

MODIFICATION OF ILLITE–MUSCOVITE CRYSTALLITE-SIZE DISTRIBUTIONS BY SAMPLE PREPARATION FOR POWDER XRD ANALYSIS

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ABSTRACT

Mean crystallite sizes of illite–muscovite have been obtained by direct measurements using TEM on ion-milled (original rock) samples and separates prepared for XRD analysis, and by XRD profile analysis of separates in a prograde sequence of metapelites from southern New Zealand. The mean crystallite sizes determined by the analyses of XRD peak profiles increase with metamorphic grade, consistent with the trend determined by TEM from ion-milled rock samples. However, the sizes obtained by TEM on the ion-milled rock samples are approximately two to four times larger than those by XRD profile analyses. This difference is greater in higher-grade than lower-grade samples. The mean sizes of crystallites measured using TEM on the separates that were used to obtain XRD profiles correspond well to those from XRD profile analyses. Further TEM and AFM observations of separates show that crystals have been broken across and cleaved along (001) planes. These relations indicate that the XRD data were obtained from samples that differ significantly from the original rock samples; the data indicate that sample preparation for XRD analysis significantly altered the original size-distributions. Crystallite-size distributions are poor approximations to lognormal in original rocks, but are modified to lognormal or nearly lognormal distributions in separates. Interpretation of growth conditions from size distributions of separates is therefore subject to error. Only size distributions of unseparated samples, or separates where the effects of the separation process are known, should be used as indicators of growth conditions.

Keywords: illite–muscovite, crystallite size, size distribution, XRD analysis, TEM measurement, diagenesis, low-grade metamorphism, anchizone, epizone, New Zealand.

SOMMAIRE

Nous avons mesuré la taille moyenne des cristallites d'illite–muscovite directement en microscopie électronique par transmission (TEM); nos mesures ont porté sur des échantillons de roche amincis par faisceau d'ions et sur des fractions séparées telles que préparées pour analyse par diffraction X, et par l'analyse de profils de ces séparés en diffraction X dans une séquence prograde de métapelites provenant du sud de la Nouvelle-Zélande. La taille moyenne des cristallites, telle que déterminée par l'analyse de profils en diffraction X, augmente avec l'intensité du métamorphisme, ce qui concorde avec les observations faites par TEM sur échantillons de roche amincis. Toutefois, la granulométrie mesurée par examen en TEM des sections de roches est plus grossière par un facteur de deux à quatre que celle déduite à partir des profils de pics en diffraction X. Ce décalage est plus important dans les échantillons de roches recristallisées à un degré de métamorphisme plus élevé. En revanche, la taille moyenne des cristallites observée en analyse TEM des séparés utilisés pour obtenir les profils en diffraction X correspond à celle qui est déduite de l'analyse des profils de pics en diffraction X. Nos études des séparés impliquant TEM et la microscopie utilisant les forces atomiques montrent que les cristaux ont été brisés au travers du plan (001) et clivés le long de ce plan lors de la séparation. Ces observations montrent que les données de diffraction X ont été obtenues sur des matériaux qui diffèrent sensiblement des

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roches originales. La préparation des échantillons pour l'analyse par diffraction X modifie sensiblement la distribution originale de la taille des grains. La distribution est au départ une faible approximation d'une distribution lognormale dans les roches originales, mais elle devient davantage lognormale ou quasiment lognormale dans les séparés. L'interprétation des conditions de croissance à partir de la distribution de la taille des grains des séparés peut donc mener à l'erreur. On doit s'en tenir aux seules distributions de tailles de grains des échantillons non séparés, ou des séparés dans lesquels les effets du processus de séparation ont été documentés, pour en déduire les conditions de croissance.

(Traduit par la Rédaction)

Mots-clés: illite–muscovite, taille des cristallites, distribution des tailles, analyse par diffraction X, mesures par microscopie électronique par transmission, diagenèse, métamorphisme de faible intensité, anchizone, épizone, Nouvelle-Zélande.

INTRODUCTION

Phyllosilicates are abundant in sediments, and in sedimentary and very low-grade metamorphic rocks. They generally have large surface-areas and exhibit a broad range of crystallite sizes. Since the sizes and the size distributions of crystals in rocks are controlled by and contain information about 1) original conditions of crystallization and 2) later modifications in response to environmental changes, it is widely accepted that crystallite size is an approximate indicator of grade of diagenesis and metamorphism (*e.g.*, Spry 1969, Cashman & Ferry 1988, Eberl *et al.* 1990). One therefore would like to measure the sizes of phyllosilicate crystallites in order to relate them and their distributions to geological events. Most measurements have been made using X-ray diffraction (XRD, *e.g.*, Kodama *et al.* 1971, Árkai & Tóth 1983, Eberl & Środoń 1988, Eberl *et al.* 1990), transmission electron microscopy (TEM, *e.g.*, Nadeau *et al.* 1984, Merriman *et al.* 1990, Árkai *et al.* 1996, Jiang *et al.* 1997) and, in a few cases, by atomic force microscopy (AFM, *e.g.*, Lindgreen *et al.* 1991).

Both powder XRD analysis and TEM methods have advantages and disadvantages. Because it is efficient and relatively inexpensive, powder XRD analysis is the most frequently used method for studying phyllosilicates. With appropriate assumptions and the aid of computer programs, XRD peak profiles of microcrystalline phyllosilicates have been deconvoluted to obtain mean size of the crystallites, distribution of crystallite sizes, and lattice strains. Kodama *et al.* (1971) developed a Fourier analysis of XRD profiles to establish the mean sizes of coherently scattering domains of microcrystalline muscovite. More recently, the Warren–Averbach technique (Warren & Averbach 1950), the Scherrer equation (Klug & Alexander 1974), Wilson's variance method (Wilson 1962, 1963a), and the Voigt single-line method (Langford 1978) have been used to determine the size of crystallites, their size distributions, and lattice strain of illite and other phyllosilicates (*e.g.*, Árkai & Tóth 1983, Eberl & Środoń 1988, Eberl *et al.* 1990, Merriman *et al.* 1990, Árkai *et al.* 1996, Warr 1996). On the other hand, the advantages of XRD are offset by several disadvantages. For example, the val-

ues obtained are indirectly measured (as opposed to direct observation by TEM) on the basis of mathematical functions that contain various approximations; the determinations are based on models with inherent assumptions, as pointed out by Lanson & Kübler (1994) and Árkai *et al.* (1996). In contrast, the size of phyllosilicate crystallites can be directly measured from high-resolution TEM images. The results obtained by the TEM method are likely to be more accurate, although they might be less precise owing to counting statistics. The TEM method has been used extensively despite the tedious nature of sample preparation and data measurement. Among the various studies in which both methods were used to obtain crystallite sizes, some investigators obtained satisfactory agreement between the two methods (*e.g.*, Eberl & Środoń 1988). In other cases, especially for the more strongly metamorphosed rocks, however, the crystallite sizes measured by TEM do not correlate well with those obtained by XRD profile analysis, the former usually being larger (*e.g.*, Merriman *et al.* 1990, Lanson & Kübler 1994, Jiang *et al.* 1997). With the exception of a few studies in which ion-milled rock samples (original textures retained) were used (Merriman *et al.* 1990, Nieto & Sánchez-Navas 1994, Árkai *et al.* 1996, Jiang *et al.* 1997), TEM measurements have commonly been made on "separates", *i.e.*, samples that have been physically disarticulated during preparation (*e.g.*, Nadeau *et al.* 1984, Inoue *et al.* 1988, Eberl *et al.* 1990). These separates also were used to obtain powder XRD patterns for profile analysis. Jiang *et al.* (1997) used TEM to compare thicknesses of illite crystallites (separates) in samples prepared for XRD analysis with original, non-disarticulated samples from a prograde sequence of pelitic rocks; they found that crystallites are up to five times thinner in the XRD samples than in the original rock samples, although both gave similar trends of increasing size of the crystallites with increasing metamorphic grade.

With increasing numbers of studies of the chemical, structural, and textural aspects of clay minerals and phyllosilicates from diverse environments, questions concerning their sizes and size distributions remain unanswered in light of conflicting results from TEM and XRD. In order to assess the true nature of the phyllosilicate-size distributions, samples from a prograde

sequence of pelitic rocks from southern New Zealand were studied by both XRD and TEM methods. XRD profiles were analyzed to derive the mean sizes of illite-muscovite crystallites using the Voigt single-line method (Langford 1978, de Keijser *et al.* 1982) and Scherrer equation. TEM observations of ion-milled rock samples were used to measure the thickness of illite-muscovite crystallites. We also used TEM to measure the thickness of illite-muscovite crystallites in separates of the same samples, but as prepared for XRD analysis. In this study, XRD-determined values are compared with the results measured by TEM. Crystallite-size distributions are presented and compared by different methods. The effect of sample preparation for XRD analysis on the crystallite-size distribution is evaluated using these data. The following three kinds of relations are quantified: 1) correlation of TEM-measured and XRD-determined mean sizes of crystallites in separates, 2) correlation of TEM-measured mean size of crystallites in separates and those in rock samples (original texture retained), and 3) correlation of TEM-measured crystallite-size distributions in separates and those in rock samples.

MATERIALS AND METHODS

Materials

A suite of 93 samples was collected from the prograde sequence within the Otago Schist and the Caples Terrane of southern New Zealand. A subset consisting of four pelitic samples with the greatest amounts of phyllosilicates was subsequently selected for the present study. The samples were chosen to cover a large range of illite crystallinity in a prograde sequence in rocks with similar bulk-compositions (Li 1996, Li *et al.* 1999). The dioctahedral phyllosilicates consist of illite and phengitic muscovite only; Na-rich white mica is absent. Powder XRD patterns from glycolated <2- μm fractions indicate only minor smectite in very low-grade samples. The values of illite crystallinity therefore have no contributions from other 1-nm phyllosilicates. The selected samples represent a range of low-temperature metamorphic conditions, varying from the prehnite-pumpellyite facies, through the pumpellyite-actinolite facies, to the chlorite zone of the greenschist facies. The

illite crystallinity indices ($\Delta 2\theta$ 0.47 to 0.18 $^\circ$) of these samples correspond to the diagenetic zone (sample D11.1), anchizone (samples D8.2 and D6), and epizone (sample D2), respectively, with a generally good correlation between decreasing illite crystallinity indices and increasing diagenetic and metamorphic grade (Table 1).

Quartz, chlorite (or stilpnomelane), illite (or muscovite), and albite are the principal minerals in these samples. In the lowest-grade sample (D11.1), coarse-grained detrital phyllosilicates and fine-grained authigenic illite and chlorite form a compactional fabric parallel to bedding. In higher-grade rocks, dissolution of detrital minerals and recrystallization of metamorphic phyllosilicates led to strong preferred orientation parallel or subparallel to bedding, resulting in slaty cleavage. The white micas vary from immature illite in the diagenetic zone to mature phengitic muscovite in the anchizone and epizone. Details of the geological background and descriptions of phyllosilicates in these rocks are given by Li (1996) and Li *et al.* (1999).

XRD analysis

Samples for XRD analysis were initially hammer-crushed and gently reduced further using a mortar and pestle, with frequent use of sieving, followed by centrifugation to obtain <2- μm fractions. Such <2- μm fractions are described as "separates" below. Slides of oriented separates were prepared by a pipette method. All powder XRD data were obtained for air-dried and ethylene-glycol-solvated <2- μm fractions using a Philips XRG 3100 automated diffractometer (at the Department of Geological Sciences, University of Michigan) and $\text{CuK}\alpha$ radiation at 35 kV and 15 mA. The diffractometer is equipped with a theta-compensating slit with a maximum divergence angle of 1 $^\circ$, a receiving slit of 0.2 mm (~0.15 $^\circ$), a graphite crystal monochromator, and a scintillation detector. A step size of 0.01 $^\circ$ 2θ and a counting time of ~6 seconds were used to obtain patterns of high intensity. Quartz was used as an internal standard. Variations in half-height peak widths among patterns recorded for each sample at different times are within $\pm 2\%$ of the mean value. Repeated measurements on the polished interlaboratory standards varied by <4% from those of Kisch, in which 0.38 and 0.21 $^\circ$ $\Delta 2\theta$ are the limits for the anchizone (Kisch 1990).

TABLE 1. ILLITE CRYSTALLINITY INDICES OF PELITIC ROCK SAMPLES (<2 μm FRACTIONS) FROM SOUTHERN NEW ZEALAND

	Metamorphic facies ¹	Illite crystallinity ($^\circ\Delta 2\theta$)		Diagenetic/metamorphic grade
		air-dried	glycolated	
D11.1	Pr-Pmp	0.47	0.46	Diagenetic zone
D8.2	Pmp-Act	0.30	0.27	Anchizone
D6.3	Pmp-Act	0.24	0.23	Anchizone
D2	Chl	0.18	0.18	Epizone

¹ Pr-Pmp: prehnite-pumpellyite facies; Pmp-Act: pumpellyite-actinolite facies; Chl: chlorite zone of the greenschist facies.

Kisch's limiting values for the anchizone are employed in this study.

TEM measurements

Sticky-wax-mounted thin sections were prepared from rock chips for TEM observations. Thin sections were cut perpendicular to both bedding and cleavage to obtain optimum orientation for TEM (001) lattice-fringe images of phyllosilicates. Images were obtained from the thin edges of carbon-coated, ion-milled specimens prepared following the method described by Li *et al.* (1994). For the diagenetic-zone sample, TEM observations were made on areas with representative authigenic illite, *i.e.*, areas free of detrital, coarser-grained white micas. Identification was based on textural relations, characteristic d -values of 001 lattice fringes, electron-diffraction patterns, and chemical compositions from analytical electron microscopy (AEM) analysis (Li 1996). For higher-grade samples, contamination by detrital white mica was less of a problem because of dissolution of detrital minerals and recrystallization of metamorphic phyllosilicates (Li 1996). Separates of XRD samples were embedded within two layers of resin to form "sandwiches", with subsequent ion milling to obtain TEM specimens. The TEM observations were made using a Philips CM12 scanning transmission electron microscope (STEM) fitted with a Kevex Quantum solid-state detector and computer system and a JEOL 2000FX TEM. The Philips CM12 STEM and the JEOL 2000FX TEM were operated at accelerating voltages of 120 and 200 kV, respectively.

Crystallite size is defined as the dimension of a coherently diffracting domain in the direction perpendicular to the diffracting plane (Klug & Alexander 1974). Size variations in other directions do not affect the diffraction relations for the plane of interest, but should be considered in integrating intensity. This integration is necessary because mean size of the crystallites derived from XRD-defined peak widths at half-maximum heights or integral widths are average values weighted by domain volumes or domain areas, not by numbers of domains (Guinier 1963, Wilson 1963b, Klug & Alexander 1974, Árkai *et al.* 1996). In illite-muscovite crystals, coherently scattering domains parallel to c^* are equal to the defect-free distances along this direction. For crystallite-size determination using the TEM approach, measured dimensions include the thicknesses parallel to c^* and the lengths parallel to the basal planes of illite-muscovite as observed in lattice-fringe images. Because the crystallites are much longer than they are thick, not all high-magnification lattice-fringe images contain both ends of the crystallites, especially in higher-grade samples. We therefore measured lengths from the low-magnification images if they could not be obtained from the high-resolution ones. Similar to the data in Warr & Nieto (1998), the lengths of the illite-muscovite crystals are considered as minimum values.

As the thickness commonly varies within a single crystallite, multiple measurements (usually 2 to 7 counts per crystallite) of thickness were made along the length of the grains. The mean thickness of the crystallites was then calculated based on 680 to 1341 domains per sample. For purposes of comparison, all TEM data presented in this study are area-weighted because the methods for determination of crystallite sizes by XRD analysis yield area-weighted values.

The TEM data were obtained from very small samples, so there is a question whether they are representative of the regional metamorphic trend. In order to optimize the probability that observations are typical of a given sample or grade, great care was taken in the choice of samples. Only samples typical of given outcrops were chosen, the grade subsequently having been confirmed as consistent with the known prograde trend. Such samples are uniform in texture at the hand-specimen level. Bulk XRD measurements determined the average mineral contents, and SEM observations of thin sections then verified that the areas subsequently chosen for TEM observations were uniform in texture and typical in mineral content. In addition, more than one thin section from each sample was used for TEM observations. Nevertheless, although the results for individual samples are relatively precise, there is a possibility of small inaccuracies as a result of lack of representation of TEM samples relative to bulk specimens, or of separates relative to ion-milled samples. However, the TEM observations are compatible with mineral relations in bulk samples, and the mineral relations vary in a regular and predictable way as a function of grade, indicating that they are accurate measures of the desired variables.

XRD profile analysis

The apparent mean size of the crystallites and lattice strains of illite-muscovite were calculated from line-profiles of the first-order (1 nm) XRD basal reflections, based on the Voigt method of Langford (1978), as modified for the Philips APD-1700 software package. The structural profiles of the basal reflections were calculated using the Stokes (1948) deconvolution method based on Fourier coefficients, which utilizes Fourier transformations of the line-profiles obtained from samples being investigated and from "standard" samples. Final calculations were performed on the profiles corrected for a standard-determined instrumental effect, and therefore were theoretically devoid of such effects. As compared to the original application of the Voigt match (Langford 1978), this procedure, also called single-line Fourier analysis, has the advantage that no errors in integral widths caused by the finite size of the crystallites and lattice strain can arise from the deconvolution itself, since Stokes's deconvolution uses no assumptions on the shapes of the sample and "standard" profiles. On the other hand, the Langford (1978)

method assumes that both profiles can be described by Voigt functions. The line-broadening caused by small crystals is described by a Cauchy (or Lorentzian) type function, whereas that caused by lattice strain is described by a Gaussian function. The integral width values resulting from these two components can be obtained from a parabolic fit to the natural logarithms of the Fourier coefficients of the structural profile. The linear coefficient is proportional to the Cauchy function, whereas the parabolic coefficient is related to the Gaussian contribution to line broadening. Having obtained these two integral width values, one can use the appropriate Scherrer equation to calculate crystallite size and strain [further details are provided in the manual of the Philips APD-1700 software package and by Árkai *et al.* (1996)]. This single-line method was applied using the IBM-PC program written by Attila Nagy for the Laboratory for Geochemical Research, Budapest. A cleavage plate of coarse muscovite from a granitic pegmatite was used as standard.

RESULTS

TEM observation of illite–muscovite in ion-milled rock samples

Typical microstructural features of illite–muscovite in ion-milled rock samples have been described by Li (1996). In diagenetic sample D11.1, the matrix phyllosilicates are dominated by fine-grained, defect-rich $1M_d$ illite with a low net negative charge (<1.5 per $O_{20}[OH]_4$), characteristic of typical authigenic illite. Illite commonly occurs as aggregates of coalescing packets of layers locally intergrown with chlorite. Illite aggregates consist of irregularly oriented bundles of thin, parallel or subparallel packets of layers (Fig. 1). The boundaries between single crystals of illite are usually difficult to discern. Crystals of detrital mica are common but easily differentiated from authigenic illite using characteristics including size, polytypism, and composition. In anchizone samples, textures involving

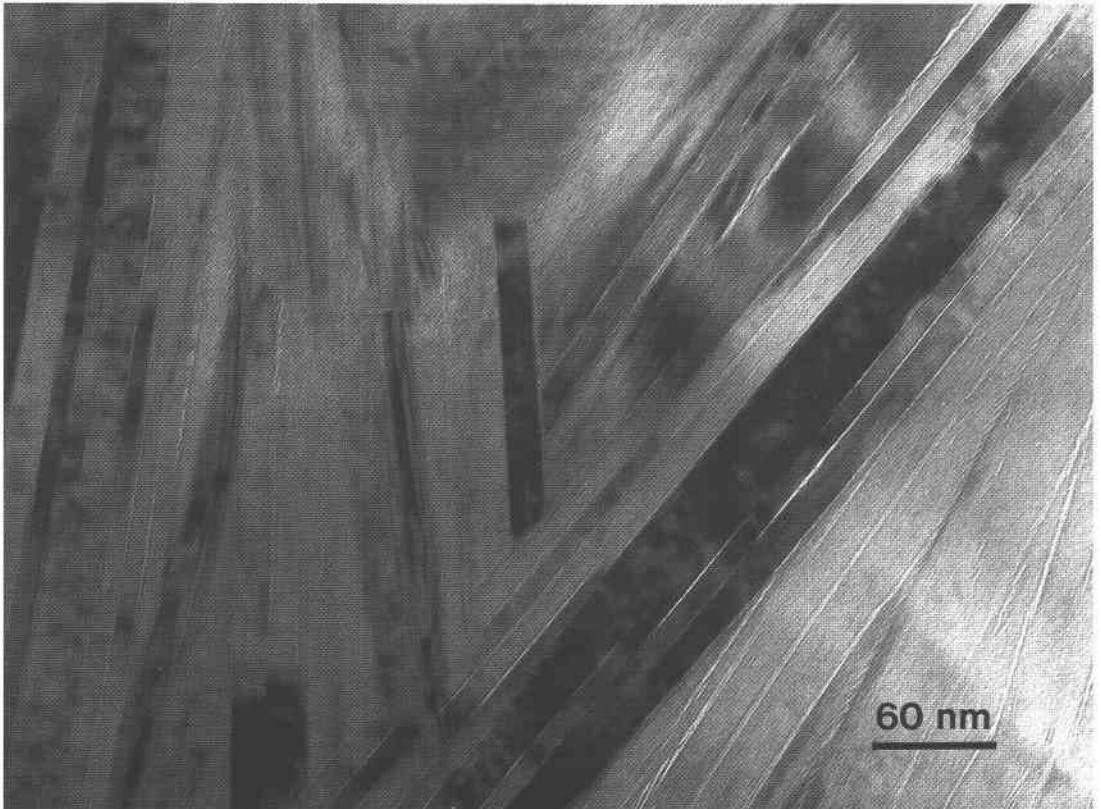


FIG. 1. Low-magnification TEM image showing aggregates of thin packets of illite in sample D11.1, taken from the diagenetic zone.

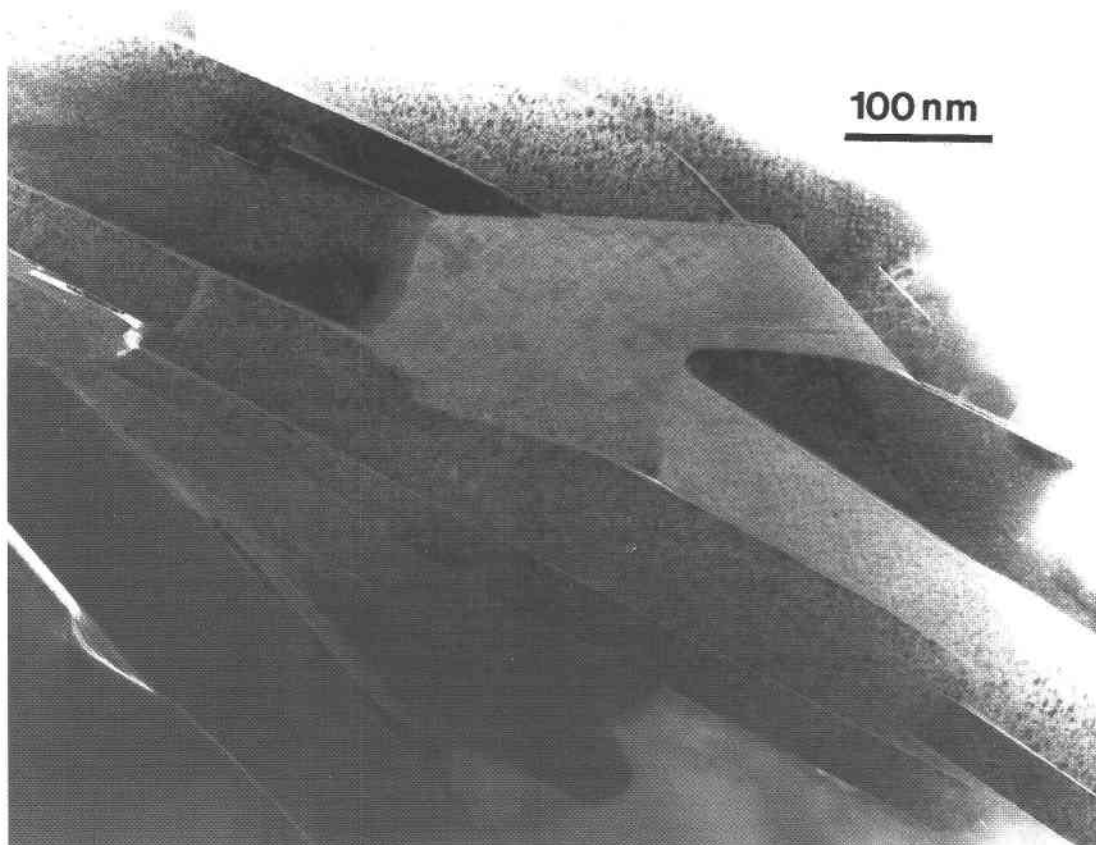


FIG. 2. TEM image showing thick packets of phengitic muscovite, with well-defined crystal boundaries and an interlocking texture, in sample D6, taken from the anchizone.

illite–muscovite vary greatly, ranging from random aggregates of small crystals similar to packets of diagenetic illite, to slightly better-defined small crystals with subhedral platy outlines, to aggregates consisting of large subparallel packets of layers. The proportion of crystal imperfections is relatively small compared to that in illite of the diagenetic zone, and the proportion of $2M_1$ relative to $1M_d$ polytypes increases from diagenetic to anchizone rocks. In the epizone, dioctahedral phyllosilicates consist of only $2M_1$ muscovite and are dominated by large crystals. They typically occur as thick packets of layers having well-defined boundaries, lacking (or almost lacking) defects and strain features. Some packets occur as parallel aggregates that form thick stacks, and others are related by interlocking features with high-angle boundaries (*e.g.*, Fig. 2). Large euhedral crystals of muscovite as thick as $1\ \mu\text{m}$ occur in the epizone (Fig. 3). In contrast to $1M_d$ illite in lower-grade samples, $2M_1$ muscovite in higher-grade samples has a net negative charge near that of nearly ideal mus-

covite. No micas having the characteristics of detrital mica were observed in such samples, and authigenic and detrital material with an orientation approximately parallel to bedding had been eliminated by dissolution, with neocrystallization in an orientation determined by tectonic stress.

The TEM-measured sizes of illite–muscovite crystallites in ion-milled rock samples are shown as frequency distributions in histograms in Figure 4. Illite in the diagenetic zone is clearly dominated by thin domains, approximately 90% of the crystallites having a thickness $<50\ \text{nm}$. In anchizone samples D8.2 and D6, the muscovite has mean crystallite thicknesses of 74 and 128 nm, and about 75% and 50% of crystallites have thicknesses $<100\ \text{nm}$, respectively. In epizone sample D2, the mean thickness of crystallites is about 337 nm, with only about 13% of crystals being $<100\ \text{nm}$, and more than 60% of crystals having a thickness $>200\ \text{nm}$, clearly demonstrating a strong trend of increasing crystallite-size with metamorphic grade. The distribu-

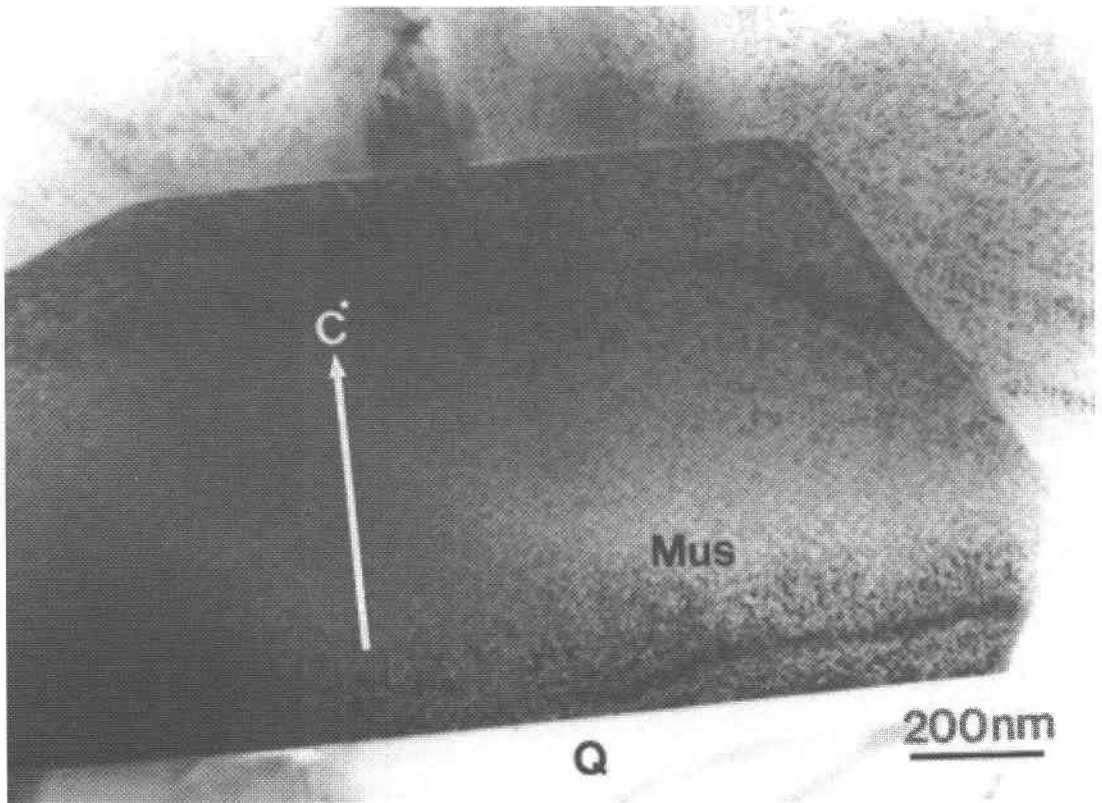


FIG. 3. Low-magnification TEM image of large crystal of muscovite with straight, defect-free layers and a well-defined outline in sample D2, taken from the epizone. The thickness of such defect-free layers can be as great as 1 μm .

tions are positively skewed toward larger thicknesses for diagenetic and anchizonal samples. Compared to diagenetic illite, the patterns of anchizonal samples D8 and D6 indicate a significant spread of the distribution profile toward larger thicknesses. However, the epizonal sample shows no apparent concentrations of domain sizes, but has a trend toward greater numbers of thick crystallites. In general, the size distributions tend to broaden and flatten, and their amplitudes tend to decrease and shift toward larger thicknesses; the profiles are positively skewed, indicating greater thicknesses with increasing metamorphic grade.

TEM observation of illite–muscovite in separates

In contrast to the relative difficulty in identifying the outlines of crystals in ion-milled (especially diagenetic) rock samples, measurements of crystallite sizes in separates are less difficult because illite–muscovite crystals in clay separates of all samples have sharply defined parallel or subparallel boundaries. Crystals are relatively defect-free compared to those in ion-milled rock samples,

perhaps owing to breakage along the intracrystalline layer terminations during separation, as also observed by Jiang *et al.* (1997). Many crystals in TEM images exhibit the influence of the (001) cleavage (Figs. 5, 6). In addition, thin packets of layers are split, bent, curved, or twisted, especially at the ends or edges of crystals (Fig. 6). Such features are rare in illite–muscovite from ion-milled rock samples. AFM images show that muscovite crystals in separates of anchizonal and epizonal samples have cleaved not only along but also have broken across (001) planes. Consequently, a decrease in length:thickness ratios of the crystallites is observed in separates relative to those in ion-milled rock samples.

Figure 7 shows frequency-distribution histograms of TEM-measured crystallite sizes of illite–muscovite from separates. In contrast to the variable distributions observed in ion-milled rock samples, all the separate samples show similar distributions, skewed to larger crystallite sizes. The median is smaller than the mean in all cases. Both the mean and median thicknesses of the measured populations increase and the distribution of thicknesses spreads out as metamorphic grade increases,

as do those of the ion-milled rock samples. However, the absolute values are significantly different from those of rock samples. With the exception of the diagenetic-

zone sample, in which the mean thicknesses of illite in separates is only slightly smaller than that in ion-milled rock samples, the mean thicknesses measured in separates of anchizone and epizone samples are up to four times smaller than those measured in ion-milled rock samples. The differences are greater for the epizonal and anchizonal samples, and smallest for the diagenetic samples.

XRD analysis and comparison with TEM results

The mean crystallite sizes and mean lattice strains determined from XRD profile analyses and mean crystallite sizes measured by TEM are listed in Table 2. Values of mean lattice strains determined by peak-profile analysis show a decreasing trend with increasing metamorphic grade, consistent with the observation of decreasing number of crystal defects in illite-muscovite with increasing grade by TEM on ion-milled rock samples (Li 1996) and similar trends described by others (e.g., Peacor 1992, Árkai *et al.* 1996, Jiang *et al.* 1997). For samples of the same rocks, the mean size of crystallites measured for separates by TEM and XRD are of the same order of magnitude. Correlation of the averages of mean sizes calculated using the XRD Voigt single-line method and Scherrer equation with those measured by TEM from the same separation yields nearly a 1:1 linear relationship: $T_{XRD} = 0.980T_{TEM} - 0.835$, $R^2 = 0.840$. On the other hand, differences between values obtained from TEM and XRD analysis of separates are small compared to differences relative to those measured on ion-milled rock samples (Table 2). The mean sizes determined by the two methods are different for all samples. The mean thickness of the crystallites measured by TEM on ion-milled rock samples is much larger than those determined by XRD profile analysis; these differences are about a factor of two to three in diagenetic and anchizonal samples and up to four in epizonal samples. However, XRD-determined mean size of crystallites increases with increasing metamorphic grade, consistent with the trend determined by TEM measurements.

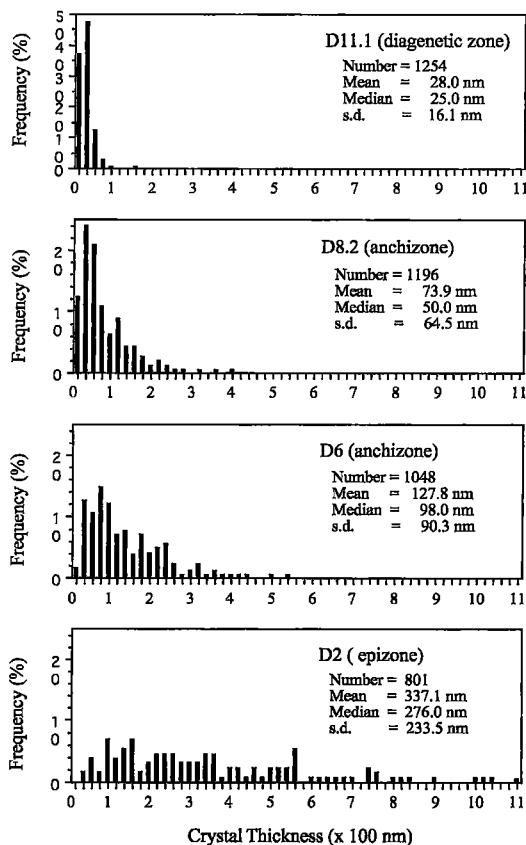


FIG. 4. Frequency histograms showing distributions of the thickness of illite-muscovite crystals in ion-milled rock samples, as measured by TEM.

TABLE 2. THICKNESSES OF ILLITE-MUSCOVITE IN PELITIC ROCKS FROM SOUTHERN NEW ZEALAND

	XRD-profile analysis						TEM measurement ¹						
	Voigt single-line method ²			Scherrer equation ³			ion-milled separates		ion-milled rock samples		s.d.		
	thickness mean (nm)	lattice strain (%)	error of fitting ⁵	air-dried mean (nm)	glycolated mean (nm)	domains (no.)	mean (nm)	median (nm)	domains (no.)	mean (nm)		median (nm)	
D11.1	14.4	1.68	0.13	17.9	18.3	1341	23.9	21.0	12.6	1254	28.0	25.0	16.1
D8.2	45.2	0.61	0.03	30.4	32.9	927	29.9	26.0	16.1	1196	73.9	50.0	64.5
D6	49.1	0.54	0.02	39.5	41.5	680	47.1	40.0	26.1	1048	127.8	98.0	90.3
D2	79.1	0.44	0.10	61.2	61.2	845	69.4	52.0	53.6	801	337.1	276.0	233.5

¹ All TEM data are area-weighted.

² Data were obtained on air-dried samples.

³ Scherrer equation: thickness = $K\lambda/\beta\cos\theta$ where $K = 0.89$, $\lambda = 1.5418$, $\theta = 4.42$, and β is peak broadening in radians derived from peak half-height width (Klug & Alexander 1974).

⁴ Standard deviation.

⁵ Error of fitting a parabola to the natural logarithms of Fourier coefficients of the line profile devoid of instrumental broadening.

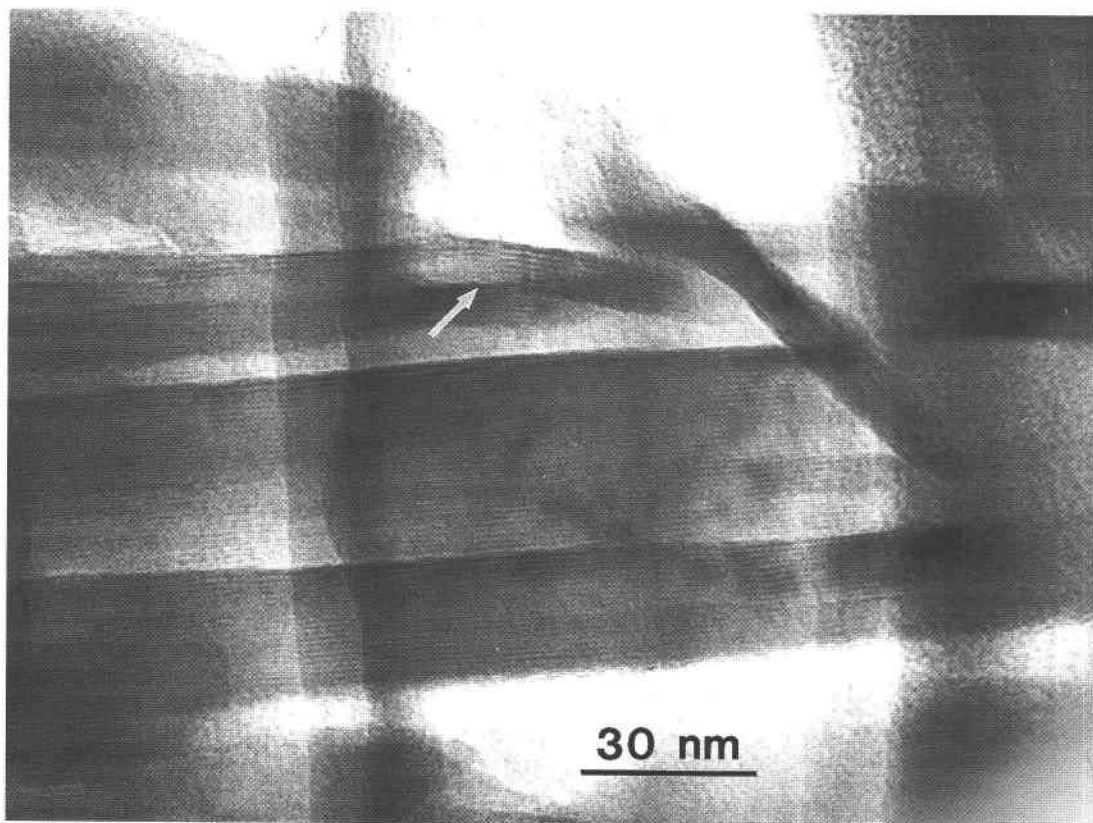


FIG. 5. TEM image showing texture of a muscovite crystal cleaved along layers in separates of sample D6, taken from the anchizone. The white arrows indicate damage due to initial crushing.

Lognormality test of size distributions measured by TEM

All of the ion-milled rock and separate samples give size distributions skewed to the larger crystallite sizes in frequency histograms. In most cases, the mode is smaller than the median, and the median is smaller than the mean, indicating possible lognormal distributions. A lognormal distribution is defined for a positive random variable X (with two parameters μ and σ^2) if $Y = \ln X$ is normally distributed with mean μ and variance σ^2 (Shimizu & Crow 1988). As a check of lognormality in the two-parameter cases, the skewness (g_1) and kurtosis (g_2) tests of normality can be applied to the transformed sample values. Normally distributed data should not possess significant g_1 skewness and g_2 kurtosis; therefore the smaller these absolute values, the closer are the data to normal distributions (Hipel *et al.* 1977).

In order to test for the approach of crystallite-size distributions to lognormal functions, the measured

thicknesses were converted to logarithmic form (*i.e.*, we used $Y_i = \ln X_i$ instead of X_i for each observation). The results from both ion-milled rock samples and separates are plotted in frequency-distribution histograms (Fig. 8). The data demonstrate a significant increase of log-transformed values with increasing metamorphic grade for both rock and separate samples, as do the measured thicknesses. The distributions of transformed values for the ion-milled rock samples are either asymmetrical or asymptotic; *e.g.*, the size distribution of muscovite in rock sample D2 has an irregular profile that does not correspond to any simple function. However, the transformed values for separates are almost all symmetrical and nearly normally distributed. The data suggest a change in crystallite-size distribution during sample preparation for XRD analysis, with the lognormality being increased for separates. When data from the same rocks are compared, this increase can also be verified by the generally decreasing absolute values of g_1 skewness and g_2 kurtosis from ion-milled rock to separate samples. The changes appear to be more significant

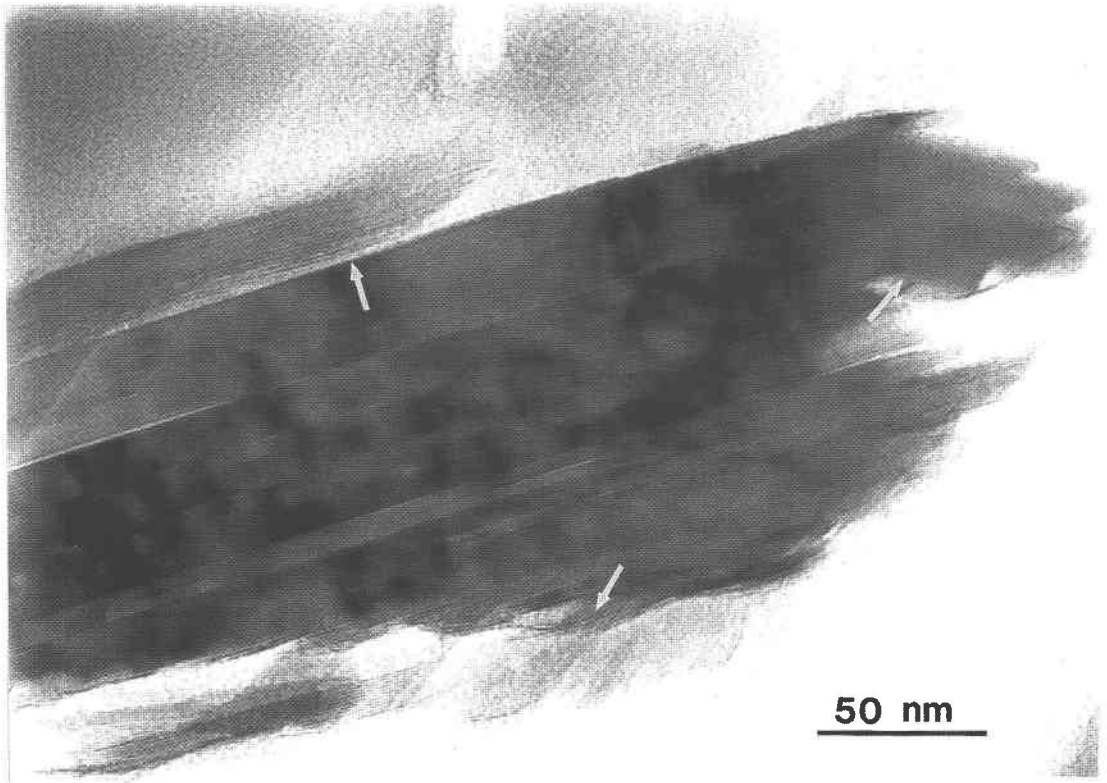


FIG. 6. TEM image of separates showing the texture of a muscovite crystal cleaved along layers in sample D6, taken from the anchizone. Packets of layers are bent and twisted along edges (indicated by white arrows); the outlines are not as straight as in the case of ion-milled rock samples.

for higher-grade samples, especially in the case of g_1 skewness.

DISCUSSION

Overview

The results described can be briefly summarized as follows: 1) With increasing diagenetic – metamorphic grade, the mean size of illite–muscovite crystallites from pelitic rocks increases. 2) There is a fairly good agreement between the data on mean crystallite-size calculated from XRD line profiles and those directly measured by TEM on the same material (*i.e.*, the $<2 \mu\text{m}$ separates). 3) In contrast, there are significant differences in mean crystallite-sizes determined either by XRD or TEM in separates and determined by TEM on selected portions of ion-milled whole-rock samples, the differences being greater in higher-grade samples. 4) There are systematic differences in crystallite-size distributions determined by TEM in the selected portions of the whole-rock samples and in the separates,

the differences also being greater with increasing grade. The size distributions in separates better approximate the lognormal type, whereas those in the whole-rock samples are rather irregular.

We interpret these data to imply that the separation process significantly alters the form of the crystal-thickness distribution, especially as measured by the mean size of crystallites, and that the cause is cleavage and breakage of original coherent crystals in the rock. That interpretation is discussed in detail below. Before discussing such relations, however, it is necessary to clarify some relations concerning the possible effects of separation. Most importantly, L.N. Warr (pers. commun., 1998) noted "...an alternative interpretation (which) lies toward the other extreme of believing that the damage observed has not significantly altered the true crystallite size of the clay fraction. Such an interpretation is based on the idea that significant differences in the size and distribution of crystallites may result from grain-size separation. Such changes in crystallite-size distributions are to be expected after separating the clay-size fraction from a whole rock, especially if the original sample

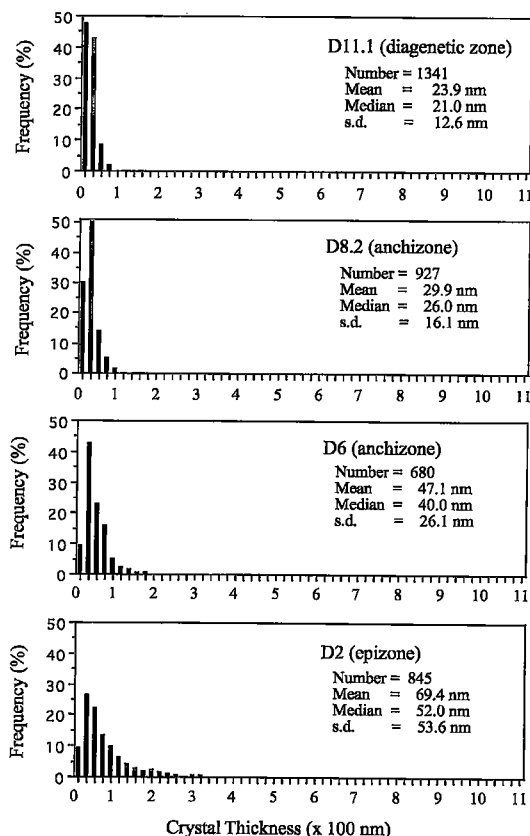


FIG. 7. Frequency histograms showing distributions of the thicknesses of illite-muscovite crystals in separates as measured by TEM. For the purpose of comparison, the horizontal axis is set in the same scale as that in Figure 4.

contains a mixture of size populations (*e.g.*, smaller authigenic and larger detrital components). That the clay-sized fractions have more log-normal distributions than the whole rock could be taken as reflecting the successful concentration of the authigenic growth fraction, which is the very reason why clay mineralogists separate the clay-size fraction in the first place." Warr's analysis refers to problems that might exist in referring a given crystallite-size distribution to a given mode of occurrence. This is a critical issue, as it is the size distributions obtained from separates that are generally used as determiners of relations such as crystal-growth theory and a variety of other relations, assuming that the separates represent (largely) the non-detrital (*i.e.*, authigenic or metamorphic) component.

The samples used in this study were carefully chosen as representative of a single prograde geological sequence, so that the modes of occurrence of the white micas represent a carefully characterized, simple pro-

gression (Li 1996), in order to minimize the contributions of multiple modes of occurrence or origin of white micas. The full sequence has been studied in detail by optical, XRD, SEM, and TEM methods, in part to define textural relations and to identify modes of occurrence of the white micas. In particular, the low-grade samples were observed by TEM to contain only two modes, detrital mica and authigenic illite. Such modes are easily distinguished by TEM and AEM on the basis of size, shape, polytypism, density of defects, and chemical composition. The measured crystal-size distributions exclude detrital grains, and represent only authigenic illite formed during the prograde event, as verified by the small standard deviations from the mean crystallite sizes (Table 2). As grade increases, the texture is modified from that of a sediment with grains preferentially oriented parallel to bedding, wherein detrital and authigenic clays are easily differentiated. The texture evolves to that of a metamorphic rock, in which both detrital and authigenic clays have been eliminated through reaction to give rise to metamorphic mica in a preferred orientation determined by tectonic stress. The crystal-size distributions as measured in ion-milled samples have only a small contribution, if any, from detrital micas. They are therefore realistic measures of the distributions of sizes of the authigenic or metamorphic illite-muscovite in the ion-milled samples, within the bounds of precision of measurements.

On the other hand, in the TEM measurements of crystal-size distributions in separates, we did not consider whether or not a given crystallite was of authigenic or metamorphic origin, or was detrital. In the lower-grade rocks containing detrital mica, there may have been some contribution of detrital crystallites to the size distributions. Because for those rocks especially, the mean size of detrital grains is much greater than that of authigenic crystallites, the separated detrital grains are inferred to also be larger than those for authigenic grains. The detrital component may actually cause the mean size of crystallites in separates to be larger than is true for the authigenic clays only. The effects of separation on the authigenic clays would then actually be more severe than is concluded below. The inclusion of detrital grains in separates could have changed the full crystal-size distributions of course, and therefore have affected the normality of the functions in an unknown fashion.

Because no detrital mica was observed in the higher-grade samples, the distributions measured for separates in this study are valid only for the metamorphic micas. Moreover, even for the highest-grade sample, the mean thickness of the crystallites is only 337 nm, much less than the assumed limiting size for separates of $<2 \mu\text{m}$. This finding implies that the crystal-size distribution for separates of such samples includes only a contribution of the metamorphic variety of white mica.

The above relations demonstrate that the effects of separation described in this study are applicable only to

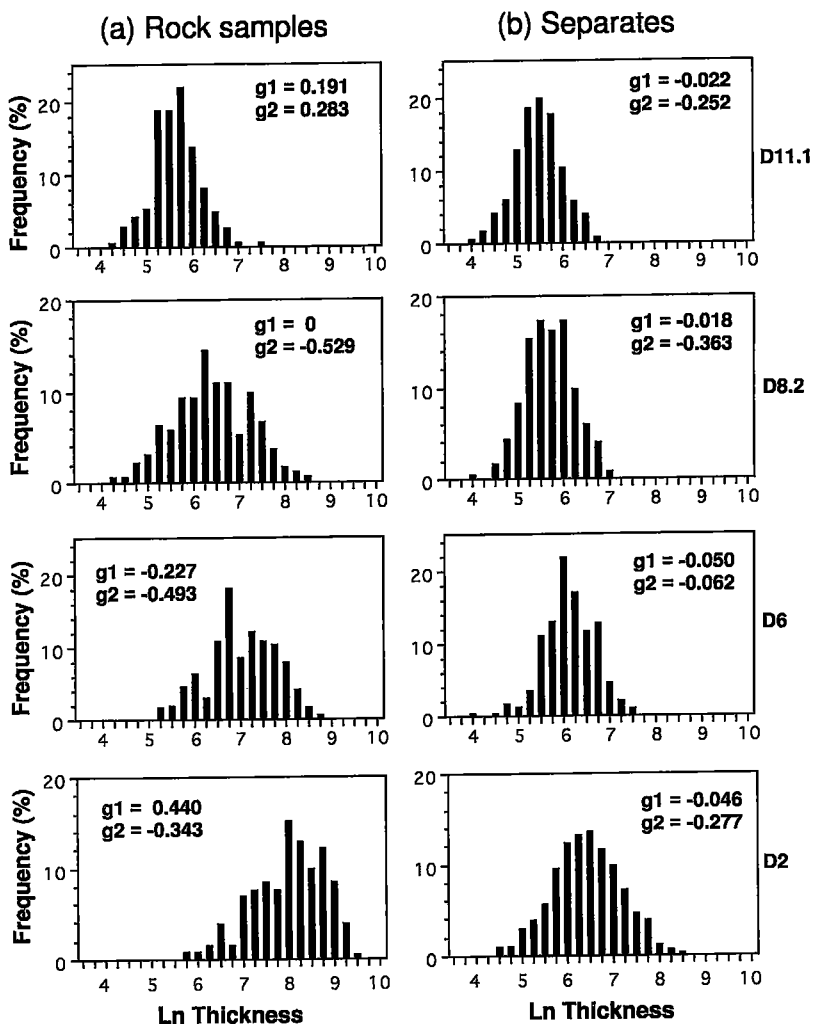


FIG. 8. Frequency histograms for logarithmic thicknesses of illite-muscovite in metapelites from southern New Zealand, as measured by TEM. (a) Ion-milled rock samples. (b) Separates.

the authigenic or metamorphic varieties of white mica, both in ion-milled samples and in separates as measured both by XRD and TEM. Nevertheless, the need for caution as expressed by L.N. Warr (see above) is appropriate for many studies, and the degree to which more than one mode of occurrence contributes to crystal-size distributions of separates should be the subject of detailed future research.

Changes in crystallite size during sample preparation

Despite the markedly different methodologies, the mean sizes of the crystallites independently determined

from XRD and TEM on the same separates are similar (nearly 1:1), and the trends of increasing size with increase in grade for both kinds of values are also similar. We therefore conclude that the Voigt peak-profile analysis, which also included values of strain, yields useful results. In addition, the crystallite sizes determined from full width at half maximum (FWHM) of peaks as a variable in the Scherrer equation are similar to those obtained by TEM and profile analysis (average differences *ca.* 6 and *ca.* 11 nm, respectively; Table 2). This agreement occurs despite the fact that the Scherrer equation assumes that the mean thickness of the crystallites is the only variable affecting FWHM, *i.e.*, there is no contri-

bution from strain. All these data indicate that XRD profile analysis is a reliable method for determining the size of crystallites in separates.

Just because XRD profile analysis provides reasonable measurements of separates, however, does not mean that it yields the original size of crystallites in the materials, which is the aim of our studies; *i.e.*, our primary concern is the crystallite sizes in the rocks rather than their dimensions in laboratory-prepared samples. The sizes in ion-milled rock samples, in which the original textures are preserved, are approximately two to four times greater than those determined using XRD analyses, the difference being greater in higher grades. The shapes and sizes were evidently modified during sample preparation for XRD analysis. TEM and AFM images show incipient cleavage in separates, many grains bounded by cleavages, thin packets that appear to be split apart from and bent or twisted at the ends or edges of crystals, and diminished densities of layer terminations. The latter is consistent with preferential cleavage along strained, but largely coherent planes, as also concluded by Warr & Nieto (1998). Crystals are also broken across cleavage planes, resulting in smaller length-to-thickness ratios in separates than in ion-milled rock samples. The mechanical work necessary to obtain the separates clearly results in reduction of the mean size of crystallites. Such changes are greater in higher-grade rocks, probably as a result of both the larger initial sizes and the interlocking texture typical of higher-grade metamorphic rocks. When disarticulated, such crystals are more likely to break along or across cleavage.

Merriman *et al.* (1990) reported similar thicknesses of illite-muscovite crystallites in XRD- and TEM-measured ion-milled samples from diagenetic mudrock, whereas for anchizonal and epizonal rocks, the mean thickness of crystallites determined by XRD analysis was three times smaller than those measured by TEM on ion-milled rock samples. As the TEM-measured size-distributions for illite crystallites are strongly skewed toward larger crystallite sizes (mode < median < mean), the TEM-measured mode rather than the mean values are correlated with the XRD-determined mean values. Lanson & Kübler (1994) studied micaceous clay from various locations and found that a Warren-Averbach analysis yields results very different from a TEM analysis. XRD-determined sizes of crystallites are much smaller than those measured by TEM. In a study of a prograde sequence of pelitic rocks from the Gaspé Peninsula, Quebec, Jiang *et al.* (1997) demonstrated that the size of illite crystallites measured by TEM on ion-milled rock samples are up to five times larger than those determined by the Voigt XRD profile analysis and TEM on separates, and that a significant cleavage effect exists in separates. Warr & Nieto (1998) examined illite-muscovite in separates prepared by ultrasonic treatment rather than grinding. Their TEM images of separates show similar cleavage-induced effects and much smaller sizes of crystallites than those in ion-milled rock sam-

ples. These collective results imply that mean sizes of crystallites calculated from XRD line profiles obtained from the <2- μm grain-size fraction are not representative of the given low-grade metamorphic rock as a whole, at least those with grades above the diagenetic zone and lower anchizone.

Changes in crystallite-size distributions and their implications for conditions of crystal growth

The mathematical forms of the size distributions are also affected during sample preparation for XRD analysis. As shown by the natural-logarithm transformation of the original data, the lognormality of crystallite-size distributions is much improved for separates compared to the ion-milled rock samples. The change appears to be more significant for higher-grade samples, in which asymptotic size-distributions of crystallites have been modified to lognormal distributions. Consequently, all separates have lognormal distributions independent of their distributions in the rock samples. It is well known that the size distribution of industrial powders produced by milling fine-grained minerals and calcined aggregates often approximates a lognormal distribution function (Reed 1995). It has been shown theoretically that grinding can produce a lognormal distribution for three-dimensional solids independent of the particular kind of size distribution considered, *i.e.*, by volume, linear dimension, or count (Epstein 1947). Although clays are two-dimensional in shape, the same relations that pertain to isotropic solids should be valid for the one-dimensional treatment of clays, *i.e.*, for measures of thickness normal to (001). This study demonstrates that as a result of cleavage, lognormal distributions could be produced by grinding clay minerals during the disaggregation process.

Among the various XRD methods of profile analysis, the Warren-Averbach method is considered by some investigators to be more effective for calculating the size of clay-mineral crystallites, as it can yield size distributions from the diffraction profiles modeled (*e.g.*, Eberl & Środoń 1988, Eberl *et al.* 1990). In most cases, this approach gives a lognormal size-distribution for clay minerals. As reviewed above, such distributions may be caused by sample preparation. Until such cause is shown not to be the case for specific samples and separation methods, the disaggregation process must be inferred to be a major factor in creating size distributions based on the data obtained in this and other studies.

Some published estimates of thickness distributions of illite crystallites determined by XRD and TEM show fairly good agreement between the two methods, and most of these size distributions are strongly skewed, resembling lognormal functions (Eberl & Środoń 1988, Eberl *et al.* 1990). On the basis of Baronnet's work (1982), such distributions were attributed to recrystallization by Ostwald ripening (*e.g.*, Eberl & Środoń 1988, Eberl *et al.* 1990), although others found that Ostwald

ripening is too simplistic a mechanism to explain changes in illite thickness and composition (e.g., Primmer 1994, Merriman *et al.* 1995, Dalla Torre *et al.* 1996, Li 1996). However, most such TEM measurements were made on separates rather than samples in which original textures are preserved. In calculating mean crystallite thickness, some methods of XRD profile analysis require assumptions concerning the shape of the size-distribution function, e.g., the integral peak-width method was developed using a specific model for the evolution of mean thickness of particles with lognormal distribution shape (Drits *et al.* 1997). This assumption may also lead to erroneous results if the original size-distribution shape is different from the assumed one. For example, in a test of XRD methods for measuring illite/smectite thicknesses, mean thicknesses calculated using an integral peak-width method assuming a lognormal distribution gave smaller values than those given by methods without any assumption regarding size-distribution shape (Eberl *et al.* 1998).

The shapes of the normalized distributions have long been considered to be indicative of the growth-controlling mechanism (e.g., Lifshitz & Slyozov 1961, Chai 1974, Baronnet 1982, 1984). The normalized distribution is obtained by replotting histograms of crystallite-size distribution in terms of the reduced coordinates: f/f_{\max} and r/r_{mean} , where f is the frequency of occurrence of a given particle radius, f_{\max} is the maximum frequency encountered, r is the particle radius, and r_{mean} is the mean particle radius. Ostwald ripening involves the reduction of surface free-energy resulting from simultaneous dissolution of small crystals and enhanced growth of large crystals in an isochemical system (Ostwald 1900). Necessary, but not sufficient, proof that Ostwald ripening has taken place is given by a steady-state profile that is independent of ripening time and of initial crystallite-size distribution (Lifshitz & Slyozov 1961). For mechanisms of crystal growth governed by surface kinetics with reaction orders greater than one, frequency distributions tend to be lognormal, but the shapes of the curves depend on the order of kinetics of the crystal-growth mechanism. Where the frequency maximum occurs at r/r_{mean} values less than one in the reduced coordinates plot, the distribution is consistent with surface-controlled reaction kinetics with reaction orders greater than one (Chai 1974, 1975, Baronnet 1982, Morse & Casey 1988), as demonstrated by the experimental work of Baronnet (1982, 1984), who found that phlogopite grows by surface-controlled second-order kinetics.

The crystallite-size distributions obtained by TEM are plotted in reduced coordinates, including both separates and ion-milled rock samples, in Figure 9. In all cases, the frequency maximum occurs at r/r_{mean} values less than one, and approximately steady-state profiles are found for the separates but not for the ion-milled rock samples. The shapes of the grain-size distributions of separates appear to match the theoretical profiles cal-

culated for surface-controlled second-order kinetics, i.e., with a growth rate controlled by spiral growth under conditions of low supersaturation (Baronnet 1982). However, the distribution shapes of illite-muscovite in ion-milled rock samples deviate from this theoretical profile, especially for the highest-grade sample. If we had not studied the ion-milled rock samples, the crystal-growth mechanism of illite-muscovite in this study would have been erroneously connected to Ostwald ripening by second-order kinetics.

Since our interest is primarily in the distribution of crystallite sizes in the rocks, any changes resulting from sample preparation will produce errors of interpretation with respect to the relation between distribution and genesis. By directly measuring the crystallite sizes of the separates, which also were used as a source of XRD data for size analysis, this study demonstrates how poor approximations to lognormal distributions improve considerably during sample separation for XRD analysis. We also show how erroneous interpretations tend to arise from separates. Lognormal size-distributions of

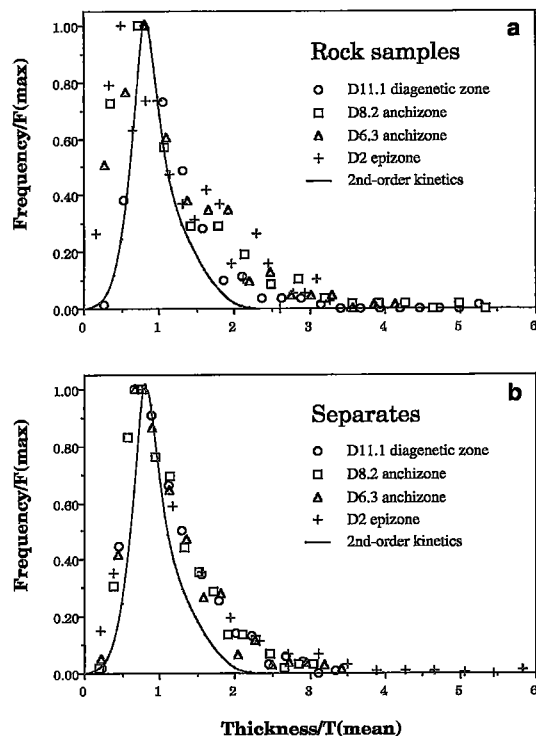


FIG. 9. Normalized frequency histogram of thickness of illite-muscovite in metapelites from southern New Zealand. The curves were calculated from the frequency histogram for crystal growth by second-order surface-controlled kinetics. (a) Ion-milled rock samples. (b) Separates.

separates have been taken as evidence for crystal-growth mechanisms, but our results suggest that such conclusions are generally not warranted. However, contrasting results were obtained on a pyrophyllite sample, for which grinding caused a lognormal distribution to be altered to an asymptotic distribution (D. Eberl, pers. commun.). Nevertheless, whether from asymptotic to lognormal or from lognormal to asymptotic, distributions of crystallite sizes can be significantly changed or modified by sample preparation. Crystallite sizes and size distributions determined from XRD are not generally a true measure of the state of crystallite sizes in rocks. They should be assumed to be meaningless as far as evidence for growth mechanisms is concerned unless data for the specific sample in question show the opposite.

Concerns and suggestions

This study has demonstrated decreases in crystallite size and changes in size distributions by cleavage along and fracture across (001) during sample separation. Such effects are serious and vary in magnitude both as a function of grade and rock types, *e.g.*, shales and bentonites, as they depend on textures. Such effects also clearly depend on separation techniques. Even though size distributions as measured by XRD are modified by the separation process, the use of XRD analysis for determination of crystallite sizes and size distributions of clay minerals has many advantages; it is easily and rapidly carried out, especially relative to the time-consuming analyses by TEM. The XRD approach also provides measurements over large numbers of crystallites and, therefore, is much more likely to give true measures of average materials, relative to the small volumes of materials analyzed by TEM. The challenge, therefore, is to carefully choose samples that display the full range of possible textures, as exemplified by rock type and grade, utilize standard techniques for separation of clays and preparation of samples for XRD (*e.g.*, Kisch 1991, Warr & Rice 1994), and compare distributions in original rocks and in separates as directly measured, *e.g.*, by TEM or AFM. In this way, the "separation function" that modifies the original size-distributions of crystallites can be determined. With knowledge of such relations, it may then be possible to obtain distributions using XRD techniques and to correct such distributions by the appropriate "separation function", assuming that it exists.

Perhaps an even more important reason not to depend on XRD-determined crystallite sizes and size distributions, is that TEM observations have shown that pelitic rocks may contain two or more generations of dioctahedral phyllosilicates, each of which may have their own crystallite sizes and size distributions (*e.g.*, Peacor 1992, Li *et al.* 1994). This is especially significant in rocks containing both diagenetic (bedding-par-

allel) and metamorphic clays that have preferential orientations parallel to slaty cleavage. XRD analysis is incapable of discriminating the sum of such functions from a single size-distribution. It is especially important to obtain quantitative data comparing the crystallite-size distributions in original rock samples and in separates for such materials.

CONCLUSIONS

Crystallite sizes of illite–muscovite in a prograde sequence of pelitic rocks from southern New Zealand have been studied using XRD and TEM. Mean thicknesses of illite crystals measured in a TEM study of separates are similar to those obtained by XRD profile analyses, indicating that XRD profile analysis may be useful and reliable for studying crystallite sizes in separates. However, mean thicknesses of illite–muscovite in ion-milled rock samples are up to four times larger than those of illite–muscovite in separates. Cleaved crystals of illite–muscovite are dominant in separates of all samples, indicating breakage of crystals along cleavage planes during sample preparation.

The above relations indicate that XRD profile analysis is a poor quantitative measure of the true size of crystallites in rock samples. The sample-preparation process for XRD analysis can significantly alter the original size-distributions; the poor approximations to lognormal distributions improve considerably during separation. Interpretation of growth conditions from size distributions of separates is therefore not warranted. Only size distributions of unseparated samples, or separates where the effects of the separation process are known, should be used as indicators of crystal-growth conditions. Our data also imply that the conventionally measured values of illite crystallinity, and all the other data (mean crystallite size, lattice strain, crystallite-size distribution) that are determined from the $< 2 \mu\text{m}$ grain-size fraction samples, at best may be representative of the given separate used for crystallinity studies, but are not directly characteristic of the whole rock studied. This is especially true at higher grades. Further integrated TEM and XRD work on whole-rock samples and various separates produced at different but well-constrained, standardized experimental conditions are needed in order to quantify the effects of sample-preparation processes.

ACKNOWLEDGEMENTS

We thank Laurence Warr and an anonymous reviewer for their constructive reviews. This work was supported by NSF grants EAR-94-18108 and EAR-97-06359 and DOE grant DE-FG03-95ER14533. The XRD peak profile analysis was supported by grant T022773 from the Hungarian Scientific Research Fund (OTKA), Budapest.

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Received November 5, 1997, revised manuscript accepted November 23, 1998.