Z. Kristallogr. Suppl. **26** (2007) 111-116

Illite crystallinity: Instrumental effect and its relation to crystallite size and lattice distortion

Salah Shata

Geology Department, Faculty of Science, Suez Canal University, Ismailia, 41522, Egypt

Keywords: Fourier analysis, Scherrer, Voigt, variance, Warren-Averbach, expandability

Abstract. Illite crystallinity (IC) monitors the continuous chemical and structural change of the illite-white mica group of phyllosilicates in high-grade diagenesis-very low-grade metamorphism (VLGM). One of the disadvantages of utilizing IC approach to delineate the diagenetic to VLGM conditions is that the measured values differ strongly between laboratories because of sample preparations and instrumental parameters. Various XRD-based methods are used for crystallite size determinations namely, the Scherrer equation, variance, Vigot method and Fourier analysis (Warren & Averbach method). The numerical variation of the crystallite size estimates obtained by these methods is due to the different assumptions made and the different physical meaning of the estimated parameters. The standardization of sample preparations, instrumental parameters should also extend to include the software methods which analyze illite crystallinity and measure the crystallite size.
The relationship between illite crystallite size and their crystallinity indices can be expressed by quadratic equation. The measured crystallite-size distributions (CSDs) for diagenetic/VLGM phyllosilicates follow the lognormal distribution.

Introduction

Illite crystallinity (IC) measured as full width at half maximum (FWHM) of the 10Å peak expressed as distance in angular width (Δ^o 2θ). The shape of the 10Å X-ray diffraction peak (XRD) of the illite white mica group has been used extensively in the last 40 years to establish progressive alteration from diagenesis to low-green schist facies conditions. When the term 'IC' was introduced, it was used cautiously [1], largely because the physical reasons for the change in the 10Å peak profile were poorly understood. The Kübler crystallinity index is a strictly empirical parameter; progress of gaining a better understanding of the factors controlling the change in the peak width has been slow. Yet, IC has been extensively used just because of the simplicity of the technique. The main restriction in comparing IC results between different laboratories is insufficient standardization [2].
A crystallite size (N) accurately termed X-ray scattering-domain size, is the more meaningful parameter to determine diagenetic and metamorphic grade. Crystallite size and the size distribution of phyllosilicates in rocks are a function of 1) the original conditions of crystallization, and 2) of later modifications in response to metamorphism or annealing [3]. Because of the required data processing, the measurement of crystallite size is used less than the FWHM

method. Several XRD-based methods are available to determine the crystallite size, yet the resultant data are not comparable.
The aim of the present study is:
1. to explore the physical meaning of IC in order to arrive on firmer ground when utilizing IC to define diagenetic and VLGM zones;
2. to review different approaches for illite crystallite size determining from XRD patterns.

Materials and methods

Fifteen samples from the Lower Palaeozoic sedimentary sequences of high-grade diagenesis and VLGM from the Gaspé Peninsula of the Quebec Appalachians were chosen with the aid of IC- and organic-matter maturation maps for the Taconian Orogenic belt [4]. For calibration processes, four rock standard composite samples from the VLG Variscan metamorphic belt of north Cornwall, southwest England [2] and other six samples supplied by the illite crystallinity working group within ICGP-294, were used.
The samples were size-fractioned by centrifugation into two main size classes, a coarse (<2 μm) and a fine (<0.1 μm) fraction. Neither sonic nor chemical treatments were applied during the sample preparation.
XRD analysis was performed on a 12 kW Rigaku D/Max 2400 automated powder diffractometer with a rotating anode. Operating conditions were 40 kV, 120 mA using a copper target. The diffractometer is equipped with a secondary monochromator and a θ-compensating slit assembly. For the sake of comparing instrumental parameters of different equipment, the XRD analyses were repeated using a Siemens D-500 automated diffractometer equipped with a graphite diffracted-beam monochromator (CuKα radiation) with the following instrumental settings: 40 kV operating voltage, 20 mA beam current, 0.01° 2θ step-size, 1 second counting time per step, 0.15 mm receiving slit, and a 2 to 40° 2θ scanning range.

Results and discussion

Two groups of parameters were extracted from XRD analysis:
(1) the 10 Å diffraction peaks measured on oriented samples and calibrated with crystallinity index standard (CIS) samples;
(2) crystallite sizes for illite applying XRD line-broadening program to the 10 Å reflections.
According to [5], the profile of an XRD peak produced by a crystalline powder is a function of four main factors: 1) sample preparation methods (dis-aggregation method, chemical treatment, cation saturation, grain size, slide preparation method, slide thickness); 2) X-ray diffractometer settings (dispersion of the incident radiation, thickness of the diffracting layer, axial divergence, width of the receiving slits, scan rate, time constant, and data processing parameters; [6]); 3) crystallite-size and domain size distribution; and 4) lattice strain (various kinds of lattice imperfections, e.g., local heterogeneity of chemical composition and lattice structure) defined relative to a given crystallographic direction
Firstly, as far as sample preparation is concerned, a complete calibration is applied to the standard samples supplied by IGCP 294, which had undergone pretreatment, to eliminate the influence of sample preparation (grinding, H_2O_2 treatment, ultrasonic, sample thickness, cation saturation and glycol salvation). As expected, the (IC) values of those samples vary as a function of the number of required treatment steps. IC deteriorates as the number of

steps increases (Fig. 1a). However, the deterioration was very small for well-crystallized samples, but increased in poorly- crystallized samples.

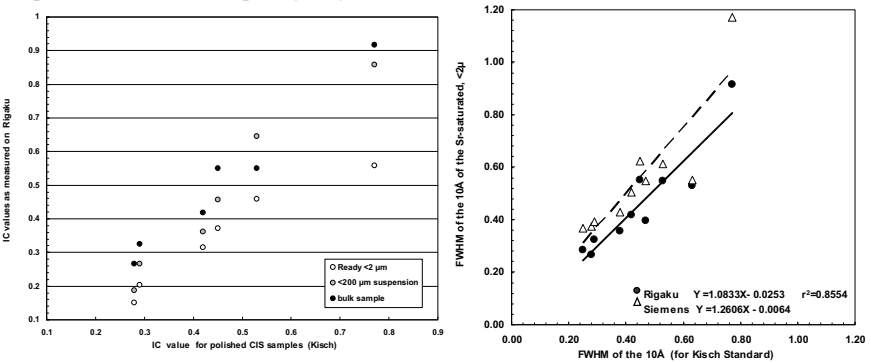

Figure 1. Calibration of illite crystallinity with CIS samples (a) Effect of sample preparation on illite crystallinity values for the <2 µm of CIS samples, (b) Calibration of illite crystallinity values measured on Siemens and Rigaku X-ray instruments.

Measurements of illite crystallinity are a function of instrumental conditions. IC values varied greatly as a function of take off angle, focal spots dimension of the tube, receiving slit width, axial divergence, and divergence slit.

Secondly, although instrumental setting of the two XRD machine were too close if not identical, yet the difference in (IC) values of the same sample run both on the Rigaku and Siemens instruments is documented. The peaks of the Rigaku patterns are sharper than the Siemens peaks (Fig. 1b). Consequently, a sample with an IC value of anchizone grade on the Rigaku pattern may yield an IC value indicating diagenetic conditions on the Siemens pattern. Line profile analysis resulted in similar crystallite size values for both data sets collected by the Rigaku and Siemens instruments. In the present study, using the WINFIT program, four crystallite-size measuring methods are compared (Fig. 2). Two main approaches have been used to calculate crystallite size and strain from XRD traces:

(i) single peak methods such as:

a-Scherrer method [7],

$$N\ (Å) = K\ \lambda / B\ \cos\theta$$

where N = volume average crystallite thickness in Å along c*,

K = constant near unity depending on the crystal shape, the indices of (hkl) reflecting plane

λ = wavelength in Å of the radiation used, θ = diffraction angle of the reflection $(001)_{10}$

$B = (\beta^2 - b^2)^{1/2}$ = corrected FWHM of the basal reflection measured in radians,

β = measured FWHM of the basal reflection of the sample in $\Delta^o 2\theta$,

b = FWHM of the instrumental standard in $\Delta^o 2\theta$

Two perquisite conditions need to be fulfilled in order to apply this equation; i.e., there is no strain-broadening effect [5]; there is no mixed layering affecting the peak width [6]. Scherrer equation is devised for defect-free material, which, however, is rarely encountered in diagenetic and low-grade metamorphic rocks.

b- Variance method [8]

The variance approach is a mathematical method to deconvolute the XRD peak profile W(2θ) into its main components:

$$W(2\theta) = Wo(2\theta) + WN(2\theta) + W\sqrt{<\varepsilon 2>}(2\theta)$$

where $W_o(2\theta)$ is the variance of the original pure line profile,
$W_N(2\theta)$ is the variance of the mean size of the coherent scattering domain, and
$W\sqrt{<\varepsilon^2>}(2\theta)$ is the variance of the lattice distortion.

c- Voigt method [9]

The Voigt method uses integral breadth. Line broadening caused by small crystallites is described by a Cauchy 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 either by mathematically or 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. Voigt function [9] should only be used where both crystallite size and microstrain affect the peak broadening

(ii) Multiple-peak Warren-Averbach method [10, 11]

Warren-Averbach analysis separates the effects of finite crystallite size and lattice strain on XRD line-broadening, using the Fourier coefficients of two or more orders of the same hkl reflections. While the line-broadening caused by crystallite size does not change as a function of diffraction order, the strain-induced broadening increases as a function of diffraction order increases.

The availability of many approaches analyzing the XRD line profile, where each method has adopted certain conditions or uses approximations in mathematical functions, leads to uncertainty. Absolute values of crystallite size are substantially different for different XRD-based methods. The relationship between illite crystallinity and crystallite size can be expressed by quadratic equation (Fig. 3). Crystallite size calculated with the different methods exhibits the same relation (quadratic equation with different constants) for every method.

The (N) and (IC) relationship produces a curve consisting of three segments (Fig. 3):

i) One is sub-horizontal representing the diagenetic material in which the effective crystallite size is small and consequently peak broadening and Kübler index are large.

ii) The anchizone is characterized by a decreasing IC with increasing metamorphic grade; the domain size increases first slightly and then, reaching the epizone, considerably.

iii) The third segment is subvertical (rapidly increasing gradient) whereas the continuous broadening of the peak is not influenced by crystallite size.

This phenomenon can be interpreted as follows: while in the diagenetic and anchimetamor phic zones with increasing grade, the domain size increases and the distortion decreases due to recrystallization. In the epizone, the increase of crystallite size is not associated with a decrease in lattice distortion. This may be due to the fact that illite–muscovite recrystallization took place in a system characterized by K-deficiency.

Ideally, the values of crystallite size and strain should be reproducible and give identical results. Analyses were repeated at least three times. However, numerical results from the 4 methods discussed for crystallite-size calculation differ strongly (Fig. 2). This is in part due to different meaning of various parameters (volume averaged sizes vs. area weighted), and in part due to the fact that most methods produce correct result only if some basic assumptions hold true. The WINFIT program[12] does not only calculate the crystallite-size and the cumulative frequency distribution (Fig. 2), but also plots a reduced curve. This curve is

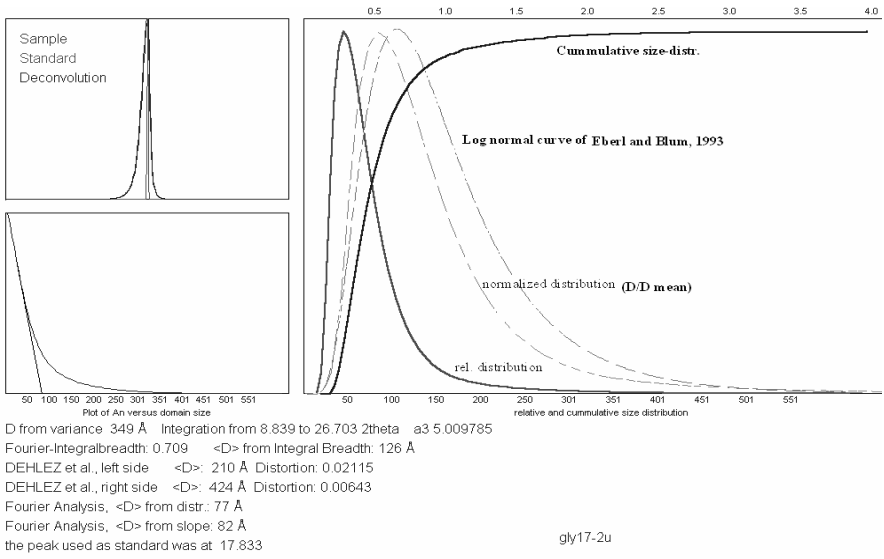

Figure 2. Determination of crystallite size and lattice strain values with different approaches, and comparing the resultant size distribution with the log normal distribution.

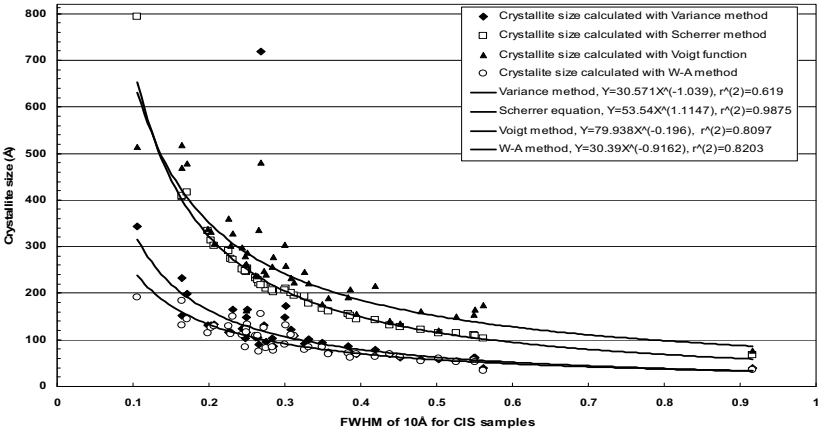

Figure 3. Comparison between different XRD processing methods calculating crystallite size

obtained by dividing crystallite size by mean crystallite size and plotting this against frequency/maximum frequency. Analysis of the Gaspé samples with the WINFIT program shows that all crystallite size distributions are asymmetrically bell shaped and positively skewed toward large coherent-scattering domain sizes. With advancing metamorphic grade, the size-frequency maximum moves to larger crystal sizes, as smaller crystals are reduced in size and eventually disappear. This curve can be compared to log-normal distributions described by [6]. For more than a decade, this CSDS curve had been interpreted to be

characteristic for crystal growth by Ostwald ripening [10]as mechanism driving illitization (Eberl and Środoń,1988). Simulations of these log-normal distributions indicate that illite particles grow from 2-nm thick illite nuclei by surface-controlled growth [12]. The illitization process begins with the dissolution of single S layers and the nucleation and growth of 2-nm thick illite. That stage is characterized by S ranging from 100 to 20% and accompanied by transformation of the clay from randomly interstratified to R3-ordered structure. When <20% S remains in illitic material, the nucleation ceases. Illite crystals may continue to grow by surface-controlled growth.

Conclusions

Illite crystallinity (IC) is an easy and rapid technique for monitoring the continuous chemical and structural change of the white mica group of phyllosilicates in high-grade diagenesis-very low-grade metamorphism (VLGM).

One of the main disadvantages of utilizing IC approach is that the measured values differ strongly between laboratories because of instrumental parameters and sample preparations. Therefore, any study not based on calibration by standards will yield spurious results, which will induce an incoherent VLGM zonation.

The standardization of sample preparations, instrumental parameters should also extend to include the software methods, which analyze IC and measure the crystallite size. Various XRD-based methods are used for crystallite size determinations namely, Scherrer method, Variance method, Voigt method, and Warren & Averbach method. The variation of the crystallite size estimates obtained by these methods is due to in the different assumptions made and the different physical meaning of the estimated parameters.

References

1. Kübler, B., 1967, *La cristallinité de l'illite et les zones tout à fait supérieures du metamorphisme.* In: Étages tectoniques, Colloque de Neuchatel 1966, À la Baconnière, Neuchatel, Suisse, pp. 105-121.
2. Warr, L.N., & Rice, A.H.N., 1994, *J. Metamorphic Geol.*, **12**, 141-152.
3. Cashman, K.V., & Ferry, M.J., 1988, *Contrib. Mineral Petrol.*, **99**, 401-415
4. Hesse, R. & Dalton, E.. 1991, *J. Metamorphic Geol*., **9**, 775-790.
5. Klug, H.P. & Alexander, L.E., 1974, *X-ray diffraction procedures for polycrystalline and amorphous materials., 2nd ed.* Wiley*, New York.*
6. Eberl, D.D., & Blum, A., 1993, Illite crystallite thickness by X-ray diffraction, In*:* Computer application to X-ray powder diffraction analysis of clay minerals, R.C. Jr. Reynolds, & J.R. Walker (eds.) *Clay Miner. Soc. Workshop Lectures 5,* A124-153.
7. Weber, F., Dunoyer de Segonzac, G. & Economou, C., 1976, *CR Somm Soc. Geol. Fr* 5, 225-227.
8. Wilson, A.J.C., 1963, *Proc. Phys. Soc*., **80**, 286-294
9. Langford, J.I. , 1978, *J. Appl. Cryst.*, **11**, 10-14
10. Eberl, D.D., and Środoń, J., 1988, *Amer. Mineral.*, **73**, 1335-1345.
11. Warren B. E., & Averbach, B.L., 1950, *J. Appl. Phys*., **21**, 595-599
12. Środoń, J., Eberl, D.D., & Drits, V.A., 2004, *Clays Clay Miner.*,