A RELATIONSHIP BETWEEN CRYSTALLOGRAPHIC PROPERTIES OF ILLITE AND CHEMICAL PROPERTIES OF EXTRACTABLE ORGANIC MATTER IN PRE-PHANEROZOIC AND PHANEROZOIC SEDIMENTS

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Abstract—Crystallographic properties of illite and chemical properties of organic matter in various mudstones ranging in age from Archean to Miocene were investigated. The breadth of the (001) X-ray powder diffraction peak of illite correlates significantly with the ratio of aliphatic to condensed-aromatic components and the degree of condensation of aromatic rings of the polar ("humic") fraction of extractable bituminous organic matter. The broader the diffraction peak, the less highly condensed and aromatic (i.e. less highly humified) is the organic matter associated with the illite. Breadth of illite diffraction peak and degree of humification of polar organic matter vary in a complex and apparently systematic way through geologic time. All of the three different suites of mudstones investigated ("calcareous," "non-calcareous," and "glacial" mudstones) gave similar patterns of secular variation. In addition, the ratio of diffraction intensities for the (002) and (001) reflections (I_{002}/I_{001}) of illite in calcareous mudstones and limestones showed a strong negative correlation with geologic age, indicating that the illites in the older rocks are enriched in magnesium with respect to aluminum.

The correlation between crystal structure of illite and degree of humification of its associated organic matter could, by itself, be interpreted as an effect of post-depositional maturation processes, whereby "crystallinity" and degree of humification both increased as functions of heat and pressure. However, the patterns of secular variation suggest that the observed variations are primary, or were pre-determined by primary characteristics of the sample materials. The possibility that the original structure and composition of the organic matter influenced post-depositional changes in the crystallographic properties of sedimentary clay minerals, or post-depositional genesis of clay, would seem to merit consideration. The demonstrated relationship between crystallographic properties of illite and the nature of the "humic" matter constitutes evidence that most of the extractable organic matter is truly indigenous to the rock in which it occurs. The results also imply that molecular structure of extractable organic matter can be used in place of the breadth of the (001) diffraction peak of illite as an index of incipient metamorphism within a single formation or stratigraphic sequence, provided the primary characteristics of the organic matter are nearly the same in all samples. This method would have the advantage of being applicable to all sediments, not just those containing illite (specifically, aluminum-rich illite).

The secular variation of the I_{002}/I_{001} ratio of illite in calcareous sediments is provisionally ascribed to diagenetic processes whereby magnesium is abstracted from pore water and groundwater and is gradually assimilated into the crystal structure.

INTRODUCTION

In previous papers I reported systematic secular variations in the chemical properties and carbon isotope composition of organic matter in a selection of sedimentary rocks spanning most of geologic time (Jackson, 1973 and 1975; Jackson and Moore, 1976; Jackson *et al.*, 1976). The sediments were "unmetamorphosed" (except for cherts and argillite from the Archean upper Onverwacht and Fig Tree groups, which represent the lower greenschist grade of metamorphism (Viljoen, M., personal communication)), and the research data suggest that most of the secular variations are primary and have paleobiological significance (Jackson, 1973 and 1975). Without further information, however, we cannot discount the possibility that differences in thermal history have contributed to some extent to the observed differences in the nature of the organic matter (McKirdy, 1974). Therefore, a quantitative study of post-depositional alteration of the sediments was undertaken using the breadth of the ~ 10 Å (001) diffraction peak of illite as a possible index of the relative severity of alteration. Crystallographic properties of illite were compared with chemical properties of organic matter, and their variations through geologic time were investigated.

Attention was focused on illite, because a number of workers have observed that within the zone of incipient metamorphism, or "anchimetamorphism", (the transition zone between diagenesis and metamorphism) the breadth of the (001) diffraction peak of this mineral decreases progressively as the degree of metamorphism increases (Weaver, 1961; Kubler, 1968; De Segonzac *et al.*, 1968; McKirdy, 1974). The

(001) reflection of sedimentary illite is considered a sensitive indicator of the relative severity of incipient metamorphism, provided the magnesium/aluminum ratio of the illite is not too high (Esquevin, 1969). A relatively broad (001) peak for illite may indicate poor "crystallinity", small crystal size, interlayer hydration, variation in the nature of the interlayer cations, and interstratification with other clay minerals such as montmorillonite or montmorillonite + chlorite (Weaver, 1961; Kubler, 1968; De Segonzac et al., 1968; McKirdy, 1974; Brown, 1961; Grim, 1968). Sharpening of the (001) peak with the onset of metamorphism is presumably caused by dehydration and collapse of expanded layers as well as crystal growth and improved "crystallinity" (Weaver, 1961).

In a comparative study of illites in different sedimentary deposits, interpretation of crystallographic measurements is undoubtedly complicated by the diverse origins of sedimentary illite and the variety of factors which may influence its formation and its structure and composition. Sedimentary illite may originate in situ by diagenesis of other clay minerals, or it may be generated by soil-forming processes or eroded from pre-existing sedimentary, metamorphic, or igneous rocks, and subsequently laid down as a detrital mineral (Keller, 1963 and 1964); furthermore, crystallographic properties of illite vary with elemental composition (Esquevin, 1969) and are modified by interstratification with other clay minerals (Weaver, 1956). Nevertheless, the research data presented in this report revealed interesting systematic variations related to variations in the nature of the organic matter.

MATERIALS AND METHODS

The rock samples that contained detectable quantities of illite comprised an assortment of shales, mudstones, argillites, and tillites—all collectively termed "mudstones" for convenience—ranging in age from early Archean to Miocene, together with two Paleozoic limestones. The samples were collected in widely separated parts of the world and represent a variety of depositional environments, though most of them were laid down under marine conditions. The mudstones were divided into three categories according to mineral composition and depositional environment: (1) "calcareous mudstones" (mudstones containing calcite or dolomite, or both), (2) "non-calcareous mudstones" (mudstones in which no carbonate minerals were detected), and (3) "glacial mudstones" (a subset of non-calcareous mudstones supposedly laid down under glacial conditions). Geologic age, rock type, and sampling locality are listed in Table 1. More detailed information on these rocks is given elsewhere (Jackson, 1975).

Weathered surfaces were removed, and the rocks were pulverized in a tungsten carbide disc mill for 5 min in 1 min bursts, and extracted with benzene–methanol (9:1). The extracts were taken to dryness,

redissolved in hexane, and fractionated on a silica-gel column by elution with hexane, benzene, and methanol, in that order. The methanol eluate, which comprised the polar fraction of the extract (hereafter termed "polar extract" for brevity), consisted largely of a type of humic substance (Jackson, 1975). The chemical properties, secular variations, and possible paleobiological significance of this humic matter are treated elsewhere (Jackson, 1973 and 1975); the nonextractable organic matter, or kerogen, in the rock samples was investigated by Jackson and Moore (1976) and by Leventhal et al. (1975), and the carbon isotope composition of both the polar extracts and the kerogen was studied by Jackson et al. (1976).

Crystallographic properties of illite were investigated by X-ray powder diffraction analysis. A portion of each pulverized, solvent-extracted, and subsequently air-dried rock sample was suspended in water, and the slurry was pipetted on to a glass slide. This preparation was allowed to dry in the air at room temperature and then analyzed with a Philips (Norelco) diffractometer employing CuKα radiation. The breadth of the $\sim 10\,Å$ (001) diffraction peak of illite was expressed as (1) peak width at 1/2 peak height ("Kubler index") (Kubler, 1968) and (2) ratio of peak height at 10.5 Å to peak height at 10 Å (the reciprocal of Weaver's "sharpness ratio") (Weaver, 1961). Inasmuch as the (001) spacing is variable, peak height was not necessarily measured literally at 10 Å and 10.5 Å. Instead, recorder response was measured at the apex of the (001) peak and at a position on the chart corresponding to 0.5 Å more than the d-spacing represented by the apex. The first measurement was designated the "10 Å" peak height, and the second measurement the "10.5 Å" peak height. The "10.5 Å" position was generally on the flank of the (001) peak. All measurements were recorded in inches, because the scale of the chart paper was in inches. Measurements were made with an engineer's scale accurate to 1/50th of an inch.

To determine whether the illites are interstratified with other clay minerals, the (001) and (002) d-spacings were measured, and the ratio d(001)/d(002) was computed. Pure illite would be expected to yield a ratio value of exactly 2, unlike interstratified clays, whose basal reflections do not form an integral series except in the case of certain kinds of ordered interstratification (Reynolds and Hower, 1970; Weaver, 1956; Brown, 1961). Other possible indications of interstratification are abnormally high (001) spacings ($>10\,Å$) (Weaver, 1956) and (001) peaks that tail off toward higher d-spacings.

Magnesium-rich and aluminum-rich illites were distinguished by computing the ratio of (002) peak intensity to (001) peak intensity (I_{002}/I_{001}). According to Esquevin (1969), the I_{002}/I_{001} ratio increases with increasing Al content, and only the more Al-rich (Mg-poor) illites—those with an I_{002}/I_{001} ratio greater than 0.3—can be used as indicators of metamorphic grade.

The X-ray powder diffraction data were plotted against geologic age, and were correlated with values for the following two parameters representing the molecular structure and composition of the polar fraction of the extractable organic matter: (1) the visible-light absorbance ratio $A_{400m\mu}/A_{500m\mu}$ (absorbance at 400 mμ divided by absorbance at 500 mμ); and (2) the ratio of aliphatic to condensed aromatic components (symbolized as $CH_2/A_{665m\mu}$), which was estimated by dividing the absorbance value for the infrared absorption band at 2910 cm^{-1} (representing aliphatic $-CH_2$ groups) by visible light absorbance at 665 mμ (representing condensed aromatic chromophores). Methods used for analysis of organic matter are described by Jackson (1975). Visible-light absorbance ratios such as $A_{400m\mu}/A_{500m\mu}$ are inversely related to the degree of condensation of aromatic rings in humic matter (Schnitzer, 1971). The more highly "humified" or "mature" humic substances are more highly condensed and aromatic (have lower

Table 1. List of rock samples, with information on geologic age, sampling location, rock type and depositional environment

Sample no.	Name of rock	Age ($\times 10^9$ years)	Location	Rock type	Comments
1	Gowganda Fm.	2.288 ± 0.087	Ontario, Canada	Argillite	Glacio-lacustrine
2	Hector Fm.	0.7	Alberta, Canada	Shale	Marine
3	Nonesuch Shale	1.05	Michigan, U.S.A.	Shale	Marginal marine
6	Kingston Peak Fm.	1.1 (?)	California, U.S.A.	Tillite	Glacio-marine (?)
9	Gunflint Iron Formation	2.0	Ontario, Canada	Shale with calcite & dolomite	Marine
18	Burgess Shale	0.540 (Cambrian)	British Columbia, Canada	Shale with calcite & dolomite	Marine
21	(no name yet)	0.827 ± 0.030	Utah, U.S.A.	Mudstone with calcite & dolomite	Marine
22	Dripping Springs Quartzite	1.3	Arizona, U.S.A.	Argillite	Marginal marine
25	Mineral Fork Tillite	0.827 ± 0.030	Utah, U.S.A.	Tillite	Probably glacio-marine
26	Nonesuch Shale	1.05	Michigan, U.S.A.	Argillite with calcite	Marginal marine
27	Bjoranes Shale	0.700 (?)	Norway	Argillite	Marine; climate glacial
28	Antrim Shale	0.350 (Devonian)	Michigan, U.S.A.	Shale with dolomite	Marine
29	Kupferschiefer	0.250 (Permian)	Germany	Limestone	Probably marine
30	Rove Shale	2.0	Minnesota, U.S.A.	Shale	Marine
31	Hoadley Fm.	1.1	Montana, U.S.A.	Shale with calcite & dolomite	Marine
32	Stoer Bay Fm.	0.935	Scotland	Shale with calcite & dolomite	Marine (?)
33	Diabaig Shale	0.751	Scotland	Shale	Marine (?)
34	Monterey Shale	0.016 (Miocene)	California, U.S.A.	Shale with calcite	Marine
35	Romney Shale	0.370 (Devonian)	Maryland, U.S.A.	Shale	Marine
36	*Didymograptus* Shale	0.490 (Ordovician)	Norway	Shale	Marine
40	Givetian Limestone	0.360 (Devonian)	Belgium	Limestone	Marine
41	Pierre Shale	0.075 (Cretaceous)	Wyoming U.S.A.	Shale	Marine
43	Urquhart Shale	1.6	Australia	Siliceous argillite with dolomite	Marine
44	Fig Tree Group	3.3	South Africa	Siliceous argillite	Marine

absorbance ratios), and are poorer in aliphatic and polar groups, i.e. are more similar to graphite. Variations in degree of "maturity" of unmetamorphosed organic matter may reflect differences in biological source material and environment of formation, but metamorphic processes invariably cause organic matter to become increasingly "mature" until it is ultimately converted to graphite (Degens, 1967; Abelson, 1967; Forsman, 1963; Bordovskiy, 1965).

For evaluation of data plots, correlation coefficients (r) and significance probabilities (P) were computed by standard statistical procedures.

RESULTS

The X-ray data for illite and the chemical data for the polar extracts are given in Tables 2 and 3, respectively. Figure 1 shows Kubler index of illite plotted against geologic age. The plots reveal a complex pattern of maxima and minima. Although more data are needed to confirm these results, it should be noted that all three suites of mudstones gave remarkably similar patterns of variation. The curves for calcareous and non-calcareous mudstones are practically identical, and even the glacial mudstones, of which there are too few to give significant results by themselves, fit the same general pattern. This would seem to indicate that the patterns of variation are not merely fortuitous, and suggests that these patterns have a general, worldwide significance transcending mere regional differences in source material, weathering conditions, depositional environment, and post-depositional history, even if we take into account the fact that a few pairs of samples come from the same stratigraphic system (samples 3 and 26, 32 and 33, and possibly 9 and 30, and 21 and 25). The 10.5 Å/10 Å peak-height ratio (Table 2) gave similar results, but there was more scatter.

Going from older to younger rocks, the curves show a gradual decline in peak width from the early
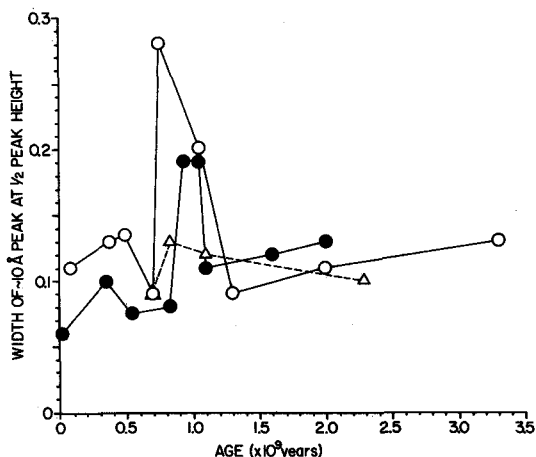

Figure 1. Width of the ~10 Å X-ray diffraction peak of illite at 1/2 peak height (Kubler index) plotted against geologic age. Explanation of symbols: calcareous mudstones ●, non-calcareous mudstones ○, glacial mudstones △.
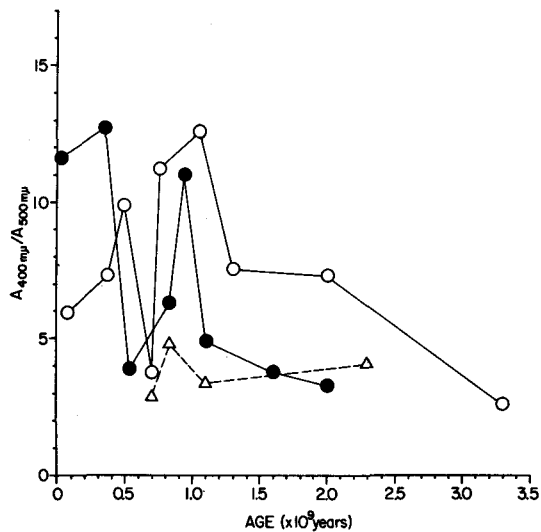

Figure 2. The $A_{400 m\mu}/A_{500 m\mu}$ ratio of the polar ("humic") fraction of the extractable bituminous organic matter plotted against geologic age. See Figure 1 for explanation of symbols.

Archean (~3.3 × 10⁹ years B. P.) to the mid-Proterozoic (1.1–1.3 × 10⁹ years B. P.), whereupon there is a steep increase in peak width culminating in a large maximum in the upper Proterozoic (0.8–1.05 × 10⁹ years B. P.); after that, we see a steep decline to a minimum at or near the boundary between the Proterozoic and Paleozoic (0.5–0.75 × 10⁹ years B. P.) followed by another maximum in the lower or middle Paleozoic (Ordovician to Devonian), declining again to relatively low values in the Mesozoic and Tertiary. Among sediments older than ~1.05 × 10⁹ years B. P., illite in non-calcareous mudstones has consistently lower peak widths than illite in calcareous mudstones, whereas among sediments 1.05 × 10⁹ years old or younger the reverse is true.

The secular variations of the $A_{400 m\mu}/A_{500 m\mu}$ and $CH_2/A_{665 m\mu}$ ratios of the polar organic extracts show a striking similarity to the secular variations of the crystal structure of illite (Figures 2–4). Polar extracts with higher $A_{400 m\mu}/A_{500 m\mu}$ and $CH_2/A_{665 m\mu}$ values —in brief, the less highly humified extracts—tend to be associated with illite characterized by a relatively broad (001) peak. Thus, as illustrated in Figures 3 and 4, the $CH_2/A_{665 m\mu}$ ratio shows a highly significant positive correlation with both the 10.5 Å/10 Å peak-height ratio and the Kubler index ($r = 0.788$ and 0.705, respectively; $P < 0.001$ for both values). Note that the 10.5 Å/10 Å ratio gave an appreciably higher correlation coefficient than did the Kubler index.

The patterns of secular variation reported here are not confined to mudstones. Various chemical data for both polar extracts and kerogen from cherts and carbonate rocks gave comparable patterns characterized in particular by a prominent peak in the upper Proterozoic (Jackson, 1973 and 1975; Jackson and Moore, 1976). For some chemical parameters, polar extracts from carbonates and cherts and from calcar-

Table 2. Measurements of X-ray diffraction parameters for illite in the rock samples. Replicate data are given for samples 3 and 22

Sample no.	Width of 10 Å peak at $\frac{1}{2}$ peak height (in.)		10.5 Å/10 Å peak-height ratio		I_{002}/I_{001}		(001) spacing (Å)	(002) spacing (Å)	$\dfrac{(001)\ \text{spacing}}{(002)\ \text{spacing}}$
1	0.10		0.137		0.274		9.91	4.97	2.00
2	0.090		0.131		0.341		9.95	4.97	2.00
3–1	0.19 $\}$ $\overline{X} =$		0.422 $\}$ $\overline{X} =$		0.511 $\}$ $\overline{X} =$		9.96	4.98	2.00
3–2	0.21 $\}$ 0.20		0.222 $\}$ 0.322		0.511 $\}$ 0.511		10.11	5.03	2.01
6	0.12		0.218		0.166		10.14	5.03	2.02
9	0.13		0.250		0.067		10.10	4.99	2.02
18	0.075		0.191		0.372		10.19	5.05	2.02
21	0.080		0.118		0.374		10.19	5.09	2.00
22–1	0.085	$\overline{X} = 0.095$	0.111 $\}$	$\overline{X} = 0.155$	0.301 $\}$	$\overline{X} = 0.299$	10.07	5.03	2.00
22–2	0.090		0.163 $\}$		0.340 $\}$		10.03	5.01	2.00
22–3	0.11	$M_d = 0.090$	0.191 $\}$	$M_d = 0.163$	0.255 $\}$	$M_d = 0.301$	10.10	4.99	2.02
25	0.13		0.224		0.272		10.03	4.96	2.02
26	0.19		0.329		0.385		10.00	4.98	2.01
27	0.090		0.197		0.425		10.13	5.04	2.01
28	0.10		0.320		0.424		10.05	5.01	2.01
29	0.14		0.185		0.50		10.04	5.02	2.00
30	0.11		0.254		0.396		9.83	4.94	1.99
31	0.11		0.224		0.160		10.42	5.10	2.05
32	0.19		0.667		0.417		10.21	5.06	2.02
33	0.28		0.494		0.302		10.48	5.10	2.05
34	0.06		0.000		—		9.85	4.90	2.01
35	0.13		0.288		0.375		10.05	4.99	2.01
36	0.135		0.348		0.342		10.00	4.98	2.01
40	0.10		0.000		0.85		10.19	5.04	2.02
41	0.11		0.000		2.86		10.05	5.10	1.97
43	0.12		0.000		0.24		10.05	4.99	2.01
44	0.13		0.155		0.44		9.95	5.01	1.99

Table 3. Spectrophotometric data for the polar ("humic") fraction of bituminous organic matter extracted from the rock samples. Replicate data are given for samples 3, 22 and 25

Sample no.	$CH_2/A_{665\,m\mu}$		$A_{400\,m\mu}/A_{500\,m\mu}$	
1	53.3		4.06	
2	82.8		3.73	
3–1	161 $\}$ $\overline{X} = 407$		8.51 $\}$ $\overline{X} = 12.6$	
3–2	653 $\}$		16.6 $\}$	
6	27.7		3.33	
9	43.8		3.29	
18	53.0		3.86	
21	183		6.28	
22–1	366 $\}$ $\overline{X} = 262$		5.20 $\}$ $\overline{X} = 7.13$	
22–2	178 $\}$		8.65 $\}$	
22–3	241 $\}$ $M_d = 241$		7.53 $\}$ $M_d = 7.53$	
25–1	82.6 $\}$ $\overline{X} = 109$		3.07 $\}$ $\overline{X} = 4.71$	
25–2	135 $\}$		6.34 $\}$	
26	381		14.0	
27	10.2		2.86	
28	225		12.7	
29	142		7.28	
30	580		7.30	
31	198		4.89	
32	788		11.0	
33	683		11.2	
34	98		11.6	
35	166		7.29	
36	393		9.87	
40	1,090		12.3	
41	74.9		5.94	
43	125		3.77	
44	59.7		2.57	

eous mudstones yielded nearly identical patterns of secular variation (Jackson, 1973 and 1975).

Computation of the I_{002}/I_{001} ratio (Table 2) showed that the illite in nearly 3/4 of the rock samples investigated is relatively aluminum-rich ($I_{002}/I_{001} \geqslant 0.3$). All of the samples with magnesium-rich illite ($I_{002}/I_{001} < 0.3$) gave low values of the $CH_2/A_{665\,m\mu}$ ratio,
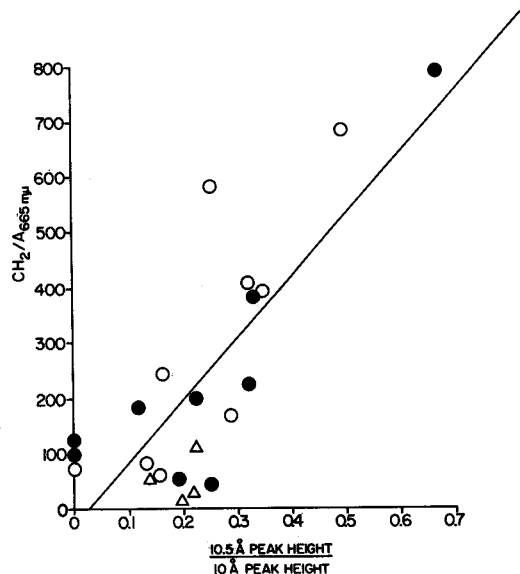

Figure 3. $CH_2/A_{665\,m\mu}$ ratio of polar organic extract plotted against 10.5 Å/10 Å peak-height ratio of illite. See Figure 1 for explanation of symbols.
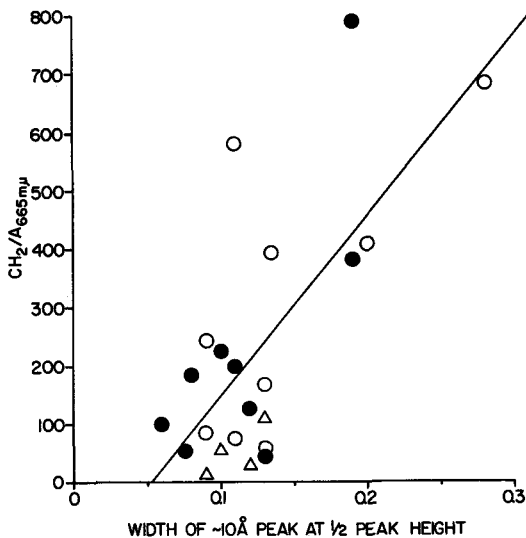
Figure 4. $CH_2/A_{665m\mu}$ ratio of polar organic extract plotted against Kubler index of illite. See Figure 1 for explanation of symbols.

Figure 5. I_{002}/I_{001} ratio of illite in calcareous mudstones ● and limestones ▲ plotted against geologic age.

10.5 Å/10 Å peak-height ratio, and Kubler index (cf. Esquevin, 1969), and are therefore clustered near the origin in each of the two plots shown in Figures 3 and 4. The samples with Mg-rich illite do not, by themselves, show any significant correlation between $CH_2/A_{665m\mu}$ ratio and (001) peak breadth. Consequently, the observed correlation between the $CH_2/A_{665m\mu}$ ratio and the 10.5 Å/10 Å peak-height ratio and Kubler index for the samples as a whole (Figures 3 and 4) is due entirely to the samples with Al-rich illite, and the correlation coefficients are increased considerably if the samples with Mg-rich illite are omitted ($r = 0.838$ and 0.742, respectively; $P < 0.001$).

The I_{002}/I_{001} values of the calcareous mudstones and limestones decrease exponentially with increasing geologic age (Figure 5) throughout the age range of this class of samples [Permian to early Proterozoic (2×10^9 years B. P.)]. Thus, the illites in the older rocks tend to be richer in magnesium with respect to aluminum than the illites in the younger rocks. The correlation between I_{002}/I_{001} ratio and age is highly significant ($r = -0.855$; $P < 0.001$), but the relationship is true only of rocks containing carbonate minerals. The I_{002}/I_{001} values of the non-calcareous and glacial mudstones showed no systematic secular variation.

About 3/4 of the samples gave $d(001)/d(002)$ values that deviated at least slightly from the ideal value of 2.00 for pure illite, mostly in the direction of higher values (Table 2). The range of values was 1.97–2.05, although most of the samples fell in the range 1.99–2.02. This would seem to indicate a minor, if not insignificant degree of interstratification with other clay minerals (probably montmorillonite or chlorite, or both). In addition, about 70% of the samples gave (001) spacings at least slightly higher than 10 Å (Table 2); the values ranged from 9.83 to
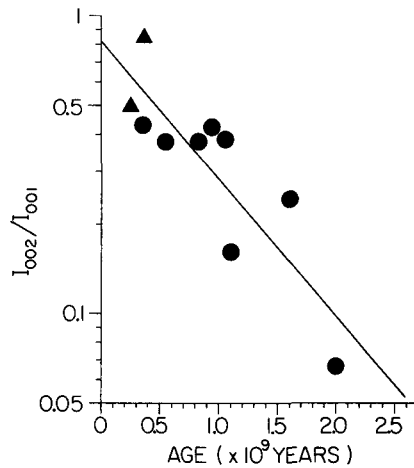
10.48 Å, but most of the samples fell in the range 9.9–10.2 Å. Samples 31 and 33, both of which are of late Proterozoic age, gave the highest $d(001)/d(002)$ values and the largest (001) spacings; presumably these two samples have the highest degree of interstratification. Note, moreover, that the broader (001) diffraction peaks tend to tail off toward higher d-spacings (Figure 6), as is commonly the case with illite (Keller, 1964; Grim, 1968). Figure 6 gives a good idea of the range of (001) peak shapes and peak widths encountered in this study. Of course, abnormally high (001) spacings, and (001) peaks skewed in the direction of higher spacings, may signify slight hydration, expansion, and degradation of illite layers (especially among the smaller crystals) (Keller, 1964; Grim, 1968) as well as interstratification of distinctly different minerals species.
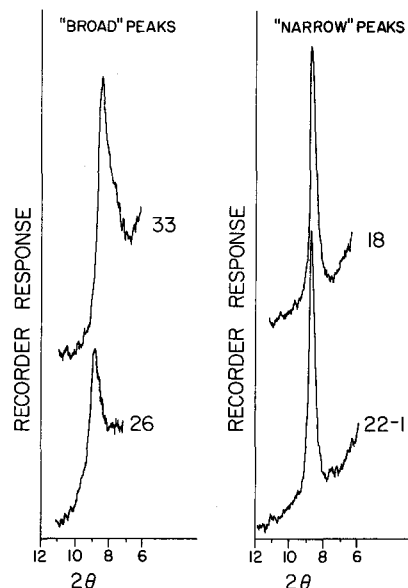

Figure 6. Examples of (001) diffraction peaks of illite, illustrating variation in peak width and shape. Sample number is given to right of each peak.

To determine whether the breadth of the (001) peak of illite is primarily related to interstratification of different mineral species or to factors such as "crystallinity," crystal size, and interlayer hydration, the 10.5 Å/10 Å peak-height ratio and Kubler index were plotted against the $d(001)/d(002)$ ratio and the (001) spacing. No correlation was found, suggesting that the degree of interstratification of other clay mineral species with the illite has little or no connection with the observed variations of the (001) peak width. We may conclude, tentatively, that the Kubler index and 10.5 Å/10 Å peak-height ratio are primarily related to factors such as crystal size, degree of "crystallinity," and expansion and hydration of illite layers, as originally claimed (Weaver, 1961; Kubler, 1968). This point need not be labored, however. It would not be realistic to insist on a sharp distinction between "poorly crystallized" illite of small crystal size containing partially hydrated and expanded layers on the one hand, and illite containing interstratified montmorillonite on the other hand.

DISCUSSION

The tendency of the more highly humified organic matter to be associated with illite of higher "crystallinity" (characterized by a relatively narrow (001) diffraction peak) could, by itself, be interpreted as an effect of post-depositional alteration. It is a recognized fact that maturation processes not only improve the "crystallinity" of illite but also make organic matter more highly condensed and aromatic, and correspondingly poorer in aliphatic and polar groups. On this interpretation, the observed variations in both the chemical properties of the organic matter and the breadth of the (001) diffraction peak of the clay would be ascribed to variations in the degree of alteration of the rock by mild post-depositional heat and pressure, and there would be no need to invoke either primary differences between sample materials or specific clay–organic interactions.

However, the observed patterns of secular variation tend to militate against such an interpretation, and suggest instead that the variations are primary or were pre-determined by primary characteristics of the sample materials, although it must be emphasized that more data are needed to confirm this tentative conclusion. It seems very unlikely that three different suites of rocks would show similar patterns of diagenetic alteration in the same intervals of geologic time. This argument becomes even more convincing if we include polar extracts from a fourth suite of rocks, the carbonates and cherts, some of whose patterns of secular variation were strikingly similar to those of the calcareous mudstones (Jackson, 1973 and 1975), even though certain differences were noted as well. Primary phenomena such as evolutionary changes in the nature of the biosphere or the atmosphere could well have exerted an influence on sediments in various depositional environments almost simultaneously all over the world, thus producing results like those described here. In contrast, post-depositional heat and pressure are more localized, and their intensity varies greatly across horizontal and vertical gradients. The occurrence of maxima and minima and abrupt changes on a seemingly worldwide basis in particular intervals of geologic time—including the middle to late Proterozoic and Proterozoic–Paleozoic transition, which are so significant for the evolution of eucaryotic organisms (Cloud, 1974)—suggests episodic evolutionary events, as discussed by Jackson (1975). The late Proterozoic reversal of the relative positions of the curves for calcareous and non-calcareous mudstones in the plots of Kubler index against age (Figure 1) fits this interpretation too and suggests a permanent biogeochemical effect of eucaryote evolution. If post-depositional maturation processes did cause a progressive change in the crystallographic properties of illite as a function of geologic age, it would probably be a long-term increase in "crystallinity" with increasing age, owing to a tendency of the more ancient sediments to be more severely altered. The peaks in the plots of Kubler index against age (Figure 1) do appear to be superimposed on a long-term trend extending all the way from the Archean to the Tertiary, but this trend indicates a *decrease* in "crystallinity" (increase in (001) peak width) with increasing age–the opposite to what would be predicted on the theory that illite "crystallinity" is a function of post-depositional maturation processes. Thus, the Fig Tree argillite (sample 44) does not have the lowest Kubler index, even though it is probably the most severely altered sample according to conventional geologic and petrographic criteria [in the opinion of M. Viljoen (personal communication), this rock represents the lower greenschist grade of metamorphism].

Why do the chemical properties of the organic matter correlate with the "crystallinity" of the illite? One possible explanation is that the clay influenced the properties of the sedimentary organic matter as a result of selective adsorption and catalytic effects. The ability of clay minerals to adsorb and catalytically transform organic compounds is well known (Weiss, 1969; Solomon, 1968; Galwey, 1972; Andreev et al., 1968; Grim, 1968; Degens and Matheja, 1970; Jackson, 1971; Paecht-Horowitz et al., 1970). However, this possibility seems unlikely in view of the observation that certain chemical properties of polar extracts from carbonates and cherts, which contain little or no clay, revealed secular variations similar to those of extracts from calcareous mudstones (Jackson, 1975); moreover, it would be difficult, on this hypothesis, to explain why illite "crystallinity" should vary through geologic time in the manner described. It would seem that a more plausible, though as yet unproven, interpretation is that the organic matter affected the "crystallinity" of the clay.

According to this hypothesis, the chemical properties of the organic matter varied through geologic

time owing to evolutionary changes in the nature of the biological source material (Jackson, 1973 and 1975), and the organic matter, in turn, influenced post-depositional changes in the crystal structure of sedimentary clay minerals, or post-depositional genesis of clay, as a result of epitaxial interactions with clay surfaces and formation of complexes with metal ions. There would be no difficulty in believing that the nature of sedimentary organic matter varied with changes in the biological source material, and it has been shown that organic compounds, including humic substances, can influence the crystallization of clay minerals and oxides (Linaeres and Huertas, 1971; Hem and Lind, 1974; Kwong and Huang, 1975; Jackson and Keller, 1970; Schwertmann, 1971; Schwertmann and Fischer, 1973; Schwertmann et al., 1968; Mackenzie, 1952; Towe and Loewnstam, 1967). We may venture to speculate, very tentatively, that the late Proterozoic peak revealed by the illite and the organic extracts represents the appearance and early expansion of eucaryotic algae followed by a decline in algal populations resulting from the emergence of protozoans and metazoans at the onset of Paleozoic time (Jackson, 1973 and 1975). The second peak corresponds approximately to the evolution of the first land plants. The data suggest that the less "humified" organic matter tended to inhibit both the post-depositional enlargement of illite crystals and the collapse of expanded, hydrated layers in the illite, presumably by forming "protective" epitaxial films on the crystal surfaces and between the partially expanded layers. The fact that the $CH_2/A_{665m\mu}$ ratio of the organic matter correlates more strongly with the 10.5 Å/10 Å peak-height ratio (which measures peak-broadening in the direction of higher d-spacings only) than with the Kubler index (which measures total peak breadth) can be interpreted as evidence that the organic matter produces relatively broad (001) peaks largely by inhibiting collapse of partially expanded illite layers.

The existence of a highly significant correlation between chemical properties of the polar extracts and crystallographic properties of illite in the matrix rock is consistent with previously cited evidence that the extractable organic matter is mostly, if not entirely, indigenous to the rock in which it occurs (Jackson, 1975; Jackson and Moore, 1976; Jackson et al., 1976). Some geochemists have warned that the extractable organic matter of ancient sedimentary rocks may include appreciable quantities of contaminants which migrated into the rocks from younger formations (Hoering, 1965; Smith et al., 1970; Nagy, 1970), but the characteristics of such contaminants would probably show little or no correlation with the properties of the clay minerals and other immobile constituents of the host rock.

The observed relationship between the properties of illite and extractable organic matter imply that under some circumstances organic matter could be used instead of, or in addition to, illite as an indicator of metamorphic grade, provided its use was restricted to comparison of different samples within one formation, stratigraphic sequence, or facies, so that the primary characteristics of the organic matter would be nearly the same in all samples (cf. McKirdy and Powell, 1974). The potential value of this proposed application of organic geochemistry is apparent when we consider that all of the multifarious sedimentary rocks investigated contain extractable polar organic matter, whereas not all sediments contain illite, let alone aluminum-rich illite, which is the only type of illite considered suitable for use as an indicator of metamorphic grade.

Finally, the progressive decrease of the I_{002}/I_{001} ratio of illites in calcareous mudstones and limestones with increasing geologic age can be attributed to a long-term diagenetic process whereby magnesium leached from carbonate minerals by groundwater and pore water is abstracted by illite and gradually incorporated into the crystal structure of the mineral. This interpretation is supported by the fact that the observed relationship is limited to rocks containing carbonate minerals, and by the fact that the plot of I_{002}/I_{001} ratio against geologic age yields a simple, continuous trend line that is apparently independent of episodic evolutionary events. With some methodological refinements to reduce the amount of scatter in the plot, the observed trend could, perhaps, be applied to the dating of sedimentary rocks.

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