Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2001: Order, disorder and crystallinity in phyllosilicates and the use of the 'Crystallinity Index'

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INTRODUCTION

The purpose of this report is to describe the appropriate use of indices relating to crystallinity, such as the 'crystallinity index', the 'Hinckley index', the 'Kübler index', and the 'Árkai index'. A 'crystalline' solid is defined as a solid consisting of atoms, ions, or molecules packed together in a periodic arrangement. A 'crystallinity index' is purported to be a measure of crystallinity, although there is uncertainty about what this means (see below). This report discusses briefly the nature of order, disorder and crystallinity in phyllosilicates and discusses why the use of a 'crystallinity index'

should be avoided. If possible, it is suggested that indices be referred to using the name of the author who originally described the parameter, as in 'Hinckley index' or 'Kübler index', or in honour of a researcher who investigated the importance of the parameter extensively, as in 'Árkai index'.

In contrast to a crystalline solid, an 'amorphous' solid is one in which the constituent components are arranged randomly. However, many variations occur between the two extremes of crystalline *vs.* amorphous. For example, one type of amorphous material might consist simply of atoms showing no order and no periodicity. Alternatively, another amorphous material may consist of atoms arranged, for example, as groups of tetrahedra (i.e. limited order) with each group displaced or rotated (e.g. without periodicity) relative to another. Thus, this

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latter material is nearly entirely amorphous, but differs from the first. Likewise, disturbance of order and periodicity may occur in crystalline materials. The terms 'order' and 'disorder' refer to the collective nature or degree of such disturbances. Although seemingly simple notions, 'crystalline' and 'amorphous' are complex concepts.

Crystalline substances may show a periodic internal structure based on direction. For example, two-dimensional periodicity is common in phyllosilicates where two adjacent sheets or layers must mesh. For example, in serpentine, the 1:1 layer must match the periodicity of adjacent layers so that hydrogen bonding is optimized to link the layers. Adjacent layers may be offset by zero shifts, $\pm a/3$ shifts, or $\pm b/3$ shifts, but hydrogen bonding is still maintained and two-dimensional periodicity within each layer remains. Most materials (not necessarily clays, however), exhibit three-dimensional periodicity. Periodicity may be related also to domains, where short-range or long-range order may exist within domain boundaries.

Many forms of order and disorder occur in phyllosilicates, including order-disorder in stacking sequences, isomorphous substitutional order-disorder where various ions or vacancies occur in certain coordination sites, and order-disorder in the arrangement of material in the interlayer. Phases involving interstratifications in phyllosilicates are common, with order-disorder in stacking of two or more kinds of layers. In addition, mosaic character, interstitial impurities, thermal or positional displacement, dislocations, and other defects may also be related to order-disorder.

In practice, 'crystallinity' is defined as the degree of perfection of translational periodicity as determined by some experimental method. Diffraction techniques are the common methodologies to ascertain periodicity, but different diffraction techniques often do not convey the same information. For example, because of the different wavelengths and imaging capabilities of X-ray and electron-diffraction methods, X-ray diffraction (XRD) experiments may suggest that the periodicity of the material in the bulk sample may be non-existent, whereas electron diffraction may indicate, for example, that the atomic arrangements within finely divided particles may be periodic. In addition to the choice of radiation, apparent crystallinity (or apparent periodicity) may be related also to sample preparation or experimental technique. For example, 'two-line' ferrihydrite is often considered amorphous or nearly amorphous because of the use of powder XRD patterns made with an improper choice of counting time and radiation. When scanned properly, however, this material may display more than six powder-diffraction peaks. As shown by accurate XRD and selected-area electron-diffraction data, both two-line and six-line ferrihydrites exist (e.g. Drits *et al.*, 1993). Similarly, 'crystallinity' appears to decrease in powder XRD experiments of oriented clay-particle aggregates when the clay particles are partially or poorly oriented. Thus, the nature of the translational periodicity and the method of sample preparation and measurement are essential aspects that must be considered in any practical procedure to describe crystallinity.

Finally, note that this report is not comprehensive in that it considers only limited aspects of 'crystallinity' and does not consider environmental factors affecting disorder (e.g. mechanical actions), industrial implications, sample preparation methodologies, etc. The purpose of this report, as given above, is to consider some crystallographic aspects of crystallinity, such that appropriate nomenclature can be applied to this concept.

THE TERM 'CRYSTALLINITY'

The term 'crystallinity' is qualitative and depends on the type of order (or disorder) as described above, the dimensional nature of the periodicity present, and the technique involved in its measurement. For phyllosilicates, which are low-symmetry materials characterized by strongly anisotropic structures, widely-varying chemical compositions, and commonly having either irregular or regular interstratifications of various structures, the meaning of 'crystallinity' is ambiguous. Furthermore, the apparent 'crystallinity' is strongly dependent on crystallographic direction. Despite this, 'crystallinity' indices have been proposed for clay minerals for the last forty years, some of which have been widely accepted and applied worldwide.

HISTORICAL BACKGROUND AND COMMENTS

Hinckley (1963) attempted to define a 'crystallinity' index to quantify 'crystallinity' by describing how characteristics of powder XRD peaks may change among samples of kaolinite. Hinckley (1963) described a procedure to measure the maxima of

the 11*l* and 02*l* powder-diffraction peaks. Brindley (1980, p. 152) noted that the measurement gives an indication of the "clarity of the two peaks, but it is not related to true peak intensities". Plançon & Zacharie (1990) noted that the procedure is incapable of quantifying the diversity of defect structures in kaolinite samples. The Clay Minerals Society Nomenclature Committee (R. Giese, pers. comm., 1998) suggested that the Hinckley index differentiates kaolinite samples containing "low" amounts of defects ('low-defect kaolinite') *vs.* "high" amounts of defects ('high-defect kaolinite'). Clearly, however, whatever the Hinckley index measures, the index is not a quantitative measure of 'crystallinity'.

Weaver (1960) was the first to realize that regular changes in shape of the first, 10 Å basal reflection of illite is a function of burial (increasing temperature and pressure). The "sharpness ratio" of Weaver (the 'Weaver index') is the ratio of intensities measured at the peak maximum (near 10 Å) and at 10.5 Å. The Weaver index increases with increasing depth in sedimentary basins. Kübler (1964) differentiated the "anchimetamorphic zone" [the "anchizone" of Dunoyer de Segonzac (1969) and others] to identify the transition between the dry-gas zone and the zone of unproductive ("overmature") rocks for hydrocarbon exploration. Kübler (1964, 1967) devised an illite "crystallinity" index (often abbreviated as IC) that relies on the full width at half maximum (FWHM) of the first, 10 Å XRD powder-diffraction peak of illite-muscovite, as measured on the <2 μm size-fraction of the air-dried clay using Cu-*K*α radiation. The Kübler index, expressed as small changes in the Bragg angle, $\Delta°2\theta$, was introduced as a method of identifying the diagenesis-anchizone and anchizone-epizone metamorphic boundaries. Standardization of sample preparation, instrumental measuring conditions, and interlaboratory calibration are needed to do this (Kisch, 1990, 1991; Warr & Rice, 1994). Other crystallinity indices have been proposed for illite, including those of Weber (1972), Flehmig (1973) and Watanabe (1988), although these have been found to be less convenient or not as reproducible.

Although the Kübler index proved to be an easy-to-use measure of grade of diagenesis and incipient metamorphism of clastic rocks, the use of the term 'illite crystallinity' is unfortunate, because it also involves illite-smectite and possibly white K-rich mica interstratifications and consequently, it is not a direct measure of the 'crystallinity'. Many authors

use the term 'crystallinity' within quotation marks (e.g. Kisch, 1983; Frey, 1987), although Kübler (1984) preferred the term "largeur de Scherrer" (LS) or "Scherrer width" (SW) instead of 'illite crystallinity'.

The FWHM values of chlorite basal reflections have also been used as measures of 'chlorite crystallinity' (see reviews by Frey, 1987 and Árkai *et al.*, 1995). For the reaction series smectite–muscovite and smectite–chlorite, Árkai (1991) correlated the "chlorite crystallinity" indices measured on the 14 Å and 7 Å basal reflections with the Kübler index scale, metabasite mineral facies, coal rank and other metamorphic grade-indicating characteristics.

Investigations have shown that the Kübler index is influenced by the mean size of crystal domains that scatter X-rays coherently (Weber *et al.*, 1976; Dunoyer de Segonzac & Bernoulli, 1976; Árkai & Tóth, 1983; Eberl & Velde, 1989; Drits *et al.*, 1997, etc.). Crystallite size, especially at lower (diagenetic) grades, seems to be strongly affected by the amount of swelling of interstratified components (e.g. Eberl & Velde, 1989). Lattice strain may also influence the Kübler index, although it is a relatively minor contribution at these low-θ angles and the percentage strain in illite-muscovite crystallites tends to be small (Árkai & Tóth, 1983; Árkai *et al.*, 1996). Jaboyedoff *et al.* (2001) suggested that the index is related to the mean number of layers and the variance of the distribution of the number of layers in the coherent scattering domain, the mean percentage of smectite layers present, the Reichweite (a parameter describing layer-stacking order), and instrumental parameters. Using TEM techniques, Merriman *et al.* (1990, 1995) showed that the Kübler index is largely controlled by the thickness of illite-muscovite crystallites.

Data from many sources (e.g. Eberl *et al.*, 1987, 1990; Merriman *et al.*, 1990, 1995; Środoń *et al.*, 1992; Árkai *et al.*, 1996, 2000; Jiang *et al.*, 1997; Li *et al.*, 1998; Warr & Nieto, 1998; Essene & Peacor, 1995) suggest that phyllosilicates in diagenetic and very low-grade metamorphic conditions do not reflect thermodynamic equilibria. Consequently, the Kübler index and the FWHM values of chlorite, as well as the structural (e.g. mean crystallite size values) and chemical characterization of these metastable phases, cannot serve as geothermometers. These parameters are only qualitative indicators of the stages the investigated phyllosilicates have reached through a

series of metastable mineral reactions (Peacor, 1992; Merriman & Peacor, 1999). Despite this, the Kübler index is a useful indicator of diagenesis and low-temperature metamorphism in different geotectonic regimes.

In summary, 'crystallinity', which may involve crystals that are three-dimensional in nature, cannot be described by one-dimensional diffraction data as in the case of the Kübler index. Thus, this index is not a true measure of 'crystallinity' because crystallinity is complex and cannot necessarily be represented by a single datum. In fact, deviations from perfect structure have specific diffraction effects that may not be measurable by documenting variations of width of a single peak; for example, effects involving diffuse scattering between peaks.

RECOMMENDATIONS

(1) It is the recommendation of this committee that the term 'crystallinity index' should not be used. However, it is appropriate to refer to a 'Hinckley index' or 'Kübler index', after those authors who initially described the parameters, or the 'Árkai index' for calibrated FWHM values of chlorite, after the researcher (Prof. Peter Árkai, Hungarian Academy of Sciences) who described the importance of this parameter extensively. In this way, the term 'crystallinity' is discriminated from parameters that may not describe all aspects of crystallinity. However, vast amounts of data exist based on 'crystallinity' or 'crystallinity indices' and reference to earlier work may be awkward without the use of these terms. Thus, limited use may be made of the term 'crystallinity', within quotation marks, only if its use is unavoidable.

(2) Because there is a continuum between phases that are amorphous and crystalline, clarifying the term 'amorphous' is important. The term 'amorphous' must be accompanied by a description of the diffraction effects or other properties that suggest the phase is, in fact, 'amorphous'. In addition, a description of the sample-preparation techniques and experimental conditions must be reported.

After the appropriate descriptions as discussed above are given, adjectival modifiers may be appropriate to describe amorphous, such as 'near amorphous', because this may be a better way to designate or describe the phase. It is appropriate also to refer to 'X-ray amorphous' to describe the amorphous state as determined by XRD techniques, or by analogy, 'electron amorphous' if determined by electron diffraction.

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