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Asymmetry of 1 nm XRD Reflection and Measurement of Illite Crystallinity

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Theoretically the X-ray emission is subjected to the Gaussian distribution and is symmetric. An X-ray diffraction peak should be symmetric, too. However all illite 1 nm (interplanar distance) peaks used for measurement of illite crystallinity (IC) are practically asymmetric. Our experimental results prove that any X-ray diffraction peak in low diffraction angle segment appears asymmetric if the diffractometer is running with a slit-fixed system. However, if the diffractometer is running with an auto-adjustable-slit system and the illumination length is fixed, the X-ray diffraction peak in low diffraction angle segment is symmetric. Those peaks derived from synchrotron radiation are symmetric in all angle ranges. The asymmetric degree (AsD) of a X-ray diffraction peak is subjected to the ratio of integrated intensities on lower and higher diffraction angle sides which are related to the X-ray illuminating length (area) on the sample. From the expression of illuminating length it is derived that with increasing diffraction angle the illuminating length decreases and therefore a X-ray diffraction peak is always asymmetric. The relationship between AsD and IC can be expressed as AsD = 0.239IC + 0.999, When illite/smectite mixed-layer phase presents the asymmetry of the illite 1 nm X-ray diffraction peak will be obviously higher than usual case and induces unusually larger IC value.

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1. Introduction

Illite crystallinity (IC) has been widely used to indicator the evolution from diagenesis to very low grade metamorphism for clastic rocks since 1960. IC is given by the FWHM of the illite 001 diffraction peak with 1 nm interplanar distance (abbreviated as 1 nm XRD peak hereafter). However, when IC is measured, the 1 nm XRD peak often demonstrates an asymmetry in some extension from weak to strong which enlarges the FWHM and causes IC to be poor. This phenomenon remains a huge puzzle among IC researchers.

The asymmetry of illite 1 nm XRD peak is explained [1, 2] as the presence of illite/smectite (I/S) mixed layer phase. However, for those illites in very good crystallinity and no presence of I/S the 1 nm XRD peak still shows some asymmetry in shape. Nevertheless chlorite (001) and (002) reflections also display the same asymmetry no matter they are broad or narrow. Those phenomena cannot be explained completely by the presence of I/S nor the presence of chlorite/smectite mixed-layer phase. The aim of this work is to try to understand the nature of asymmetry of a single XRD peak and then to discuss its influence on IC measurement.

2. Methods

In order to overcome the deviation between laboratories, the Synchrotron Radiation Facility in Beijing (BSRF) and that in Shanghai (SSRF) and the data from Spring-8 in Japan and data from laboratory diffractometer are employed. IC measurement is performed according to the recommendation by Kisch [3]. Following routine operating conditions are used: for X'Pert Pro MPD diffractometer, Cu radiation, Ni filter, 40 kV by 40 mA, 1° divergence slit, 2° anti-scatter slit, 6.6 mm receiving slit, X'celerator detector, 0.017° 2θ step size, 20 s counting time, $10 \times 15 \times 1$ mm^3 powder sample holder, programmable-divergence-slit and programmable-receiving-slit are installed when needed; BSRF: Bragg–Brentano mode, $\lambda = 1.54$ Å, 0.02° 2θ step size, 1 s counting time, $10 \times 15 \times 0.8$ mm^3 powder sample holder; SSRF: Bragg–Brentano mode, $\lambda = 1.24$ Å, 0.02° 2θ step size, 1 s counting time, $10 \times 15 \times 0.8$ mm^3 powder sample holder; Spring8: Debye–Scherrer mode, $\lambda = 0.77597$ Å, imaging plate detector, 10 min exposure time, ϕ0.2 mm glass capillary. The humidity is controlled at about 30% during measurement. Single crystal of muscovite is used as a standard to monitor the instrumental broadening. Quartz and gypsum are used for comparison with clay minerals. Deconvolution technique is used to simulate the K_{α_1} and K_{α_2} components of X-ray as well as those single reflections of I/S, illite, chlorite, etc. The disagreement factors are all below 3%. The illuminating lengths of illite 1 nm peaks in different ICs from 0.1 to 0.5 (°$\Delta 2\theta$) with Cu radiation are calculated at divergence angle $\alpha = 1°$ and goniometer radius $R = 200$ mm [4], the pseudo-Voigt function is used to simulate the 1 nm peak of illite and parameter η is set at 0.82 according to the characteristic of illite from the Helvetic sediments, Switzerland.

3. Result and discussions

3.1. Result

Following conclusions can be drown from Fig. 1: (i) single reflections in low diffraction angle range produced by

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synchrotron radiation are actually symmetric; (ii) single reflections in the same range produced by diffractometer equipped with a theta-compensating slit system are symmetric; (iii) single reflections collected with a curve detector are symmetric; (iv) those single reflections in low diffraction angle range measured by diffractometers with a fixed slit system are asymmetric.

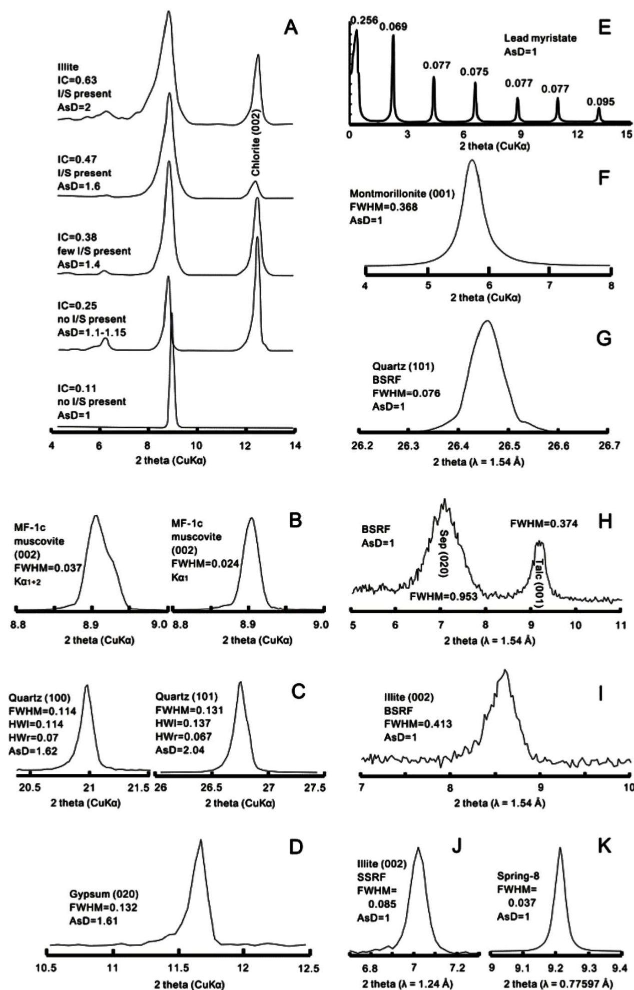

Fig. 1. (A–D) Asymmetry. (A) Illite and chlorite reflections measured with D5000 [13]; (B) muscovite measured with X'Pert Pro MPD, left: with K_α component and right: with K_{α_1} only; (C) quartz measured with X'Pert Pro MPD; (D) gypsum measured with X'Pert Pro MPD. (E–K) Symmetry. (E) Lead myristate measured with a diffractometer installed with a theta-compensating slit system [14]; (F) montmorillonite measured with a diffractometer installed with a curve detector [15]; (G) quartz measured in BSRF; (H) sepiolite (Sep) and talc measured in BSRF; (I, J) illite measured in SSRF; (K) measured in Spring-8.

3.2. Discussion

There are five parameters describing the shape of a XRD peak: position, FWHM, maximum, shape-coefficient and asymmetry [5, 6]. Each of them contains a physical meaning [7–9]. Because AsD is given by the ratio of $\mathrm{FWHM}_{\mathrm{low-angle-side}}$ to $\mathrm{FWHM}_{\mathrm{high-angle-side}}$ [5, 6] or of integrated intensity (equate to FWHM × maximum × shape-coefficient), therefore, FWHM, maximum and shape-coefficient seem to be linked to AsD. However, domain size (related to FWHM), nature of absorption to X-ray and concentration of a phase in mixture (related to maximum) and lattice strain and distortion (related to shape-coefficient) are all internal factors of minerals themselves and have no relation with the asymmetry of a XRD peak. The asymmetry of a single XRD reflection must come from external factors.

There have been five interpretations for asymmetry of a single XRD peak so far: (i) axial divergence [9–11]; (ii) layer structure [4]; (iii) secondary reflex [1, 2]; (iv) sample transparency [10, 12]; (v) mode of irradiation or geometric condition [12]. Among them (ii) and (iv) there are internal factors and the others are external factors. From Fig. 1, these single peaks of clay minerals (Fig. 1H–J) and non-clay minerals (Fig. 1G) and those produced from synchrotron radiation (Fig. 1G-J;), from diffractometers installed with a theta-compensating slit system (Fig. 1E) or with a curve detector (Fig. 1F,K) do not show any asymmetry in shape, meanwhile those of clay and non-clay minerals measured by diffractometers with a slit-fixed system show asymmetry (Fig. 1A–D) therefore above interpretations are imperfect or need further consideration in the sense of testing.

3.3. Our interpretation

From the Gaussian distribution (symmetry) of X-ray emission [16–20] and those asymmetric single peaks measured, we realize that the asymmetry of a single XRD reflection measured is a theta-dependent phenomenon or in other word is an illumination phenomenon, when the illumination of X-ray is the same on both lower and higher diffraction angle sides, the single peak is symmetric, and when illumination is different on two sides, the single peak will be asymmetric. The lower the theta is, the larger the illumination is, thus from lower angle side to higher angle side of a reflection it is always tailing on lower diffraction side. Figure 2 sketches this "theta-dependent illumination phenomenon". Schreiner [14] gave a good example (Fig. 1E) and all diffractometers installed with a slit auto-adjustable system would produce symmetry peaks if the illuminant length is fixed. Curve detector with the Debye–Scherrer optics can overcome this illuminant difference on two sides of a reflection and therefore it produces symmetry peaks. Synchrotron radiation is a kind of X-ray with very high energy and is nearly perfect parallel. Its illuminant length is only 1 mm or 1/20 of diffractometer mostly and the illuminant difference between two sides of a reflection is so small that its asymmetric degree is lower than detectable level and actually produces symmetry peak.

3.4. Influence on illite crystallinity measurement

As discussed above, scanning across the centre of a XRD peak induces a theta variation and hence produces the variation of illumination on two sides of the peak if slit is fixed. This leads illite 1 nm peak tailing on lower

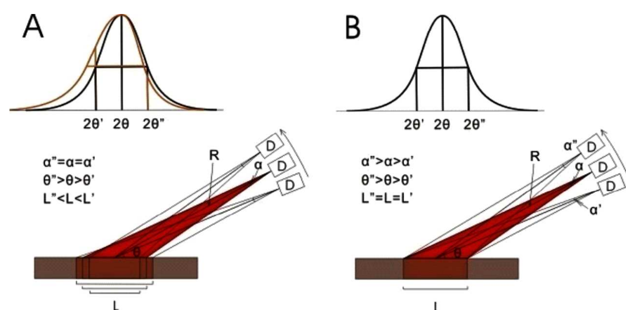

Fig. 2. Sketch of X-ray illumination: α — divergence angle, R — distance from sample to detector (D), θ — the Bragg angle and L — illuminant length. (A) (α is fixed): when X-ray scanning a reflection from lower θ' through θ to higher θ'', the illuminant length changes from L' to L to L'' and the intensity changes from higher to middle to lower. This makes a reflection asymmetry and tailing on lower diffraction angle side. (B) (L is fixed): during the course of scanning, it gets the same intensity on both reflection sides and results in symmetric peak.

TABLE I

Data of AsD and IC.

AsD*	1.023	1.046	1.070	1.095	1.120
IC	0.1	0.2	0.3	0.4	0.5

*measured from simulated 1 nm reflections of illite; AsD = 1 at IC = 0 is assumed (see Sect. 2. Methods)

angle side and directly enlarges the IC value some extension. The relationship between AsD and IC is deduced from illumination length and the shape of a XRD refection as (see Table I):

$$\text{AsD} = 0.239\text{IC} + 0.999 \quad (R^2 = 0.999). \tag{1}$$

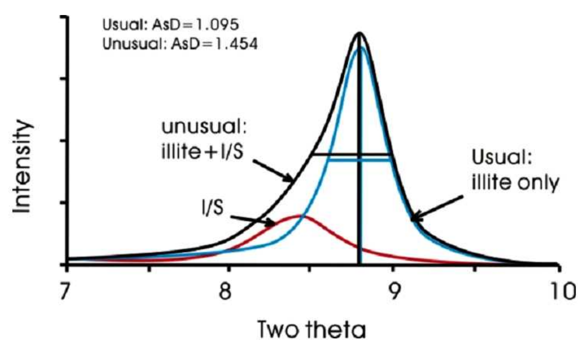

Fig. 3. Impact of I/S on IC measurement. Vertical lines indicate peak position and maximum, horizontal lines mark the FWHMs.

When I/S presents in air-dried state, the first peak position of I/S (001/001) ranges between 1.5 nm and 1 nm. For most I/S mixed-layer in $R \geq 1$ ordering type, the first peak position of I/S will be >1 nm and close to 1 nm and therefore this first I/S peak will occur on the lower diffraction angle side of illite 1 nm peak, such that the theta-dependent illumination asymmetry of illite 1 nm peak will become more heavier than usual case (see Fig. 3). Because of the interference from I/S, this derives a larger AsD than normal one by Eq. (1).

4. Conclusions

It is concluded that (i) any diffractometer with a slit-fixed system makes XRD peak asymmetric in low diffraction angle range; (ii) there exists a relationship between asymmetric degree and illite crystallinity; (iii) only if the asymmetric degree is higher than normal level could the I/S be presented.

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