are concerned mainly with the broad XRD reflections for illites formed within the diagenetic zone. For such illites, differences in peak width related to factors 1 and 2 should result in only small interlaboratory errors, especially if similar XRD slit configurations are used. Thus, the primary crystal-chemical factors causing differences in 'crystallinity' indices for various illites are crystallite-size distribution and structural distortions.

Illite crystallite-size distribution is more correctly termed X-ray-scattering-domain size distribution. X-ray scattering domains for illite may terminate either at basal particle surfaces of individual illite crystals (which are the fundamental illite particles of McHardy *et al.*, 1982, and Nadeau *et al.*, 1984a, 1984b; see Fig. 1A), at basal particle surfaces at the top and bottom of stacks of illite crystallites (at the top and bottom of coherently diffracting

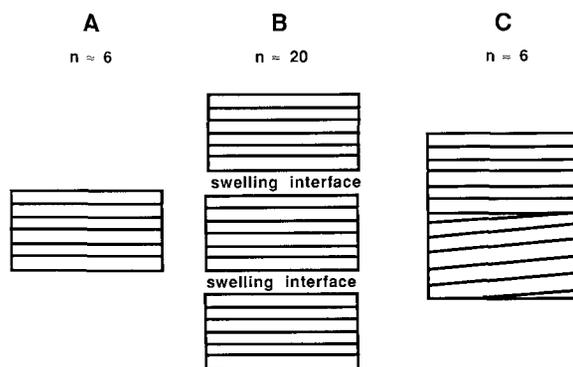


FIG. 1. Different arrangements of fundamental illite particles that give rise to different X-ray scattering domain sizes (n). Each small rectangle represents an individual illite layer within an illite particle. A = single fundamental illite particle in which the X-ray scattering domain size terminates at the top and bottom of the particle. B = fundamental illite particles in a stacked configuration (MacEwan crystallite) in which X-ray scattering domain size terminates at the top and bottom of the MacEwan crystallite. C = single fundamental illite particle broken into two diffracting domains in which X-ray scattering domain size terminates at the top or bottom of the crystal and at the defect.

MacEwan crystallites; Fig. 1B), or at stacking faults within illite crystallites (Fig. 1C). It is the size and distribution of these scattering domains that affect peak broadening (Klug & Alexander, 1974).

The most important structural distortion affecting the width of the illite 001 reflection is swelling (expansion along c^*), which, according to the concept of interparticle diffraction (Nadeau *et al.*, 1984a, 1984b), results from interactions between hydrated, basal particle surfaces in stacks of fundamental illite particles (Fig. 1B). The relations among the amount of this interparticle swelling (expandability, in percent), the weighted mean thickness of the fundamental illite particles parallel to c^* (T), and the mean number of particles (S) in stacks of fundamental illite particles that diffract coherently by interparticle diffraction (MacEwan crystallites) is: $\text{expandability} (\%) = 100(S - 1)/(ST - 1)$ (Eberl & Środoń, 1988).

METHODS

Because the width of the illite 001 peak is related to two crystal-chemical factors (domain size and swelling), two measurements, rather than a single 'crystallinity' index measurement, are needed to differentiate each effect. The first of the two measurements proposed is the width at half-height of the 001 illite reflection (the half-height width of the 005 illite reflection works equally well), with the XRD background determined on the high 2θ angle side of the reflection, rather than as an average of the background on both sides of the reflection as is used for the Kubler 'crystallinity' index (Fig. 2). The background is measured in the former manner to avoid a reversal in values undergone by the 'crystallinity' index at the larger expandabilities when background is measured by the traditional method. The second measurement is the Środoń intensity ratio (I_r ; Środoń, 1984), which is defined, using maximum illite XRD peak intensities, as:

$$I_r = [001/003]_{\text{air-dried}} \div [001/003]_{\text{glycolated}}$$

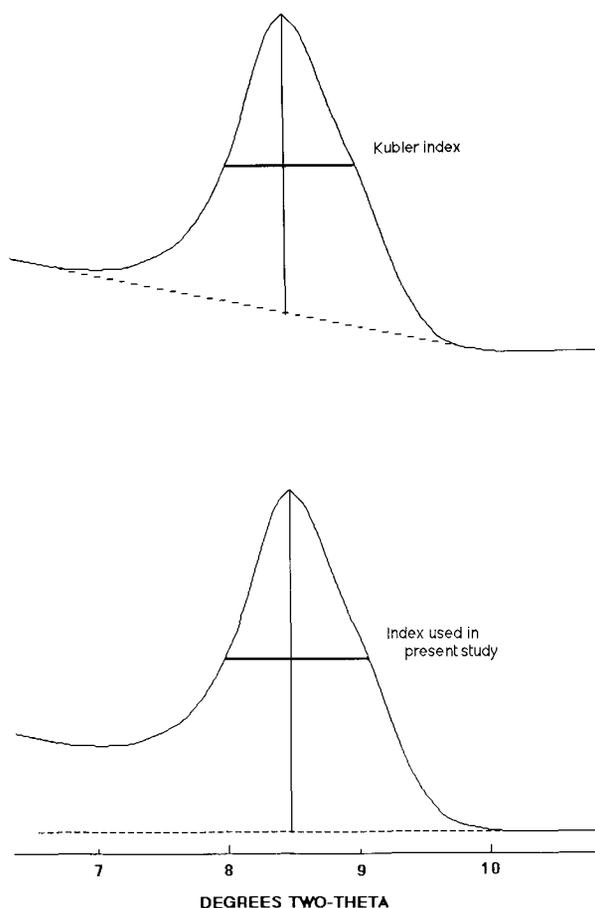


FIG. 2. Two methods for interpreting the background when measuring width at half-height of the illite 001 peak on XRD.

This ratio is very sensitive to the presence of swelling layers in illite. If $I_r > 1.0$, the illite has swelled to some degree; if $I_r = 1.0$, the illite has no detectable tendency to swell. After trying several other parameters, the modified 'crystallinity' index and the intensity ratio were found to be the best measurements for separating the two peak-broadening effects because 'crystallinity' index is more responsive to changes in domain size, whereas intensity ratio is more responsive to changes in expandability.

The modified 'crystallinity' index, which differs significantly from the Kubler index only for X-ray scattering domain sizes ($n \leq 10$ layers, or for expandabilities $\geq 6\%$ swelling layers, is plotted against Środoń's intensity ratio in Fig. 3 for various mean X-ray scattering domain sizes (labelled " n ") and for various percentages of swelling layers (labelled as $\%$). Also labelled in the figure are three metamorphic zones that are defined on the basis of the Kubler index (Kisch, 1983). This figure was constructed from calculations made for mixed-layer illite/smectite using Reynolds' NEWMOD computer program (Reynolds, 1980; program available from R. C. Reynolds, Dept. of Earth Sciences, Dartmouth College, Hanover, NH

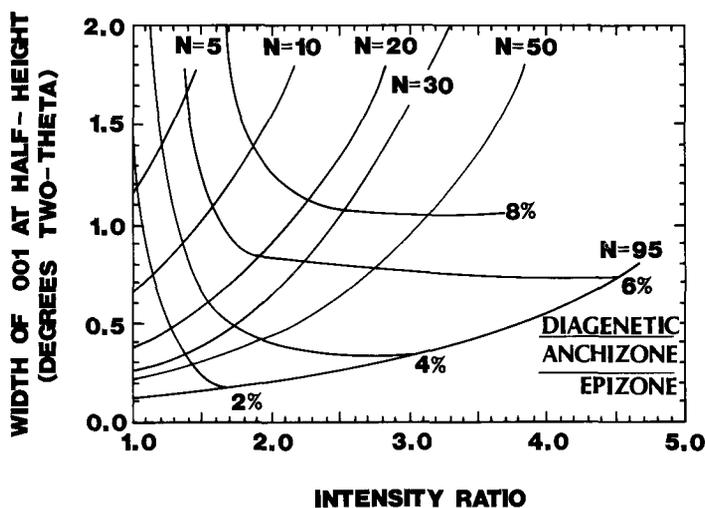


FIG. 3. A net used to determine mean XRD scattering domain size (n) and percentage of swelling layers (%) for illite using the proposed 'crystallinity' index, and the Šrodoń intensity ratio.

03755, USA). The parameters used in the calculation were: $K = 0.9$ (see Eberl & Šrodoń, 1988); $Fe = 0.2$; $reichweite = 3$; $\lambda = 1.5418 \text{ \AA}$; soller slit 1 = 6.6° ; soller slit 2 = 2° ; divergence slit = 1° ; quartz reference intensity = 10000cps; d_{001} illite = 9.98 \AA ; d_{001} smectite (2-water layers) = 15 \AA ; d_{001} smectite (2-glycol layers) = 16.9 \AA ; exchange cation = Sr; no theta-compensating slit; goniometer radius = 20 cm; sample length = 3.6 cm; mass absorption coefficient (mustar) = 45; orientation function (sigmatar) = 12; and exchange capacity = 0.36 equivalent per 4(Si + Al). Expandability was varied between 0% and 10%, and calculations were made for the following X-ray scattering domain sizes: 3–7, 8–12, 18–22, 28–32, 48–52 and 93–97 layers, with the proportions of n all equal to 1.

Care needs to be taken during sample preparation to ensure that sample data plotted on Fig. 3 are valid. Similar concerns have been expressed by Kisch & Frey (1987) for measuring the 'crystallinity' index. The $< 2 \mu\text{m}$ (or finer) size fraction must be used to minimize the quantity of detrital micas and quartz because these phases interfere with measurement of peak width and intensity. The sample needs to be Sr- (or Ca-) saturated, so that the "structural distortion" caused by swelling has a constant thickness; other exchange cations, such as Mg, Na and K, may cause only partial expansion of some of the interparticle layers (see Fig. 4 in Eberl *et al.*, 1987), which could result in spurious peak-width measurements. The sample needs to be relatively thick on the XRD slide (*e.g.* $> 8 \text{ mg/cm}^2$), so that the sample swells to its full potential. Conversely, one could prepare an extremely thin sample that diffracted as though it had a single plane of illite particles on the XRD slide. For such a sample, $I_r = 1.0$; therefore no swelling can occur, and the 'crystallinity' index would depend only on n for individual illite particles (Fig. 2A and 2C; see also Table 5 in Eberl *et al.*, 1987). The 'crystallinity' index needs to be measured using air-dried samples, and the same XRD slide needs to be glycolated overnight at 60°C in order to determine the Šrodoń intensity ratio. It would be best to ensure that differential settling does not occur during preparation of XRD clay slides by using a rapid suction method for preparing oriented mounts (*e.g.* Drever, 1973).

However, this procedure was not used in the present study in which oriented clay preparations were prepared simply by drying suspensions on glass slides.

RESULTS AND DISCUSSION

The modified 'crystallinity' index and the intensity ratio measured for an illite sample can be plotted on Fig. 3 to determine approximately the mean X-ray scattering domain size and expandability without the use of expensive and time-consuming transmission electron microscopy techniques. The figure indicates that neither the 'crystallinity' index nor the intensity ratio alone provide a complete characterization of an illite. For example, an illite having a 'crystallinity' index of 1.0 could have a variety of expandabilities depending on n . The determinations made from Fig. 3 are approximate only because, in addition to swelling, other types of "structural distortions" could lead to XRD peak broadening: for example, the presence of coherently diffracting chlorite layers in illite crystals (Ahn *et al.*, 1988) could affect peak width. In addition, multi-modal illite particle size distributions also could lead to inaccuracies.

Data for Sr-saturated illites from a variety of locations are plotted in Fig. 4. The data appear to form two groups, one of which centres around $n = 30$ layers (open symbols) and the other of which centres around $n = 10$ layers (solid symbols). The two groups meet at 0% expandable between the boundaries for the diagenetic zone ('crystallinity' index = 0.42; see Fig. 3) and the epizone ('crystallinity' index = 0.25). According to Kisch (1983), expandability is lost at the anchizone-epizone boundary. Based on the limited data plotted in Fig. 4, illites from a given locality generally have a similar value of n .

The origin of the trends in Fig. 4 is open to speculation. According to crystal growth theory (Baronnet, 1982, 1984), crystallization of illite particles having a small value of n would be

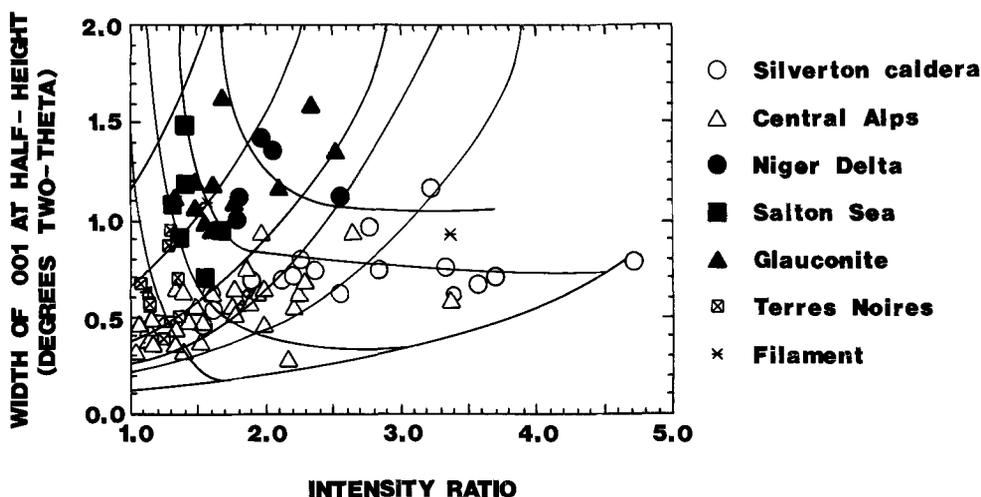


FIG. 4. The net from Fig. 3 on to which have been plotted data for illites from a variety of locations. These illites have been described in the following papers: Silverton caldera (Eberl *et al.*, 1987); Central Alps (Hunziker *et al.*, 1986); Niger Delta (Velde *et al.*, 1986); Salton Sea (Jennings & Thompson, 1986); glauconites (Thompson & Hower, 1975); Terres Noires (Guilhaumou *et al.*, 1988); filament (Środoń & Eberl, 1984).

favoured by pore fluids that are highly supersaturated with respect to illite solubility. Under these conditions, crystal growth would take place mainly by surface spreading, during which nucleation and subsequent layer growth could occur on the surfaces of previously nucleated illite particles. This type of crystal growth, which follows first-order reaction kinetics, could cause many stacking faults within the illite particles, or could cause rough basal surfaces on the illite particles that would disturb interparticle swelling. Both effects would result in a small value of n . This type of crystal growth would be expected to take place, for example, either in rocks that have undergone burial diagenesis, or in rocks that have been either hydrothermally or regionally metamorphosed, provided that the rocks contained amorphous silica, smectite, or other relatively soluble substances that can elevate concentrations in the pore solution of one or more of the components that form illite. Such a growth mechanism has been identified for sericite by electron microscopic investigations of clay crystals that grew during regional metamorphism (Sunagawa *et al.*, 1975).

Formation of illite particles with a large value of n , however, would be favoured by pore fluids that are slightly supersaturated with respect to illite solubility. Under these conditions, illite crystals would have a spiral growth pattern, which follows a second-order rate equation. Spiral growth would result in few stacking faults and would be expected to take place, for example, either in relatively dilute hydrothermal systems or in regionally metamorphosed terrains in which the degree of illite supersaturation was a function of illite particle-size distributions as illite underwent Ostwald ripening (Eberl & Środoń, 1988). This growth mechanism has been identified by electron microscope investigations of clay crystals formed by hydrothermal metasomatism (Sunagawa *et al.*, 1975).

Researchers studying low-grade metamorphic rocks in the Eastern Alps have reported that illites from shale have a larger Kubler index (*i.e.* a smaller n) than do illites from adjacent carbonate rocks (Krumm, 1984; Kralik *et al.*, 1987). Reasoning from crystal growth theory, one can speculate that pore solutions in the shale were more highly supersaturated with respect to illite than were pore solutions in the carbonates, thereby yielding a smaller n and a larger Kubler index for illites formed in the shale. In addition, different crystal growth rates for illites in different chemical environments might result in differences in expandability and, therefore, in different Kubler indices for illites that have been subjected to the same P-T conditions.

The obvious disadvantage to using the proposed methods is that it is more time consuming than is the Kubler method. However, the proposed method provides more information concerning metamorphic trends in the anchizone and diagenetic zone, particularly in comparing rocks from different regions. An even more detailed method than the method proposed here would be to measure actual particle-size distributions for illites, an approach that has been discussed in a recent paper (Eberl & Środoń, 1988).

ACKNOWLEDGMENTS

DDE thanks the French Centre National de la Recherche Scientifique for supporting four months of research at the Ecole Normale Supérieure. The authors thank Joan Fitzpatrick, Martin Kralick, R.J. Merriman, P.H. Nadeau, Richard Pollastro, Jan Środoń, Philip Rosenberg and M.J. Wilson for reviewing the original manuscript, and Martin Frey and Graham Thompson for providing the illite and glauconite samples used.

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