THE TRANSFORMATION OF ILLITE TO MUSCOVITE IN PELITIC ROCKS: CONSTRAINTS FROM X-RAY DIFFRACTION

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Abstract—The boundary between diagenesis and metamorphism most likely involves the change of illite into mica. Observations of this change can be made using decomposed X-ray diffraction (XRD) spectra of illitic clay mineral assemblages in pelitic sedimentary rocks.

XRD analysis of the (003) diffraction peak of diagenetic illites indicates that there are 2 components, one of small coherent diffraction domains and another of larger domain size. Peak width, shape and position define these fractions. The smaller domain size material in diagenetic rocks is highly illitic (>95%) but contains some smectite layers and can be best described by Gaussian shapes. The grains with larger diffracting domains show no expanding layers.

Metamorphic illites (probably muscovites) show no smectite interlayers in any fraction. In the transition from sedimentary and diagenetic to metamorphic illites, new grains of smectite-free illite are formed at the expense of the older minerals. This suggests that the new metamorphic minerals are recrystallized phases. Metamorphism of illites then produces new mica phases.

Key Words—Decomposition, Diagenesis, Illite, Metamorphism.

INTRODUCTION

The geological zone between sedimentary and metamorphic domains observed in pelites (rocks composed essentially of clay minerals and detrital mica, with some feldspar and quartz) has been of interest to geologists for some time. This geological zone is called "diagenesis" (Dunoyer de Segonzac 1970; Frey 1987b). In pelitic rocks clay minerals evolve due to diagenesis. The boundary between diagenetic and metamorphic domains should involve recrystallization of mineral components in a rock (Weaver 1989). However, this criterion is difficult to observe using normal petrographic methods on clay-rich samples. In order to overcome this problem it has been necessary to study mineral reactions which are common to a large range of rock types in order to establish a criterion of transformation from diagenesis to metamorphism (Winkler 1976; Frey 1987a). In such studies, where the thermal boundaries are based upon laboratory experiments, it was assumed that the diagenetic clay mineral assemblages evolved much more slowly than the key reaction that produces new metamorphic minerals. The use of such key mineral reactions such as those producing pyrophyllite is unfortunately often limited to specific bulk compositions, often not present in a series of sedimentary/metamorphic rocks. Pyrophyllite is a rare mineral in pelitic rocks (Velde 1968).

In general, it is preferable to define a diagenesis–metamorphism boundary in a specific compositional context (pelitic rocks) using omnipresent minerals such as illites or the illite–smectite (I–S) mixed-layered mineral series. Due to the very common presence of smectite in early diagenesis of pelitic sediments and the more common presence of illite in mature pelites, the smectite-to-illite conversion has been considered an important indicator of the change of sediment into metamorphic rock (Weaver 1989). This reaction takes place during sedimentation and burial of sediments. At the end of the smectite-to-illite reaction the illite basal peak reflections dominate XRD spectrum in the broad envelope that represents the presence of several clays. Kübler (1968), then many others, used the crystallinity index of illite (essentially the peak width at half height) as an indicator of the limits of the domains of diagenesis and the different lowest grades of metamorphism (anchi- and epi-). The lower the smectite content of the different phases present, the more narrow the illite XRD peak becomes. The presence of larger crystal diffracting domains further narrows the illite (or mica) peak. The illite crystallinity index describes the global change in the evolution of the I–S and the end-product illite phases in sediments and sedimentary rocks.

It is the object of this paper to use XRD methods to investigate more closely the evolution of the different components of the I–S and illite during the course of different types of geologic events in order to observe the transition to a metamorphic mineral assemblage. Several different geologic settings are used in order to test the importance of thermal versus time factors in reaction kinetics. This approach is not a redefinition of the crystallinity index of illite but a refinement of the assessment of the transition from diagenesis to metamorphism.

If possible, we wish to establish whether or not the metamorphism of diagenetic illite involves recrystal-

lization and if such a recrystallization can be taken as the definition of metamorphism in pelitic rocks.

EXPERIMENTAL METHODS

X-Ray Diffraction

XRD is the primary tool used in this study to define the illite crystallinity. The <2 μm fraction was studied in order to represent the whole clay fraction. The <2 μm separates were deposited on a glass slide having been concentrated using $SrCl_2$ as a flocculating agent.

The physical basis for the interpretation of the diagrams used here is given in Reynolds (1980), Moore and Reynolds (1989) and Lanson and Besson (1992). These studies have shown that one can produce a model diffractogram that can be compared very closely to natural mineral assemblages with reasonable accuracy. Such work is based upon the physics of the diffraction of X-rays in crystalline matter. Despite a solid theoretical basis, there are nevertheless some differences between the observed diffraction patterns and those predicted, which create some problems of interpretation (Lanson and Velde 1992). However, the agreement between predicted peak positions and widths (the 2 variables that can be measured in a 1-dimensional analysis) is so great that it is reasonable to simulate XRD diagrams in order to explain changes observed in natural mineral structures. Certainly errors will be made but the general pattern of change will be valid.

In the present study no attempt has been made to observe the thickness of crystallites by electron microscopic methods. One can assume that the overall distribution of particle size of the clay crystallites is somewhat lognormal (Warr and Rice 1994; Merriman et al. 1990). Until now, there has been no direct relation established between the crystal thicknesses of illitic clay particles and the sizes of the diffracting domains in them as determined by XRD methods (Dalla Torre et al. 1996). The estimation of coherent diffracting domains producing the XRD patterns commonly observed for sedimentary rocks, in our study as well as in those using the illite crystallinity method, is based only upon calculations of the physics of X-ray diffraction. The difference between these domains and actual crystallite sizes can possibly be very important. The coherent diffracting domain is defect-free. It is quite possible, and very probable, that a given crystallite will present several diffracting domains within its boundaries due to defects in the crystallite structure. Hence the correlation between XRD domains and crystallite thickness measured by electron microscope methods is not necessary (Dalla Torre et al. 1996). However, the XRD method integrates a very large number of crystallites and diffracting domains into its determination while electron microscope methods use only a very small number of grain observations among those present in a given clay sample.

The samples studied show only examples where no significant quartz or feldspar was present that would have interfered with a determination of the 003 diffraction peaks.

To obtain representative data, we use the XRD method for estimating differences in the composition and crystallite diffracting domains of illitic materials in different sequences of high-grade diagenetic pelitic rocks.

XRD Methods and Decomposition

XRD diagrams were obtained on oriented samples using a Philips diffractometer with a stepping motor. One hundred points per °2θ were counted between 35 to 60 s each. The DECOMPRX program of Lanson (1990) was used to decompose the spectra. It considers the $K\alpha_1$ and $K\alpha_2$ doublets which can be assigned different shape parameters, Gaussian or Lorentzian (G or L). Hence one can produce G/G, G/L, L/G or L/L shapes where the first shape represents 60% of the shape function. This is in fact a limited form of a Pirson function. In the present study the peaks were fitted with either G/G, G/L or L/G functions. These peaks are in any event always symmetric.

Figure 1 shows the decompositions for the (001) and (003) peaks for ground muscovite.

Phase Fractions and Attribution of Decomposed Diffraction Peaks

In diagenetic clay-mineral assemblages the presence of several phases, illite and non-illite, of similar composition and structure leads inevitably to the existence of overlapping diffraction peaks on an XRD diagram. These have been analyzed in the present paper according to the protocol given in Lanson and Besson (1992) and Lanson and Velde (1992). Other methods of establishing the number of peaks with different shape criteria have of course been used (Stern et al. 1991; Wang et al. 1995), but the results are quite similar, giving the same number of peaks found at the same range of positions in the diagrams.

The first-order basal spacing of illite or micaceous mineral diffraction maxima for diagenetic and low-grade metamorphic samples has been observed to be asymmetric (Kübler 1968; and more recently Wang et al. 1995) The form of this band, which is in fact an assemblage of several peaks, has been the subject of many papers which use its width at half height to determine the evolution of illite and other phases through what is called the "illite crystallinity index" (Kübler 1968; Kisch, 1987, 1990; Robinson et al. 1990; Warr and Rice 1994). However, recent applications of numerical treatment indicate that there are several possible methods to describe an asymmetric diffraction maximum. New methods suggest that the asymmetry of the first-order illite peak is in fact due to the existence of several different clay-mineral phases in the

Crushed muscovite   **(OO1)**

DB= 9.95A
Form = L/G
WHH= 0.133
POS= 8.88

DB= 10.11A
Form = G/G
WHH= 0.337
POS= 8.735

CI = 0.12 (°2Θ)

RF= 99.27%

(OO3)

RF=99.55%

DB=3.32A
Form =L/G
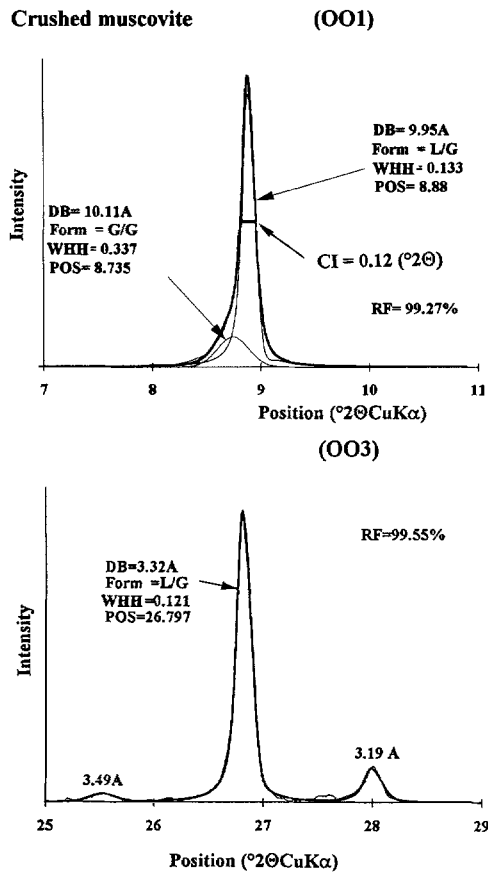WHH =0.121
POS=26.797

3.49A   3.19 A

Figure 1. Decomposed spectrum of finely ground muscovite mica for the (001) peaks. CI = Kübler crystallinity index measurement. WHH = width at half height, POS = peak position in °2θ. Peak shape G = Gaussian, L = Lorentzian for $K\alpha_1$ and $K\alpha_2$ components of the peaks. G/L indicates a fit with a Gaussien $K\alpha_1$ and Lorentzian $K\alpha_2$ component. Note that the small peak at 10.11 Å is not present in the (003) peaks and hence is considered to be an instrumental artifact.

(a)

(b)

CI = 0.52 (°2Θ)

PCI
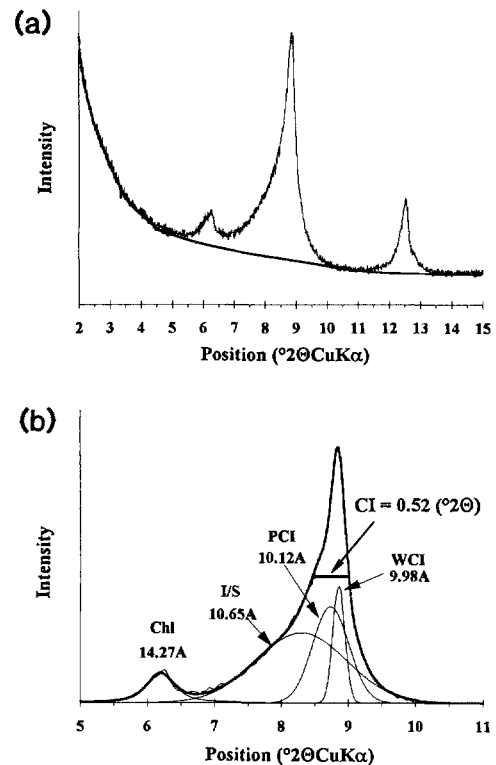10.12A

I/S
10.65A

WCI
9.98A

Chl
14.27A

Figure 2. Illustration of the procedures used to extract the component peaks from the complex 001 XRD bands for diagenetic clays: a) air-dried sample with indication of the background for the spectrum; b) decomposed spectrum after background stripping. Component peaks are Chl = chlorite, I–S = low expandability illite–smectite mineral, PCI = poorly crystallized, fine-grained or small coherent diffracting domain illite material, WCI = well-crystallized illite or mica grains with coherent diffracting domain above 30 layer units. CI = Kübler crystallinity index measurement.

sedimentary materials. One method used to model the asymmetric peak is to use a combination of peak shapes, symmetric or asymmetric, using 1 peak to describe the total diffraction band. A second method is an attempt to attribute the observed asymmetry of the illite band complex to a combination of different symmetric peaks that represent different grain populations or diffraction domains within grain populations (Lanson 1990; Stern et al. 1991; Wang et al. 1995). We use this second approach in the present paper. Three peaks can be identified for the primary diffraction maximum near 10 Å (the (001) peak) in rocks that show advanced stages of diagenesis. Correspondence between these peaks and mineral grain shapes and compositions has been established by Lanson and Champion (1991). It is then possible to attribute the existence of different mineral populations to the peaks of the decomposition routine. The method is illustrated

in Figure 2. We observe the same 3 peaks in both the (001) and (003) peak regions of the spectra. Correspondence between observed and calculated peak positions for I–S minerals is reasonable (Moore and Reynolds 1989; Lanson and Besson 1992).

Studies by Lanson and Besson (1992) showed that the first-order peak of the I–S minerals is the strongest but the true shape and positions of the peaks are less easy to interpret. However, the (003) peak is less subject to shifts and asymmetric broadening due to experimental artifacts. In the present study greatest emphasis is placed on these (003) peaks. This illite peak is frequently masked by the presence of large amounts of quartz and, to a lesser extent, chlorite. Therefore our method should not to be used in a universal way but only where, as is the case for our samples, a nearly pure illitic fraction is present. In any event there should be a strong correlation between the determinations by decomposition for both (001) and (003) peaks in the same sample. The correlations take into
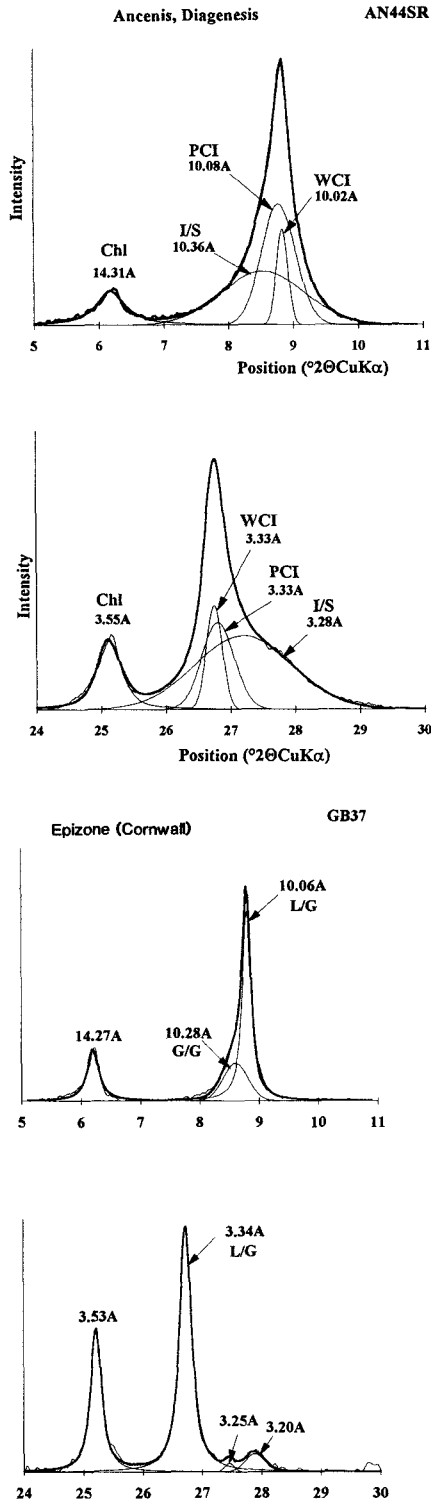
Figure 3.   Two examples of (001) and (003) peaks showing the correspondence between the 2 diffracting regions. WCI = well-crystallized illite with a large coherent diffracting domain, PCI = poorly crystallized illite with a small coherent diffracting domain, I/S = interstratified illite–smectite with <95% illite layers, Chl = chlorite, L = Lorentzian peak shape, G = Gaussian peak shape.

consideration the effects of interlayering of smectite and mica layers (Moore and Reynolds 1989). Figure 3 shows the (001) and (003) bands for 2 samples.

Identification of Phases

The 001/002 I–S peak (<90% illite) is usually broad (>1 °2θ CuKα radiation width at half height) and the diffraction maxima can be adequately described by a single Gaussian-shaped band. *This peak changes position and intensity upon glycolation.*

The complex illite band, taking out the I–S component, shows a remaining diffraction maximum that is asymmetric. It is known that instrumental band broadening in the 10-Å region produces the effect of only a very small (10% surface of the primary peak) and narrow satellite peak to low 2θ values for diffraction spectra of ground pegmatitic muscovite (Figure 1). The (003) peak for this diffraction maximum is symmetric and can be described by 1 peak. It is adequately described by a Gaussian–Lorentzian or Lorentzian–Gaussian shape. This is called the well-crystallized illite (WCI).

In decomposing the illite peak complex from a diagenetic mineral assemblage containing an I–S phase, one is left with a third peak, called the unidentified band by Wang et al. (1995). Work by Lanson and Champion (1991), Lanson and Besson (1992) and Lanson and Velde (1992) indicate that this peak is in fact due to the small diffraction domain material of near illitic composition. This is called PCI (poorly crystallized illite). This peak is best described with a Gaussian–Gaussian shape. *Its position is not displaced by glycolation.*

These 3 peaks will be followed in the (003) reflection zone, where the effects producing asymmetry are less important than in the (001) peak area.

SAMPLES STUDIED

Samples were selected for the present study in order to follow the latest stages of the smectite-to-illite reaction, that is, approaching metamorphism. The objective in sampling was to obtain sedimentary materials that had experienced the greatest "amount" of diagenesis, that is, those furthest advanced in the reaction sequence of smectite-to-illite change enhanced by normal burial processes. A second step is to observe further changes effected by regional or contact metamorphism. The first criterion was that of time. The oldest samples formed at the lowest temperatures were chosen in a basin which had not experienced a notable tectonic event (folding or thrust faulting). This was done in order to assess whether or not the smectite-to-illite reaction can be completed in low-temperature environments within a reasonable geological time framework. Results for sediments in the Paleozoic Illinois Basin are presented to this end.

Knowing the initial state of reaction advancement under low temperatures (diagenesis) over long periods of time, the next step was to obtain samples where tectonic events had affected the previous clay mineral assemblages. In such circumstances rock deformation and some thermal increase are to be expected. Higher temperatures produce regional metamorphism, that is, occurring on the 1–10 kilometric scale in more or less parallel mineralogical facies bands. The samples chosen for these types of geologic event were Paleozoic in age. In some cases the Paleozoic sediments were subsequently affected by Hercynian tectonic or metamorphic events. Samples from Brittany and southwestern England were used as examples of diagenetic–metamorphic series.

The XRD definitions of diagenesis, anchi- and epimetamorphism used for these samples in the present study are based upon the classical illite crystallinity index (Kübler 1968; Robinson et al. 1990, Warr and Rice 1994) where the limit between diagenesis is between 0.42 and 0.5 °2θ peak width at half height with CuKα radiation, and between anchizone and epizone near 0.25 °2θ peak width. They are the same as those of Kisch (1987) and only slightly different from those of Kisch (1990) and Warr and Rice (1994). Although these definitions have been changed since the early work, we use those used in the initial publications on samples from Great Britain in order to avoid confusion. The object of this paper is not to redefine epizone and anchizone terminology.

Diagenesis

1) Three series of samples from the Paleozoic Illinois Basin are used here to represent clay mineral evolution under low-temperature conditions (Gharrabi and Velde 1995). The geographical setting is given in their paper. The ages of the sediments range from Pennsylvanian to Ordovician. Two series of samples from deep bore holes and another sequence of samples taken from the same stratigraphic horizon (New Albany Shale, of upper Devonian–lower Mississippian age) from wells at different points going from the northwest of the basin to the southern tip of the Illinois portion of the basin were investigated. The results show a high degree of clay mineral reaction maturity (near 95% illite for the I–S minerals) and they do not evolve greatly as a function of actual depth (200–2500 m). Maximum temperatures attained for the deepest samples probably did not exceed 120 °C according to the kinetic formulations of the smectite-to-illite reaction/transformation according to vitrinite reflectance values (Velde and Vasseur 1992).

2) Outcrop samples were taken in the southern Brittany paleozoic (Carboniferous) Ancenis Basin (Maine et Loire, France). Here a small sedimentary basin was affected by general tectonic movements of large-scale folding and minor faulting during the Hercynian orog-

eny. No slaty cleavage was seen in the samples and no low-grade metamorphic minerals such as pyrophyllite or chloritoid were found (visual and thin section observations of the authors).

3) Several samples of diagenetic grade were taken from the Devonian in Cornwall in the area described by Primmer (1985). These rocks are part of a basin little affected by tectonics. No schistosity or folding has been noted. The entire depth–temperature history for these samples cannot be estimated.

Tectonic and Regional Metamorphic Environments

1) Two sets of samples were collected from western Brittany, in the Carhaix Basin and the Veryarch area near Brest. These samples come from the portion of the Armorican Massif that was subjected to granitic intrusion as well as strong tectonic movements during the Hyercinian orogeny. Signs of thermal metamorphism on a regional scale (pyrophyllite, chloritoid) are described by Paradis et al. (1983) for rocks near the Veryarch sector. Schistosity, folding and faulting are also apparent. The samples studied occur in the regions where these conditions are not apparent. In the Carhaix area of the Châteaulin Basin, fold schistosity is evident (Sagon 1976). One finds the prehnite–pumpyllite facies in metabasites and pyrophyllite–chloritoid–margarite in places in the pelites.

2) Samples were collected from the now-classic north coastal Cornwall area (GB) between Bude and Padstow which is used as a type area in the determination of illite crystallinity (Warr et al. 1991; Warr and Rice 1994). Samples were taken along the line shown in these papers. In this sequence, Devono–Carboniferous sedimentary rocks were considered to be in the diagenetic zone (Bude area) and affected by a complex series of orogenic events as well as batholitic granite intrusion (Warr et al. 1991), all of which brought the rocks into the anchizone (Padstowe area) and epimetamorphic zones (Tintagel). The metamorphic facies reach prehnite–pumpellyite in basic rocks and biotite facies in pelites (Robinson 1987; Primmer 1985; Warr et al. 1991). Estimations of 200–300 °C are given by these authors for rocks identified as being in the anchizone. Pyrophyllite and paragonite are present in some samples of the anchizone and chloritoid in some of the epizone samples.

EXPERIMENTAL RESULTS

Experimental results are presented as a function of peak position (in °2θ CuKα radiation) and peak width (°2θ). Data are given for the (003) peak complex because there is less instrumental effect of peak shapes and asymmetric background intensity variation. The abbreviation WHH indicates the width at half height of the peak. On the graphs, curves indicate positions and widths for a given diffraction domain size. The dots on the curves indicate the results of calculations
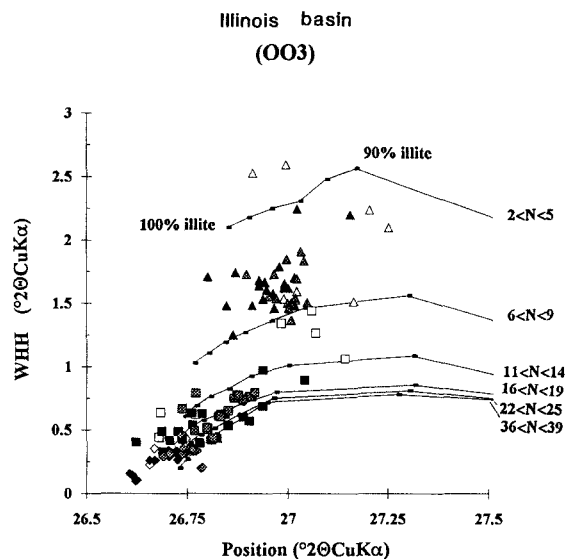
Illinois basin
(OO3)

Figure 4. Results for Illinois Basin samples presented as a function of peak width (WHH = width at half height) and peak position. Triangles indicate I–S peaks, squares indicate PCI peaks, diamonds indicate WCI peaks, open and solid figures indicate samples from deep wells, shaded figures indicate New Albany series of samples from different depths in different wells. In the (003) figure the lines indicate iso = diffracting domain thickness values (n = layers) and the dots on the lines indicate the different percent smectite layers present in the crystallites, 0 to 5 layers. Samples studied were Sr-saturated, in air-dried state.

for different percent smectite in an ordered I–S structure (type $R = 1$). I–S with small diffracting domains is found higher on the diagram and I–S with more smectite layers present is found to the right on the diagram. Three types of material identified are micas, found near the lower left-hand side of the diagram; PCI (small domain diffraction sizes), found usually at peak widths of 1 to 1.5 degrees; and I–S interstratified minerals with a peak width near 2 °2θ. In the different diagrams, different symbols indicate the different mineral types (Lanson and Velde 1992).

Diagenesis in an Old Sedimentary Basin

Results for the Illinois Basin Paleozoic samples show that the peaks for the (003) reflections follow the calculated trends reasonably closely. They show positions that indicate low expandabilities and varying diffraction domain size. The present authors have observed this effect in several other basins of younger age. There are 3 groupings: the I–S peaks near 2–5 diffracting domain layers, the PCI near 6–9 layer domains and the mica with large numbers of coherent diffracting domains (WCI). Most analyses indicate that there are some expandable layers present in small quantities in the PCI and WCI material. This is shown graphically in Figure 4.

Tectonic Areas

Figure 5 gives the peak position–peak width diagrams for the Brittany samples: Ancenis in the diagenetic zone, Veyrach in the anchizone and Carhaix in the epizone. These zones are established according to illite crystallinity index criteria given by the authors cited above. Figure 6 shows the results for the Cornwall samples in the diagenesis, anchizone and epizone sectors.

OBSERVATIONS

Diagenetic Facies

The Illinois Basin samples (Figure 4) are taken as a type series of samples of diagenesis over long periods of time under low-temperature conditions. I–S peaks indicate small diffracting domain sizes (<6 layers) and a range in smectite content between 2 and 10 percent. In the Paleozoic Brittany (Ancenis Basin) samples (Figure 5) that were affected by an orogenic episode, the peak positions for samples in the diagenetic zone show differences from the diagenetic trend of the Illinois Basin. The I–S minerals (triangles) show <90% illite content and their diffracting domain size is near 7 layers. The PCIs with smaller diffracting domain size than the micaceous peak reflections show low smectite content (<90%) which indicates a domain size of 14–25 layers. In the Devonian Cornwall diagenesis samples, the I–S peak positions are very similar to those in the Ancenis basin; however, they indicate smaller diffracting domains and more smectite layers (higher peak position in the diagram).

Hence the diffraction characteristics in the Illinois Basin, Brittany and Cornwall samples are similar for samples designated as diagenetic.

Anchizonal Samples

BRITTANY. In Brittany, in the Veyrach Anchizonal region, the I–S phase is not apparent and the peak used to identify small coherent diffracting domain micaceous material (PCI) indicates that there is no smectite component present when seen on the (003) peak width–position plots. The illite peaks show no smectite component but they indicate a small diffracting domain. It seems that there is new, fine-grained totally mica material present here. The small diffraction domain band attribution shows different peak positions in thermally affected materials compared to those in diagenetic samples.

CORNWALL. The samples from Cornwall designated as anchizonal by illite crystallinity measurements show the presence of some I–S component in the initial stages of anchizone facies. However, the diffracting domain size of these samples seems to be greater than in other series and there is a slightly lower smectite content. The PCI fractions, small domain size of the micaceous material (<90% expandable layers), indi-
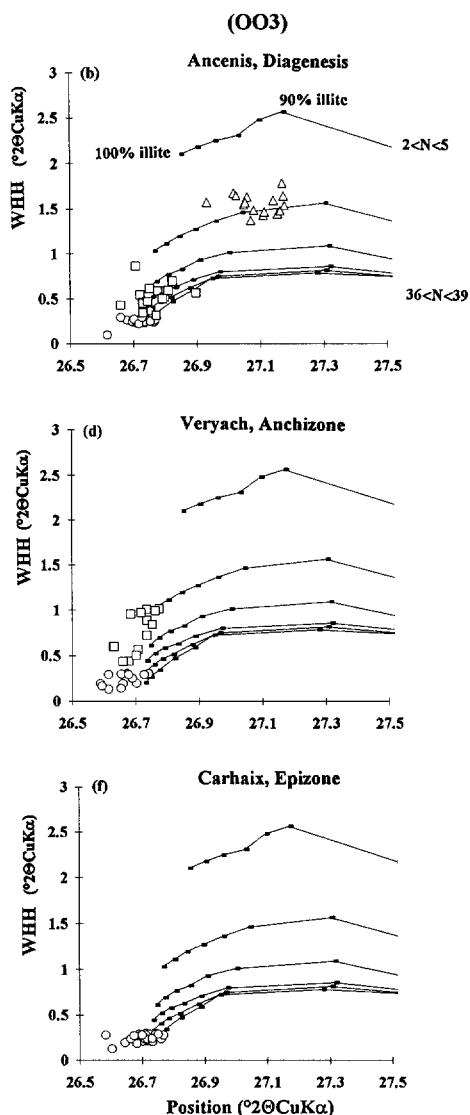
Figure 5.   Results for decomposed XRD spectra for samples from the 3 areas in Brittany: a) Ancenis diagenetic; b) Veryach anchizone and Carhaix epizone samples. WHH = decomposed peak width at half height. All samples in air-dried state.

Figure 6.   Decomposition results for diagrams of peak width at half height (WHH) and peak position for the Cornwall samples.

cate a very low smectite content and a relatively larger diffracting domain (Figure 6).

Epizonal Samples

Finally, the most transformed Brittany samples, from the Carhaix area, where pyrophyllite and chloritöid have been found in some rocks, have no I–S component, no small diffracting domain (PCI) illite and only a coarse-grained mica peak. In the (003) region, a single Lorentzian–Gaussian peak can be used to decompose the diagram.
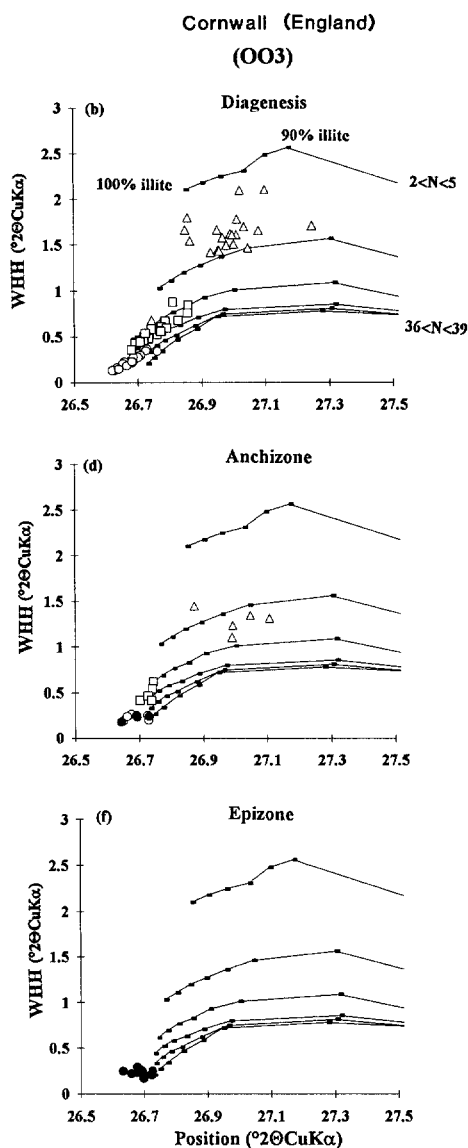
The upper anchizone and epizone samples from Cornwall show diffraction bands almost identical to those in the Carhaix area samples of Brittany.

Proportions of the Diffraction Peaks

The relative proportions of the different types of diffracting domain mineral illite and I–S mineral fractions of the rocks studied vary in a rather systematic manner. If one uses peak surface areas as a method to compare relative amounts of the mineral fractions present, the relations of I–S, small diffracting domain illite and coarse-grained or large domain size mica can be compared as in Figure 7. The diagenetic and tectonic series
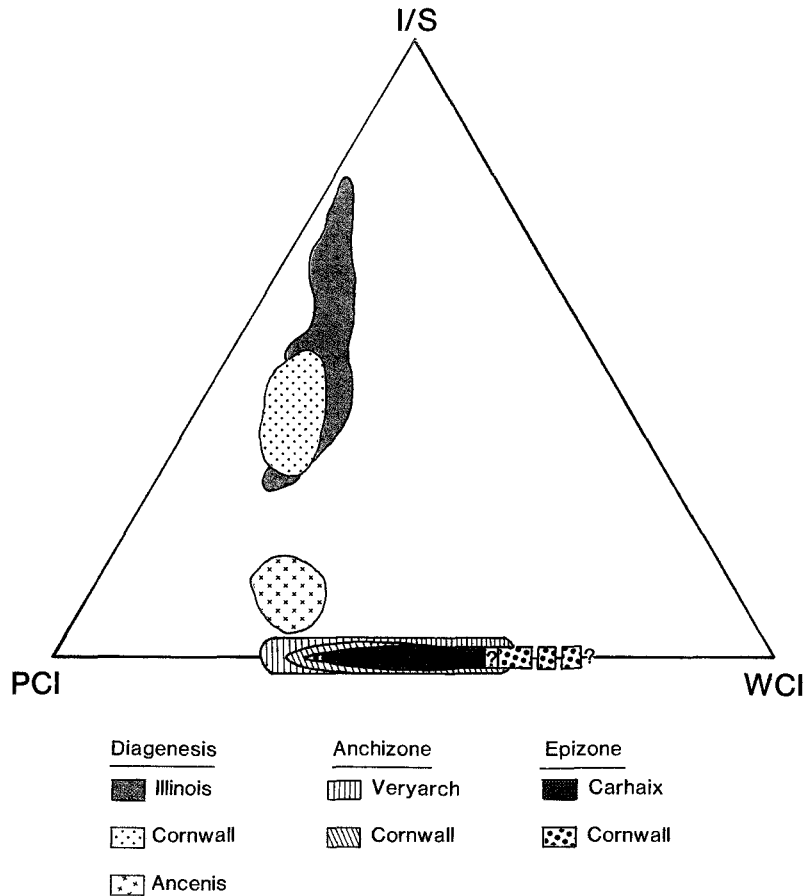
Figure 7.   Relative abundance of the mineral fractions using the areas of the decomposed peaks for the I–S, fine-grained illite (PCI = poorly crystallized illite) and coarse-grained or large diffracting domain illite–mica (WCI = well-crystallized illite).

follow the same trends of initially high I–S content followed by a decrease in I–S and a relative increase in coarse-grained or large diffracting domain size illite–mica relative to more poorly crystallized illite.

DISCUSSION

The sequence of samples taken from Cornwall was chosen in order to verify and compare the measurement of previously performed methods of the Kübler Index of illite crystallinity with those of XRD spectra decomposition of the (001) diffraction peak. The peak width at half height of our samples compares very closely with those reported by Primmer (1985) and Warr et al. (1991) for samples from the same area. By measuring the width of our peak envelopes at half height, the same values are found as those given in previous studies and hence the sample preparation procedures are sufficiently comparable. Further, we compared our diffraction band envelopes on standards kindly supplied by H. Kisch (personal communication) which give results identical to his. The only advantage of the decomposition method used here is that one can

follow the different populations of minerals or diffracting domains size materials (defined by the size of diffracting domains and by response to glycol-solvation) with greater precision than in using the crystallinity index, which measures several diffracting domain and mineral (I–S) populations at the same time. Illite crystallinity index methods are certainly as valid as decomposition techniques when used to describe regional metamorphic trends (see Stern et al. 1991; Wang et al. 1995).

Based upon our observations of the (003) diffraction peaks, the evolution of the illitic clay mineral populations in the last stages of the smectite-to-illite, then-mica reaction can be grouped into 4 stages:

1) The advanced stages of diagenesis where an identifiable mixed-layer mineral responding to glycolation indicates the presence of *I–S minerals containing up to 95% illite*. These mineral grains in the latest stages of diagenesis do not seem to change significantly in composition (smectite content) over long periods of time at low temperatures. I–S persists in slightly tectonically affected rocks, those showing no schistosity.

The progress of the smectite-to-illite reaction (production of an illitic phase) seems to evolve by a decrease in the proportion of I–S in favor of illite (Gharrabi and Velde 1995). The small diffracting domain illite grains contain a minor but distinct smectite component of <5% even though they show no effect of glycol solvation. The proportion of these materials compared to those with large diffracting domains determines the width and asymmetry of the illite peak in the illite crystallinity index measurement because the I–S abundance is too low to be included in the measurement.

2) The loss of I–S phases leaves only the illite mineral grains represented in XRD traces. The small diffracting domain crystallite component (<14 coherently diffracting layers) *contains <5% smectite layers.*

3) The next step in the evolution is the presence of large diffracting domain illite coexisting with a significant amount of *small diffracting domain illites that contain no smectite layers.*

4) Finally all mica grains all have a *diffracting domain greater than 30 layers.* The diffraction diagram of these phases can be described by a single symmetric Lorentzian–Gaussian shape band for the (003) peak (Figure 3b).

In terms of crystal genesis and mineral transformation, it appears that the latter stages of the smectite-to-illite reaction during diagenesis are marked by a loss of highly illitic I–S rather than a total conversion of I–S to illite through gradual change of composition. The smectite layer content of the last I–S phases is near 5%. The illitic material with small diffracting domain sizes (peak width 0.3–0.8 °2θ CuKα) present with the I–S phases contains several percent smectite. Hence diagenetic illitic and illite-rich minerals always contain some smectite.

The loss of smectitic mineral grains (either I–S or small diffracting domain illite) seems to be accompanied by the formation of small diffracting domain, smectite-free mica. This suggests that a portion of the I–S and small illite crystals in the diagenetic sedimentary pelitic composition rocks recrystallized to form a new mineral phase. The fine-grained mica material then coarsened-under thermal influence and a mica mineral or muscovite characterized by XRD appeared. This change from smectitic minerals (I–S and illite) to micaceous ones could be called a metamorphic change, using the criterion of mineral recrystallization.

What is Illite?

The next obvious question is *what is illite?*, an old question, and what is the new mica mineral observed to form in the initial stages of metamorphism? It is not known whether this new material has a K content of 1.0 ions per 22 anionic charges; thus it would be a true mica. However, it has been established that the composition of diagenetic illite layers in I–S minerals is near 0.8–0.9 (Velde and Brusewitz 1986; Eberl and

Środoń 1988; Meunier and Velde 1989). Since this micaceous material is the precipitating phase on clays in late diagenesis, such a low K-content mica-like material should persist as diagenesis enriches the clays in this illite component. If the diagenetic, poorly crystallized, small diffracting domain illite (containing a trace of smectite) recrystallizes as we believe has been demonstrated above, the recrystallization would only be caused by the fact that illite is not a mica. The new mica mineral formed at higher temperatures could well be a true mica with K 1.0 ions/$O_{10}(OH)_2$. In this case diagenetic, low-charge illite is unstable at high temperatures, and a true mica is formed at certain temperature–time conditions. In this analysis might lie the answer to "what is illite?"

Illite is then not a mica (high-temperature phase), and hence not a part of the mica solid solutions. In pelitic composition rocks, micas are then either metamorphic or magmatic minerals. There is a solid solution gap between illite and mica. Whether or not illite is metastable with respect to mica is another question. Since it persists for long periods at low temperatures (400 Ma y), its metastability is well assured.

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