Physical meaning and applications of the illite Kübler index: measuring reaction progress in low-grade metamorphism

Isabel Abad

Departamento de Geología. Universidad de Jaén. 23071 Jaén. Spain.

Introduction

Diagenetic and metamorphic processes that take place at temperatures lower than greenschist facies (< 300ºC) give rise to rocks characterised by a lack of chemical and textural equilibrium and by very fine-grained minerals forming intergrowths at such a small scale that they cannot be recognized under the petrographic microscope. In addition, in clastic lithologies there is commonly an absence of changes in mineral paragenesis, making it difficult or impossible to apply the criteria normally used for higher grades based on the petrogenetic grid of mineral association equilibria or on true geothermometers.

For many years, geologists working on rocks formed under such conditions have searched for alternative criteria to characterise low-grade metamorphic PT conditions. In many cases these criteria have been based on the crystal-chemical aspects of phyllosilicates. The only significant changes to be observed throughout this range of diagenetic-metamorphic conditions are a progressive increase in the crystalline domain size together with a decrease in the number of defects (Frey, 1987); consequently, crystallinity measurement and the calculation of crystallite size (X-ray scattering domain-size) have been used extensively for the evaluation of the diagenetic and low-temperature metamorphic history of phyllosilicate-bearing rocks.

During the 1960s, regional studies of clay mineralogy in relation to very low-grade metamorphism led to the development of XRD-based clay mineral "crystallinity" techniques for indexing the transition from diagenesis to metamorphism. The term "crystallinity" is commonly applied to illite, although the crystallinity of other sheet silicates (e.g. chlorite and kaolinite) can also be determined. The first illite "crystallinity" indices were applied in petroleum exploration to detect diagenetic stages, primarily to characterise the ultimate evolution stages before metamorphism (to identify the transition from dry-gas phase to unproductive rocks, i.e., the transition from deep diagenesis to anchizone).

Currently, the most common method used for determining grade in metapelitic sequences is the Kübler index of illite "crystallinity", which measures changes in the shape of the first basal reflection of dioctahedral illite-muscovite at an X-ray diffraction (XRD) spacing of approximately 10 Å. It was introduced by Kübler (1967) as a method of identifying the transitional anchimetamorphic zone between diagenesis and the epimetamorphic zone of low-grade metamorphism in metapelitic sequences. The subsequent definition of the anchizone using the Kübler index also defined the prograde limit of diagenesis and the onset of the epizone (Kisch 1990, 1991). In the last few decades, with the development of computerised XRD treatments, "crystallinity" methods have essentially been applied to the anchizone and its immediate limits, for which the method is most accurate. The field of application has therefore gone well beyond petroleum exploration to regional geology studies (palaeotectonic and geodynamic reconstructions) of low-grade metamorphic orogenic belts. In recent years, as well as the traditional use of XRD, the development of high-resolution transmission electron microscopy (HRTEM) has allowed the criteria developed by powder diffraction to be verified and has also aided in understanding their physical meaning. Such has been the case of the Kübler index, among others.

The aim of this paper is to review the origin, significance, advantages, and limitations of the illite Kübler index, the most common and straightforward parameter for the characterisation of diagenetic and very low-grade metamorphism in clastic sedimentary rocks.

Illite "crystallinity" indices

Several illite "crystallinity" indices have been proposed for studies of very low-grade metamorphism and basin maturity over the last forty years.

Weaver (1960) was the first to realize that regular changes in the shape of the first, 10 Å, basal reflection of illite are a function of burial (increasing temperature and pressure). The Weaver index is the ratio of the height of the 10 Å basal reflection to that of the reflection at 10.5 Å and it increases as the peak becomes narrower (with increasing depth in sedimentary basins).

The Kübler index, first proposed by Kübler (1964) and refined by Kübler (1967, 1968) and Dunoyer de Segonzac et al. (1968), measures the full width at half maximum intensity (FWHM) of the first, 10 Å, X-ray powder-diffraction peak of dioctahedral illite-muscovite (i.e. the Scherrer width), as measured on the <2μm size-fraction of air-dried clay specimens using Cu-Kα radiation. Values decrease as peaks become narrower since the illite-muscovite crystallites thicken in prograde metapelitic sequences. This 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, instrument-measurement conditions, and interlaboratory calibration are necessary to achieve this (Kisch, 1990, 1991; Warr and Rice, 1994).

A further "crystallinity" index is the Weber index (Weber, 1972), which expresses the half-height width of the 10 Å illite reflection as a ratio with respect to the width of the (100) peak of a quartz standard. This ratio decreases as peaks become narrower, making "crystallinity" values comparable when different laboratories use the same quartz standard.

Nonetheless, the index introduced by Kübler (hereafter KI according to the recommendation of the AIPEA in Guggenheim et al., 2002) quickly became popular and began to be widely used because of its simplicity and reproducibility. The KI is also an improvement on the Weaver index, which was found to be less accurate experimentally (Kübler, 1967). The limits of the anchizone, the zone of incipient or very low-grade metamorphism, are defined on the KI scale at 0.42 $\Delta°2\theta$ CuKα for the diagenesis/anchizone boundary, and at 0.25 $\Delta°2\theta$ CuKα for the anchizone/epizone boundary. Kübler (1967) selected these limits on the basis of certain mineralogical changes: the lower anchizone limit coincides with the upper-grade limit of the existence of liquid hydrocarbons and the dickite to pyrophyllite transformation; the upper anchizone limit is associated with the appearance of greenschist facies minerals, such as chloritoid.

Recommendations for the use of the Kübler index

KI measurements are simple and quick. However, the delimitation of KI zones still remains controversial at present, mostly due to the numerous factors affecting standardization and inter-laboratory calibration of the KI scale (Kisch et al., 2004). Frey (1987) reviewed the variables that influence the KI values and reported them to include, among others: sample preparation, instrumental conditions, and the presence of other micaceous minerals in the samples.

We can distinguish three categories of laboratory and measurement procedures:

1) Sample-preparation procedures (grinding and grain-size separation methods, clay-layer thickness sedimented on glass slides, etc.). An attempt to minimize these effects was the recommendation for uniform preparation procedures by the IGCP 294 IC working group (Kisch, 1991). The main points of this recommendation are related to crushing, oriented mounts and

cation saturation, and ethylene glycol solvation. KI is traditionally measured on oriented mounts of <2 μm fraction on air-dried oriented aggregates that contain more than 2.5 mg/cm^2 of sample (Warr and Rice, 1994).

2) X-ray diffractometer settings adopted for measurement of the FWHM values (scan rates, time constants, slit widths, use of filters, counting sensitivity, etc.). The KI is very sensitive to any change in these settings (Warr and Rice, 1994). The effects of these factors have been studied by Kisch (1990) and can be monitored by the comparison on polished-slate interlaboratory standards. KI measurements must be performed using Ni-filtered CuKα radiation (40 kV and 30 mA) with a scan rate of 1–0.5º2θmin^{-1} for the range of 7-10º2θ. The transition from one diffractometer to another requires many calibrations.

Robinson et al. (1990) calculated the percentage of mean error produced by the combined effects of sample-preparation techniques, machine variations, and intra-sample and inter-sample variations, concluding that the smallest errors are associated with machine variation (5%). These authors recommended that the intervals used to contour KI data should not be less than 0.1 Δº2θ if the contouring is to have a high degree of confidence (>0.8).

3) Techniques used for measuring or determining the "raw" (uncalibrated) FWHM values. The effects of this factor can be ruled out if the FWHM values of the investigated samples and the standards used for calibration are measured in the same way. That is, the values obtained must be corrected using standards. The correlation between laboratories has been a long-running problem of KI measurements. Warr and Rice (1994) proposed an international standarized scale to express KI, termed the "Crystallinity Index Standard" (CIS). This scale maintains the boundaries proposed by Kübler for the low- and high-grade limits of the anchizone: 0.42 and 0.25 Δº2θ respectively. A set of four interlaboratory standards are provided by these authors in the form of chips that must be prepared and measured by every laboratory in a routine way. The chips are four pelitic rocks from the Variscan low-temperature metamorphic belt of North Cornwall (SW Great Britain) that range from diagenetic to epizonal grades (SW1, 2, 4 and 6). In addition, there is a muscovite instrumental standard (MF1) that is a flake (parallel to 001) from a euhedral crystal of muscovite obtained from a granite pegmatite in India. The mean of three repeat measurements must be plotted against the CIS values. A regression analysis derived from the plot allows a correction to be made as part of a spread-sheet calculation in the form of: $KI_{(CIS)}=a*KI_{(mylab)}-b$. This equation, determined for each laboratory, allows data sets produced by different research groups to be directly and quantitatively compared. This entire process is called interlaboratory standardization.

In spite of the advantages of the international standarized scale to express the KI, Kisch et al. (2004) criticized the standardization. These authors consider the limits of the anchizone produced by the "CIS" scale of Warr and Rice (1994) to be higher than those obtained by other laboratories and have presented various reasons that might explain this anomaly. Kisch et al. (2004) recommend reporting the calibration regressions used and the uncalibrated data in all papers reporting on the KI. Their criticism mainly concerns the comparison of the new scale with the traditional values, which they consider the weak point of the proposed standardization process; however, they in no way question the necessity and convenience of a tool to make the values generated in different labs compatible with each other.

The presence of other micaceous mineral phases with XRD peaks coincident with or adjacent to the illite reflection (such as detrital mica, paragonite, and illite/paragonite or R3 illite/smectite mixed-layers) is another factor that may in practice influence the shape of the 10 Å illite peak and distort the KI values. The presence of detrital mica sharpens the diffraction peaks, although the use of the <2 μm fraction largely reduces this effect. In addition, the effects of detrital micas decrease with burial and disappear almost completely in the anchizone (Kübler and Jaboyedoff, 2000). The influence of the illite/smectite mixed-layers on the 10 Å illite peak width can be analysed by means of a statistical comparison with the less-affected 5 Å peak. These two peaks (10 and 5 Å) are affected differently by the overlap of other 10 Å phases. The illite/smectite mixed-layers produce a tail in the 10 Å peak towards lower angles, causing significant asymmetrical broadening that disappears after ethylene-glycol treatment (Nieto and Sánchez-Navas, 1994; Battaglia et al., 2004). Nevertheless, when illite/smectite mixed-layers are absent, the widths of the two peaks are very similar. Diagenetic KI values are less accurate due to the sensitivity of expandable layers produced mainly by changes in relative humidity (Kübler, 1967). In fact, the absence of expandable layers in illites is one of the characteristics used to define the anchizone.

Moreover, paragonite peaks also differentiate quite well from the second mica reflection. Thus, a KI measurement carried out on the second mica peak may be free of paragonite and illite/smectite mixed-layer effects (Battaglia et al., 2004). In any case and according to Frey (1987), rock samples that contain paragonite and/or margarite should be excluded from the "crystallinity" studies. Small portions of Na- or Ca-micas either forming discrete, sometimes intimately, intergrown phases or mixed-layers may cause considerable peak broadening and shifts in KI. Nevertheless, at higher anchizonal and epizonal grades paragonite usually forms a separate phase that is much more easily identified than that of the K-Na micas. Finally, NH_4-illite (tobelite) is also frequently found in metapelites (Nieto, 2002) and its first basal reflection hardly differs from that of illite-muscovite. In this case, since the relation of tobelite and illite is almost unknown at present, the effect cannot be isolated.

Physical meaning of the Kübler index

The Kübler index was initially used with caution because the physical reasons for the change in the 10 Å peak were poorly understood. Currently, it is well known that line broadening is the result of two factors, domain size (crystallite size) and lattice strain (imperfection). That is, the 10 Å peak width of illite in an XRD pattern is a function of several interdependent parameters. Excluding the factors mentioned above (e.g. instrumental peak broadening), the thickness of the illite-muscovite crystallites is the main parameter that controls XRD peak width, with lattice strain and other imperfections being secondary contributors.

Before the use of HRTEM for lattice resolution, the only possible estimations of domain size and defect content in poorly crystalline minerals were based on indirect mathematical calculations on the XRD spectra (e.g. Warren and Averbach, 1950; Árkai and Tóth, 1983). The traditional Scherrer equation, for instance, relates the FWHM of an XRD peak to the crystallite size measured normal to the diffraction plane, assuming defect-free material and eliminating instrumental broadening (Klug and Alexander, 1974). Weber et al. (1976) were amongst the first scientists to apply the Scherrer equation to the 10 Å peak. Certainly, the use of HRTEM has permitted recognition of mineral microstructure at the lattice level, making possible the direct measurement of phyllosilicate packets. However, it must not be forgotten that XRD yields average results, whereas HRTEM produces a crystallite thickness distribution for each sample (Figure 1). Although complementary, the results obtained by the two techniques are often incompatible; nonetheless, for the subject addressed here the two methods are congruent (e.g. Warr and Nieto, 1998).

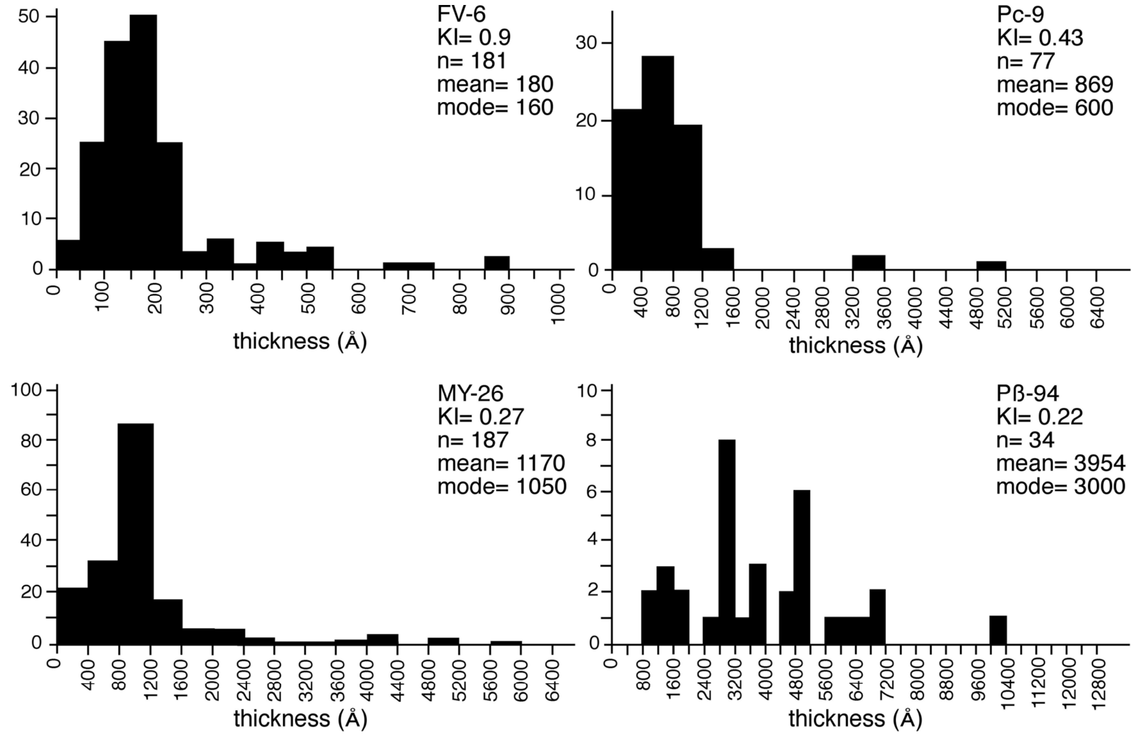

FIGURE 1. *Histograms of thickness distribution of micas measured on lattice-fringe images (based on data from Abad et al. 2001, Nieto and Sánchez-Navas, 1994).*

Much research has centred on the physical significance of the KI, focusing on correlating KI data with measurements of illite-muscovite crystallite thickness in lattice-fringe images (Merriman et al., 1990; Nieto and Sánchez-Navas, 1994; Warr and Rice, 1994; Jiang et al., 1997). Some of these authors have even applied the Scherrer formula and compared the value obtained with the KIs determined by XRD and HRTEM measurements, finding a good agreement (e.g. Merriman et al., 1990). These observations led to an interpretation of the anchizone limit values in terms of crystallite size. Despite the differences among authors on the means of defining what a coherent scattering domain in a lattice-fringe image is, all the literature agrees that the KI quite faithfully reflects the evolution of the thickness of the illite-muscovite packets. Merriman and Peacor (1999) summarized current knowledge on this relationship; their Figure 2.19. indicates that the sizes predicted by Scherrer's equation are very close to those found in various research works and the limits of the anchizone (0.42 and 0.25 $\Delta°2\theta$) are shown as crystallite sizes (220 and 520 Å respectively). The differences in criteria and the wide dispersion in sizes at the sample level (Figurel) are the reasons for the differences in detail among the various papers published regarding the limits of the anchizone in terms of size of the crystalline domain. Therefore, once the initial methodological problems were overcome by means of the proposal for standardization by Warr and Rice (1994), the KI came to be considered a good statistical indicator of the wide range of sizes present in a very low-grade pelite.

Nevertheless, no detailed combined KI and HRTEM studies have been dedicated to the study of expandable layers. Most studies do not take into account the expandable layers of illite material although they are often present and affect the KI values and limits (Kübler and Jaboyedoff, 2000). Jaboyedoff et al. (2001) proposed a method for the physical interpretation of KI based on KI measurements on both air-dried and ethylene-glycolated samples. This method can determine the mean number of layers in coherent scattering domains (i.e. illite particle size) and the smectite-layer percentage in illite/smectite minerals for a given stacking order since the KI is sensitive to low percentages of expandable layers.

The number of defects is not easy to quantify in lattice-fringe images, although we know that wavy layers, edge dislocations, curved layers, and variable-stacking sequences are examples of lattice distortion that may contribute to the broadening of XRD peaks. Therefore, the characterisation of lattice strain by TEM and its correlation with KI data is much more difficult than the KI comparison with measurements of illite-crystallite thickness. Strain-induced defect migration contributes to the polytypic transformation from the 1Md illite polytype of smectite-rich I/S to dominant $2M_1$ polytypism in illite-rich I/S (Dong and Peacor, 1996). The increased dominance of $2M_1$ illite directly influences crystal thickening (Dong et al., 1997) and hence KI. In summary, strain decreases with increasing metamorphic grade, which implies the increasing perfection of crystals (Árkai et al., 1996).

Applications of the Kübler index

Research data suggest that phyllosilicates in diagenetic and low-temperature metamorphic conditions do not reflect thermodynamic equilibria (Abad et al., 2001, 2003a, b; Árkai et al., 1996, 2000; Merriman et al., 1995; Warr and Nieto, 1998). Consequently, criteria such as the KI, polytypism, crystallite size values, chemical characterisation of the metastable sheet silicates, or the amount of lattice strain in low-grade rocks cannot serve as geothermometers. These parameters are only qualitative indicators of the stages the phyllosilicates have reached through a series of metastable mineral reactions (Merriman and Peacor, 1999). This situation is compatible with the Ostwald Step Rule (Morse and Casey, 1988) and emphasizes the notion of reaction progress: metastable phyllosilicates undergoing reactions towards the state of stable chemical and textural equilibrium reached in greenschist-facies samples (Essene and Peacor, 1995).

Illite is the first phase to produce a 10 Å peak in the smectite-illite/smectite-illite-muscovite reaction series, so that a given KI value is a function of the reaction progress of dioctahedral phyllosilicates in low-grade rocks and represents a state controlled by kinetic factors whenever the smectite-to-illite reaction has progressed to >80% illite. Consequently, a state of reaction progress can be ascribed to any assemblage, using one of the so-called geothermometers previously cited. Some of the more relevant kinetic factors to be taken into account in the control of reaction progress are fluid activity, thermal energy, and strain associated with overburden and tectonic stress. Essene and Peacor (1995) point out that, where these geological variables are approximately equal, there should be a close correlation between reaction progress (measured by KI, for instance) and metamorphic grade (temperature). Nonetheless, these correlations must be undertaken very cautiously since there is no true equilibrium.

Prograde changes in KI are consequently an inseparable part of the progress of interrelated reactions, such as the reduction in smectite interlayers, polytypic transformations, and a decrease in compositional heterogeneity of series members. Moreover, although this index is not the only indicator of reaction progress in the series, the KI is very sensitive from the onset of deep diagenesis to the beginning of the epizone in different geotectonic regimes, and is a specific index of the anchizone. As a consequence, up to three zones can be distinguished in the very low-grade metapelitic sequences—deep diagenetic zone (KI>0.42); anchizone (0.42>KI>0.25), and epizone (KI<0.25). These three zones are also indicators of the pelitic lithology and associated microfabrics (see Table 1).

For many years, studies on sequences affected by low-temperature metamophism have focused on regimes with intermediate-pressure regional metamorphism. The phengite component of dioctahedral micas and the *b* unit cell dimension of K-white mica, which is dependent on the degree of phengitization, can be used for estimating the pressure in metamorphic processes (Merriman and Peacor, 1999). This is very useful for the identification of the geotectonic context (a compressive or extensional regime), although the KI cannot be expanded to terranes with

TABLE 1. *Metapelitic zones showing associated lithologies and microfabrics. Illite Kübler index and other indicators of reaction progress in the smectite-I/S-illite-muscovite series of clay minerals used to index the zones. Correlation with metamorphic facies, fluid zones, maturation stages some organic maturity indices (shynthesis from Kisch, 1987; Merriman and Frey, 1999; Merriman and Peacor, 1999).*

Metapelitic zone (depth, km)	Temperature (°C)	KI (Δ°2Θ)	% illite in I/S	TEM mean illite crystallite thickness (Å)	Illite-muscovite polytype	Typical pelitic lithologies	Characteristic microfabrics	Metamorphic facies	Fluid zone	Maturation stages	Vitrinite reflectance Rr%	Conodont alteration index (CAI)
Shallow diagenetic zone										Diagenesis		1
3.5-4	~100	~1.00	60-80		$1M_d$	shale/		zeolite	HHC		0.50	
Deep diagenetic zone					(1M?)	mudstone	bedding-parallel (S_0)			Catagenesis	1.35	2 3
6.5-8	~200	0.42	~90	200							2.00	
Low anchizone					$2M_1$ (3T)		crenulated (S_0)					4
		0.30	95	400		slate	slaty	prehnite-pumpellyte	CH_4	Metagenesis	3.00	
High anchizone							cleavage (S_1)					5
10-12	~300	0.25	>99	500							4.00	5.5
Epizone					$2M_1$ (3T)	slate (phyllite)	(S_{1+})	greenschist	H_2O			

pressure gradients other than intermediate (Kisch, 1987). This has also been confirmed for high pressure by do Campo and Nieto (2003) and for contact metamorphism by Abad (2002).

A statistical treatment of KI data is possible when there are enough measurements for each formation in a stratigraphic succession or even in a tectonostratigraphic sequence. The KI range and the means have been used, for example, to detect patterns of burial metamorphism (Davies et al., 1997) and high-strain zones (Roberts et al., 1991).

The use of cross-sections with KI data is useful to understanding the relationship between tectonics and very low-grade metamorphism; some authors (Frey et al., 1980; Breitschmid, 1982) have even combined KI annotations with vitrinite reflectance and fluid-inclusion data (see next section). A further possibility is to draw isocryst maps (white-mica "crystallinity" maps) as long as an evenly spaced distribution of metapelites is possible. Many regional studies have used these maps (introduced by Roberts and Merriman, 1985), including Awan and Woodcock (1991) and Roberts et al. (1990), among others. The contoured maps are valuable tools for deducing episodes of different nature; in addition, metamorphic cross-sections can be drawn from the maps to reconstruct the structural and metamorphic history of a region (e.g. Roberts et al., 1996; Warr et al., 1996).

Correlation of Kübler index with other indicators of very low-grade metamorphism

Although the Kübler index is the most common and straightforward technique to establish thermal evolution in very low- to low-grade rocks, there are other methods for the characterisation of diagenesis and low-temperature metamorphism, such as metabasite mineral facies, vitrinite reflectance, conodont colour alteration index and fluid inclusion microthermometry, among others. For each method there exists specific terminology to designate the metamorphic grade. The use of one criterion or another depends on the nature of the materials studied. In this regard, the characterisation of low-temperature conditions by mineral assemblages can be very useful in metabasic rocks, for instance. Moreover, if these rocks are intercalated in a sedimentary sequence, the KI data from the clastic rocks can be correlated with the metamorphic zones based on the mineral assemblages of the metabasites (e.g. Abad et al., 2001).

Vitrinite reflectance (%Rr) is the most widely used indicator of thermal maturity in sedimentary rocks containing disseminated organic particles (Sweeney and Burnham, 1990; Ernst and Ferreiro-Mählmann, 2004). It is very effective for estimating the maximum temperatures that sedimentary rocks have experienced from dispersed organic particles and is also used to indicate maturation or rank of coal. When this indicator is correlated with KI data, one of the problems arising is that mineral and organic materials may react differently to the physical conditions of sedimentary burial. In some cases, when the geothermal gradient is higher than normal, the temperature suggested by the KI data may be lower than that indicated by vitrinite reflectance, perhaps due to the slow reaction rate of clay minerals (Srodon, 1979; Aoyagi and Asakawa, 1984). In addition, the internal strain can increase vitrinite maturity and also favour illite crystal growth.

Another index of low-grade metamorphism based on organic features is the conodont colour alteration index (Epstein et al., 1977). The CAI method is based on analysis of the colour changes that the organic matter in conodont elements undergoes as a response to incresase temperature with time. Whereas the KI is limited to clastic sedimentary rocks, the CAI is an organic indicator that enables the low-temperature characterisation of other lithologies, such as carbonate rocks (Rejebian et al., 1987). These two indicators are complementary and several authors have correlated them (Gawlick et al., 1994; Paull et al. 1996; García-López et al., 1997 and 2001; Brime et al., 2001; among others) and even correlated the KI, the CAI, and the Rr (Kovacs and Árkai, 1987). This research shows that CAI values corresponding to the diagenesis-anchizone and anchizone-epizone metamorphic boundaries can vary in different regions.

Therefore, more studies based on KI and CAI data are needed to establish correlations between these two low-temperature-metamorphism parameters.

Fluid inclusion data are very interesting in the study of very low-grade metamorphism in some regions. This technique is based on microthermometry in fluid inclusions, mainly in quartz grains or veins. Mullis (1987) proposed three fluid zones on the basis of microthermometry in quartz veins: a fluid zone of higher hydrocarbons at T<200ºC, a methane zone (T=200-270ºC), and a water zone (T>270ºC). However, the cogenetic nature of the analysed inclusions and rocks is not always easy to recognize.

Although less common, the crystallinity of chlorite (Árkai, 1991), kaolinite (Brauckmann and Füchtbauer, 1983), and pyrophyllite (Ianovici et al., 1981) has also been used as a metamorphism indicator. The applicability of chlorite crystallinity (ChC) for indicating grades in metaclastic rocks was statistically proven by Árkai et al. (1995) and was extended to meta-igneous rocks by Árkai and Ghabrial (1997). Nevertheless, it is not as widely used as the KI to determine reaction progress. Several regional studies using ChC have found a poor correlation with KI data (Dalla Torre et al., 1996a; Wang et al., 1996; among others), which suggests ChC may be a less reliable indicator of regional metapelitic reaction progress than the KI. Reasons for this lack of reliability include the fact that chlorite tends to retain more dislocations than illite in anchizonal and epizonal metapelites, which contributes to polygonization and segmentation of the crystals, thus generating subgrains and reducing the overall crystallite size. As well, the smectite-to-chlorite transition has few intermediate phases and they can persist at higher metapelitic grades than illite/smectite in the dioctahedral phyllosilicate series.

Several authors have attempted to correlate the KI values with the role of fluids in pressure-solution processes to generate schistosity. Others have undertaken to demonstrate that KI values are higher in the hinges of folds than in the limbs (Costa and Bonazzi, 1991; Fernández-Caliani and Galán, 1992), but strain is poorly documented in these folds. There is almost no quantification of deformation based on the type of fold and the temporal relationships between the deformation phase and the metamorphic conditions (Kübler and Jaboyedoff, 2000).

In conclusion, different attempts for correlating metapelitic zones (KI) with other indicators of basin maturity (mineral assemblages in metabasites, coal rank, conodont alteration index, fluid inclusion data, etc.) have been carried out by numerous authors (Frey, 1986; Kisch, 1980 and 1987; Árkai, 1983; Rahn et al., 1994; Dalla Torre et al., 1996b; among others), but the proposed boundaries are still broad and transitional in nature. Table 1 is a chart showing a correlation between the reaction progress in the smectite-illite/smectite-illite-muscovite series of clay minerals with metapelitic zones, crystallite domain sizes, KI, fluid zone, and some organic maturity indices (Rr and CAI). In short, the diagenesis-anchizone boundary (KI= 0.42 Δº2θ) is correlated with the onset of metagenesis at Rr= 2.0% and CAI>4 with a minimum temperature of 200 ºC (Mullis et al., 1993) and the anchizone-epizone boundary (KI=0.25 Δº2θ) is indexed at Rr>4%, CAI>5.5 (García-López et al., 2001), with the transition from anchizone to epizone occurring at approximately 300 ºC (Bucher and Frey, 1994).

Summary

KI is a valid tool, successfully applied to many fine-clastic metasedimentary sequences to detect the anchizonal limits in sedimentary basins and in the outer fold-and-thrust zones of orogenic belts. It is very useful for petrogenetic purposes in geodynamic and palaeotectonic reconstructions and regional comparisons. Notwithstanding, we should not forget the warning by Kisch (1987) against automatically expanding its use to terranes with pressure gradients other than intermediate.

The accuracy of KI decreases as one moves away from the anchizone towards either diagenesis or epizone. The only features differentiating the samples corresponding to the distinct grades are quantitative, related to packet size (= crystal size) and number of defects (Árkai and

Tóth, 1983). In the light of the TEM data now available, it is not surprising to note the remarkably good performance of the KI, particularly once the initial methodological problems were overcome by means of the proposal for standardization by Warr and Rice (1994).

KI is a measure of states of metastable equilibrium, a measurement of reaction progress of dioctahedral phyllosilicates in low-grade metamorphic rocks. Although reaction progress is affected by various factors, the contribution of temperature is quite significant, which is what makes it so relevant for the correlation of the KI with low-grade metabasic rocks and other mineral and organic maturity indicators. The joint use of these indicators is, at present, the best way to establish the thermal conditions in very low-grade metamorphic environments.

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