Clay Mineral Formation and Transformation in Rocks and Soils [and Discussion]

D. D. Eberl, V. C. Farmer and R. M. Barrer

Phil. Trans. R. Soc. Lond. A 1984 **311**, 241-257
doi: 10.1098/rsta.1984.0026

Phil. Trans. R. Soc. Lond. A **311**, 241–257 (1984) [241]
Printed in Great Britain

Clay mineral formation and transformation in rocks and soils

By D. D. Eberl

U.S. Geological Survey, Federal Center, Mail Stop 420, *Denver, Colorado* 80225, *U.S.A.*

Three mechanisms for clay mineral formation (inheritance, neoformation, and transformation) operating in three geological environments (weathering, sedimentary, and diagenetic-hydrothermal) yield nine possibilities for the origin of clay minerals in nature. Several of these possibilities are discussed in terms of the rock cycle. The mineralogy of clays neoformed in the weathering environment is a function of solution chemistry, with the most dilute solutions favouring formation of the least soluble clays. After erosion and transportation, these clays may be deposited on the ocean floor in a lateral sequence that depends on floccule size. Clays undergo little reaction in the ocean, except for ion exchange and the neoformation of smectite; therefore, most clays found on the ocean floor are inherited from adjacent continents. Upon burial and heating, however, dioctahedral smectite reacts in the diagenetic environment to yield mixed-layer illite–smectite, and finally illite. With uplift and weathering, the cycle begins again.

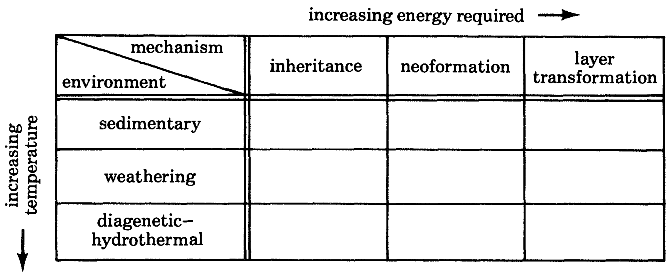
INTRODUCTION

Three questions may arise when clay is observed in nature. What is the clay? How did it form? Under what conditions did it form? The answers to these questions are the substance of the science of clay mineral petrology.

An answer to the first question requires an analysis of the clay's chemical composition and crystal structure, topics discussed by Brown (this symposium) and in books by Grim (1968) and Brindley & Brown (1980).

The second question concerns mechanisms of clay formation. This paper will consider three mechanisms, generally based on ideas of Esquevin (1958) and Millot (1970). These mechanisms are: (i) inheritance, (ii) neoformation and (iii) transformation. Origin by inheritance simply means that a clay mineral found in a natural deposit originated from reactions that occurred in another area during a previous stage in the rock cycle, and that the clay is stable enough to remain inert in its present environment. Its stability may result either from slow reaction rates or from being in chemical equilibrium. Origin by neoformation means that the clay has precipitated from solution or has formed from reaction of amorphous material. Origin by transformation requires that the clay has kept some of its inherited structure intact while undergoing chemical reaction. This reaction may take two forms: (i) ion exchange, in which loosely bound ions are exchanged with those of the environment; and (ii) layer transformation, in which the arrangements of tightly bound octahedral, tetrahedral, or fixed interlayer cations are modified. Layer transformation will be emphasized in this discussion because the results of this type of reaction are better preserved in the geological record. From a geological perspective, it is important to determine which mechanism gave rise to clays in a natural deposit. Clays that have inherited their crystal structures are indicators of provenance, and provide information about environmental conditions in the sediment source area. Neoformed clays have precipitated in response to *in situ* conditions, past or present. Transformed clays carry both types of information, having inherited characteristics from the source area and having reacted in response to *in situ* changes in environment.

The third question of interest to the clay petrologist concerns the clay's environment of formation. This environment can be described in terms of temperature, pressure, chemical composition and reaction time. In order to generalize this discussion, however, these variables are condensed into three geological situations, the conditions within each of which vary over a limited range. The situations, again based on the ideas of Esquevin (1958) and Millot (1970), are: (i) the weathering environment, (ii) the sedimentary environment, and (iii) the diagenetic–hydrothermal environment. The weathering environment is the upper zone of the Earth's crust that is at or near the atmospheric interface, where temperature and pressure vary over the relatively narrow range of Earth surface conditions. Reaction times are therefore relatively short, usually of the order of thousands of years, because the upper layers of a soil undergo continuous erosion, and solution composition is variable, depending mainly on original rock type, rainfall, evaporation and drainage. The sedimentary environment most often is found near or below sea level or lake level, in depressed areas of the crust, and refers to the zone near the sediment–water interface. In the most common sedimentary environment for clays, the ocean floor, temperatures are generally lower and restricted to a narrower range than those found in the weathering environment, pressures may range to more than 1 kilobar† in the deepest parts of the ocean, and the composition is that of sea water or related pore water. Reaction time, generally measured in millions of years, depends on rates of sedimentation and subsidence, and on rates of sea floor subduction, processes that move clays into higher temperature environments. The diagenetic–hydrothermal environment includes all zones that have been in contact with hot water. Clays in this situation may experience a wide range of environmental conditions.



mechanism / environment	inheritance	neoformation	layer transformation
sedimentary			
weathering			
diagenetic–hydrothermal			

FIGURE 1. Nine possibilities for the formation of clay minerals in Nature (after Esquevin 1958 and Millot 1970).

The three mechanisms for mineral formation operating in three geological environments yield nine possibilities for the evolution of clay minerals (figure 1). Although exceptions are numerous, a pattern exists relating mechanism to environment. Generally, inheritance dominates in the sedimentary environment where reaction rates are slow, whereas layer transformation, a mechanism that can require large inputs of energy, becomes prevalent in the higher temperature diagenetic–hydrothermal environment. Between these extremes is the weathering environment in which examples of all three mechanisms are common.

Several of the nine possibilities given in figure 1 will be discussed in terms of a simplified rock

---

† 1 bar = 10^5 Pa.

cycle (figure 2). Clays neoformed from crystalline rock in the weathering environment will be traced as they are transported into the sedimentary environment, buried and heated in the diagenetic–hydrothermal environment, and eventually recrystallized during metamorphism. With uplift and weathering, the cycle begins again.

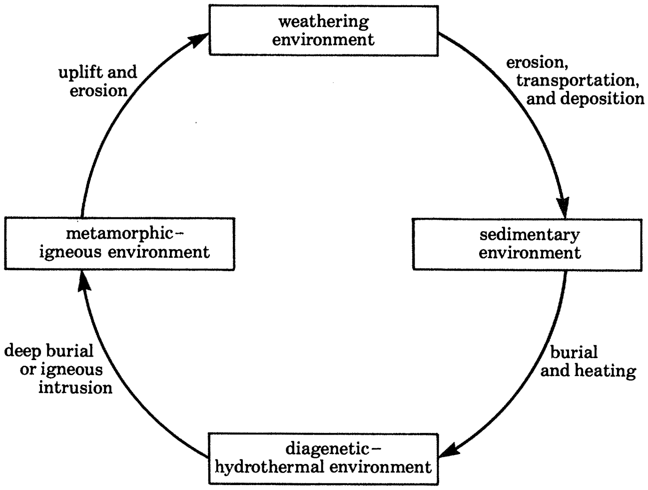


Figure 2. A simplified version of the rock cycle.

NEOFORMATION IN THE WEATHERING ENVIRONMENT

Let the cycle as depicted in figure 2 begin with a crystalline rock. The type of clay mineral neoformed from this rock in the weathering environment may change as a function of climate, drainage, original rock type, vegetation and weathering time. Bates (1962) studied weathering in the Hawaiian Islands, an area in which rock type (basalt) is constant, and clay neoformation could be observed mainly as a function of rainfall and drainage. Bates found that smectite forms on the dry, leeward sides of the islands, where rainfall is 0–50 cm a^{-1}, whereas gibbsite forms on the windward sides and in the mountains, where rainfall can be more than 1000 cm a^{-1}. Halloysite predominates in zones with intermediate rainfall. Bates's study illustrates the simple principle that clay minerals composed of the more soluble elements (for example, smectite) are formed in environments where these ions can accumulate (for example, in a dry climate or in a poorly drained soil), whereas clays composed of the least soluble elements (for example, gibbsite) form under severe leaching conditions (for example, on a hilltop in the wet tropics) where only sparingly soluble elements such as aluminium and ferric iron can remain. Kaolinite minerals form in intermediate zones where silicon, as well as aluminium, can be retained.

In a complementary study, Clemency (1975) examined a deeply weathered outcrop near São Paulo, Brazil, a situation in which climate, vegetation, and time were constant, and mineralogy could be studied as a function of original rock type. The outcrop consisted of reddish kaolinite, formed by weathering of a precursor schist or gneiss, and two greenish dykes, composed of ferric iron-rich smectite, formed by weathering of amphibolite. Once again, clay mineralogy could be attributed to differences in leaching intensity because the smectite-rich dyke rock was much less permeable than the kaolinite-rich host rock, thereby enabling soluble ions to accumulate in the dyke.

These patterns of neoformation also were found by Barshad (1966) in a study of weathering in the foothills of the Sierra Nevada mountains in California. The weathering products of acid and basic igneous rocks were studied as a function of rainfall (figure 3). The same pattern emerged: smectite forms in the dry climate, gibbsite in the wet, and kaolinite in the intermedite. Patterns for other clays shown in figure 3 may arise from inheritance or transformation mechanisms as well as from neoformation.

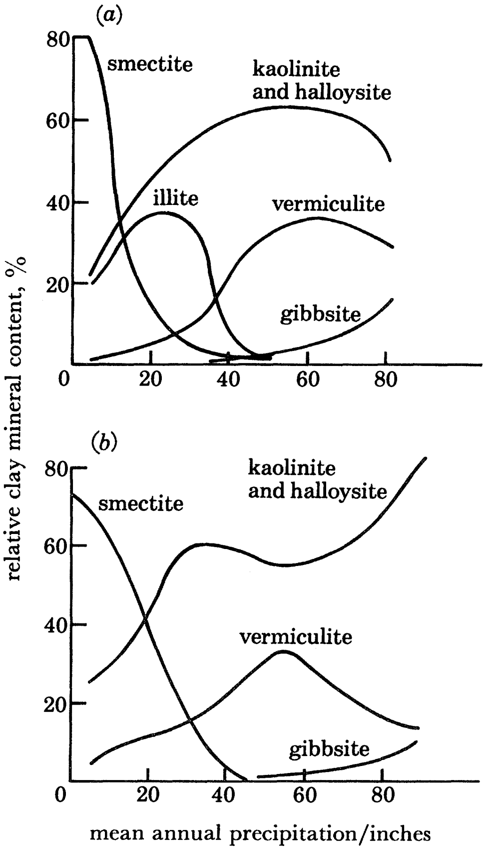


FIGURE 3. The effect of precipitation on the frequency distribution of the clay minerals in the surface layer of residual soils from acid (*a*) and basic (*b*) igneous rocks in California (from Barshad 1966). 1 inch = 2.54×10^{-2} m.

The above examples illustrate the importance of soil-solution chemistry in determining the mineralogy of a neoformed clay, and that the variables of climate, drainage, rock type, and vegetation are important insofar as they affect solution chemistry. A clay mineral may be neoformed when its solubility in a soil solution has been exceeded, given favourable reaction rates. This principle can be represented quantitatively in stability diagrams (for example, figure 4); these diagrams are constructed from thermochemical data as outlined by Garrels & Christ (1965) and Drever (1982). If a soil-solution composition lies within one of the mineral stability fields, as shown in figure 4, then that mineral should be neoformed at equilibrium. Geological evidence qualitatively supports these thermodynamic predictions. Moving from the smectite field in figure 4 to the lower left, and keeping pH constant, one passes through stability fields for smectite, kaolinite, and gibbsite as solution composition becomes more dilute, thereby duplicating mineralogical patterns found with increasing rainfall in Hawaii and in the Sierra Nevada foothills, and with increasing permeability in the outcrop near São Paulo.

These patterns for clay mineral neoformation have been used in relation to geology, for example, to study variations in palaeoclimate. Thompson *et al.* (1982) traced four major changes in precipitation in the northern Rocky Mountains during the Tertiary era by studying fauna, sedimentary structures, sediment accumulation, and clay mineralogy in continental

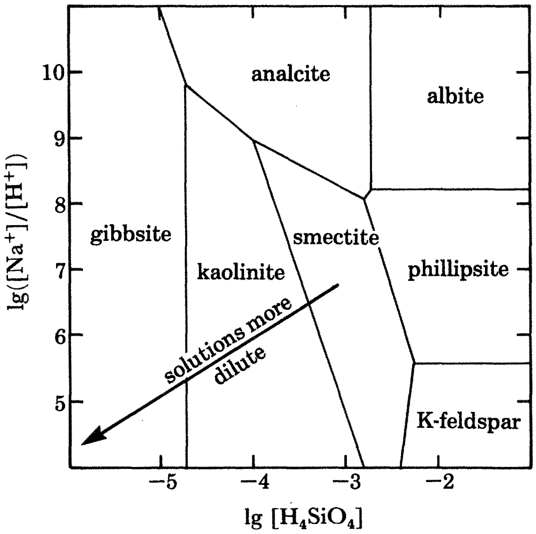


Figure 4. An example of a stability diagram for the system Na_2O–K_2O–Al_2O_3–SiO_2–H_2O drawn for $\lg([K^+]/[H^+]) = 4$. The bracketed species are activities (from Drever 1982).

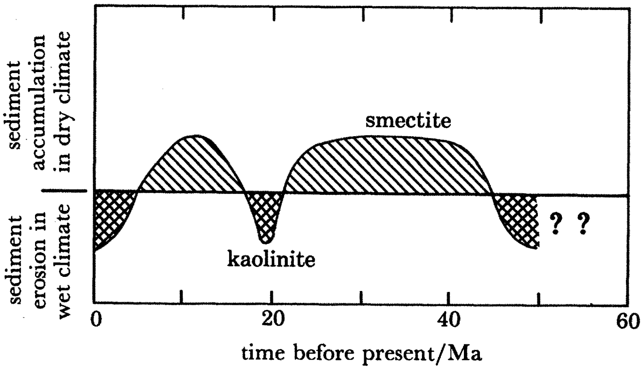


Figure 5. Erosion and deposition patterns through time in basins in Montana and Idaho. The vertical axis is in arbitrary units (after Thompson *et al.* 1982).

clastics found in intermontane basins. They found that wet climates, which were synchronous with times of sediment removal from the basins, are characterized by red, kaolinite-rich palaeosols that underlay unconformities (figure 5). These saprolitic rocks are similar to many modern soils formed in the wet tropics. Dry periods, which corresponded to times of sediment accumulation in the basins, are characterized by sediment types (for example, evaporites) and by fossils (for example, camels) formed in arid to semiarid climates, and by a clay mineralogy that is exclusively smectite.

Exceptions to the trends depicted in figures 3 and 4 are found in rocks and soils that contain significant amounts of organic matter and living organisms. Here chelating agents such as organic acids may render aluminium and iron more mobile than the more soluble elements (Huang & Keller 1970), and crystallization processes may be extremely slow. Weathering under these conditions may yield non-crystalline or poorly ordered materials and organomineral complexes (Wilson & Jones 1983).

Neoformation has been highlighted in this discussion of the weathering environment, but inheritance and transformation also are important mechanisms functioning in a soil. Inheritance dominates where weathering is mainly mechanical, such as under climatic conditions found in polar regions. Layer transformation, such as leaching of interlayer potassium from illite to form soil vermiculite (Weaver 1958), or precipitation of aluminium hydroxide interlayers in smectite to form soil chlorite (Rich 1968), is important in zones of intermediate weathering intensity, whereas neoformation prevails under more severe chemical weathering conditions. Thus, mechanisms of clay formation in the weathering environment are related approximately to latitude, with inheritance abundant near the poles, and neoformation dominant in the wet tropics. Of course there are many exceptions to these trends. For example, Reynolds (1971) described neoformation of gibbsite above the snowline in the northern Cascade Mountains of Washington State. The rocks in this area are exposed to high insolation and melt-water runoff during spring and summer and therefore undergo intense leaching during part of the year. Weathering of other rocks in this region leads to a neoformation of smectite and to a transformation of phlogopite into vermiculite, thereby demonstrating the importance of local chemical environment to clay mineral formation.

INHERITANCE IN THE SEDIMENTARY ENVIRONMENT

In the second stage of the cycle (figure 2), clays are eroded and transported to the ocean floor. Transportation into regions adjacent to continents is mainly by water, and sedimentation rates may be large. Clays are transported into regions far from continental shelves and slopes mainly by wind, and sedimentation rates may be very small. Minimal changes in composition are undergone by clays during transportation and deposition, and are primarily confined to ion-exchange reactions. On entering the ocean, the dominant exchangeable ions on clays from the Amazon River system, for example, change from Ca^{2+} (80%) to Na^+ and Mg^{2+} (about 38% each), with a significant increase in K^+ (9%) (Sayles & Margelsdorf 1979). This K^+ may be fixed in soil vermiculite and thereby transform it back into illiite (Weaver 1959).

By far the most important origin for clays on the ocean floor is inheritance from adjacent continents. Pelagic clays generally correspond both in mineralogy and in relative abundance to clays being supplied by rivers that are eroding adjacent terrestrial zones (Weaver 1959; Biscaye 1965; Griffin *et al.* 1968; Lisitzin 1972). The latitudinal distribution found for clays in the weathering environment leads to a bipolar distribution for marine clays. Chlorite and illite, minerals generally inherited in soils forming on diagenetic or low-grade metamorphic rocks, are common in marine sediments that adjoin land areas with cold climates, where mechanical weathering dominates, whereas kaolinite and gibbsite, clays neoformed in soil undergoing intense chemical leaching, are common in marine sediments bordering equatorial, humid zones (for example, figure 6). Potassium–argon age dates of oceanic illite confirm that it has been derived by inheritance from the continents rather than by neoformation or transformation reactions occurring on the ocean floor, and that it has not undergone extensive alteration (Hurley *et al.* 1963; Lisitzin 1972).

The distribution of smectite on the ocean floor is not as regular as that found for the other minerals, and may result from neoformation of smectite in the marine environment and in diverse continental environments. Griffin *et al.* (1968), for example, found that there is more smectite in the southern oceans because of greater volcanic activity, and Hein *et al.* (1979) suggest that smectite forms at a uniform rate over much of the north Pacific deep sea floor.

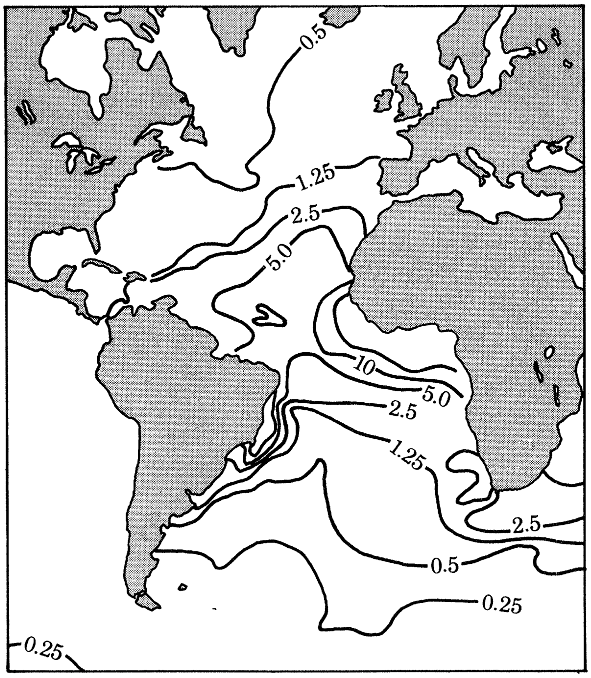


Figure 6. Kaolinite–chlorite ratio for the under 2 μm size fraction of deep sea sediments (from Biscaye 1965).

Glauconite also is neoformed (and transformed) in the ocean on continental shelves (Odin & Matter 1981). Neoformation of oceanic smectite indicates that smectite could be thermodynamically stable in seawater, although metastability resulting from slow reaction is also a strong possibility (Eberl & Hower 1976). The apparent stability of most clays in the ocean, however, results from slow reaction rates. It is unlikely that clay minerals formed in diverse terrestrial environments would be in equilibrium with the same seawater solution.

When a mixture of waterborne clay minerals enters the ocean, differential settling is expected, thereby giving rise to a systematic distribution of inherited clay minerals with distance from shore. The experiments of Whitehouse *et al.* (1960) give the following general sequence for settling rate under quiet conditions at 26 °C in seawater with approximately normal composition:

$$\text{illite } (15.8\ \text{m d}^{-1}) > \text{chlorite} > \text{kaolinite } (11.8\ \text{m d}^{-1}) \gg \text{montmorillonite } (1.3\ \text{m d}^{-1}).$$

Settling rates for clays in saline water were found to depend on floccule size rather than on grain size. Relative settling rates were not greatly changed by changes in temperature, organic matter, or salinity, with the exception that decreasing salinity caused the settling rate for chlorite to fall slightly below that for kaolinite. The experimental pattern has been observed in nature, for example, in recent sediments of the Niger delta (Porrenga 1966). Smectite in these sediments increases, relative to kaolinite, with water depth and distance from shore. This simple pattern for lateral clay mineral distribution may be altered by having several source rivers for a basin, and by complicating wind, density, and, or, sea current patterns. Conversely, these currents can be traced by studying the distribution of inherited clays (for example, Sawhney & Frink 1978).

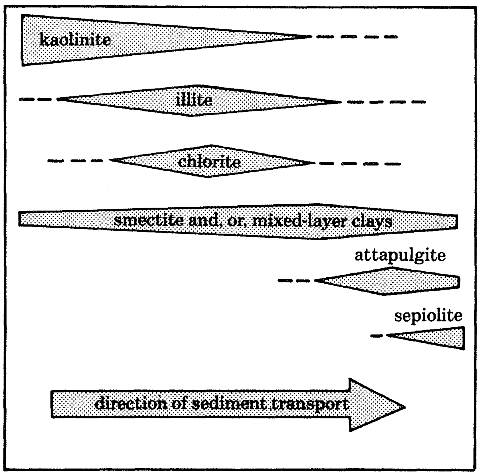


Figure 7. Generalized lateral variations in clay mineral assemblages with direction of transport (from Parham 1966).

Parham (1966), and many workers before him, studied lateral variations of clay minerals in sediments of various ages and lithologies and found a systematic pattern with distance from shore (figure 7). These trends do not agree with those of Whitehouse *et al.* (1960), and may reflect the effect of burial diagenesis, in the case of illite, and neoformation, in the case of chlorite, attapulgite, and sepiolite, on trends that originated from differential settling. Exceptions to the trends shown in figure 7 are legion, but studies of such trends have proven to be useful: maps of the relative amounts of kaolinite, illite, and chlorite have been used to define the margins and centres of ancient sedimentary basins in the search for oil.

TRANSFORMATION AND NEOFORMATION IN THE DIAGENETIC–HYDROTHERMAL ENVIRONMENT

Clays deposited in a sedimentary environment such as a subsiding basin, are buried, heated, and eventually enter the diagenetic environment (figure 2). An important reaction occurring in shales formed from muds that originally contained smectite is the gradual conversion of smectite into mixed-layer illite–smectite (I–S) with increasing burial depth and increasing temperature (figure 8*a*). Perry & Hower (1970) found that this reaction begins at about 60 °C in U.S. Gulf Coast sediments. Initially, the distribution of illite and smectite layers in I–S is random, but it becomes ordered when about 65% of the layers are illite. Neoformation of chlorite accompanies this reaction (figure 8*b*) as does dissolution of detrital potassium feldspar (figure 8*c*). Generally, the overall reaction is (Hower *et al.* 1976):

$$\text{K-feldspar} + \text{smectite} \rightarrow \text{I–S} + \text{chlorite} + \text{quartz},$$

although the stoichiometry of this reaction is as yet unclear (Boles & Franks 1979). The extent of this reaction in shales is most likely a function of time, temperature and porewater composition (Hower 1981).

The reaction of smectite to I–S is considered to proceed by transformation, although this mechanism has not been proven. Chemical data from U.S. Gulf Coast burial sequences indicate that Al^{3+} substitutes for Si^{4+} in the clays' tetrahedral sheets, thereby increasing the negative charge on smectite interlayers (Weaver & Beck 1971; Hower *et al.* 1976). When a critical layer charge is reached, interlayer potassium dehydrates, thereby transforming expanded smectite interlayers into nonexpanding illite interlayers. The layer charge required for interlayer potassium dehydration is about -0.75 equivalents per half unit cell (Eberl 1980). Interlayer cations with hydration energies greater than that of potassium require greater layer charges for dehydration. Potassium is greatly preferred over these other cations in interlayers that have reached a charge of -0.75, because dehydrated potassium has a much smaller ionic radius than hydrated cations and, therefore, according to Coulomb's law, is adsorbed with greater energy. Thus, burial diagenesis tends to concentrate potassium in illite because K^+ is the first ion of abundance to dehydrate in response to increasing layer charge.

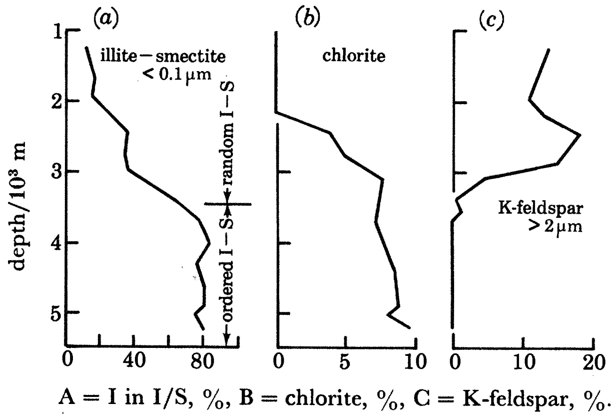


FIGURE 8. Depth-dependent changes in composition of illite–smectite (*a*), percentage chlorite (*b*), and percentage K-feldspar (*c*) from the Matagorda well (data from Hower *et al.* 1976; figure from Hower 1981).

This transformation of smectite into illite may affect the generation of oil in sedimentary basins. The tops of most oil bearing horizons in the U.S. Gulf Coast Tertiary occur in the depth interval where the reaction takes place (figure 9). Although this correlation may be fortuitous, there are several reasons why this reaction could help produce oil: fine-grained smectite layers initially may protect organic matter from oxidation and then catalyse its transformation into petroleum (Johns 1979); water released by the fixation of interlayer potassium may aid in flushing hydrocarbons out of source rocks and into reservoirs (Weaver 1960; Perry & Hower 1972); and pore space resulting from the collapse of smectite layers could provide pathways through source rocks for petroleum migration.

Trends in the reaction found with increasing temperature for clays in shales (figure 8) are not necessarily applicable to rocks with different chemical compositions. For example, hydrothermal alteration of basalts at ocean ridges produces saponites, interstratified chlorite–smectites, and chlorite with increasing temperature (Kristmannsdottir 1979), and figure 10 shows a comparison between temperature-dependent mineral assemblages found in shales, sandstones, and volcanic rocks (Hoffman & Hower 1979). In addition, laboratory studies of hydrothermal systems of more diverse compositions have shown that the conversion of smectite into I–S by fixation of interlayer potassium is but one example of a more general type of reaction, in which smectite may be converted into a variety of mixed-layer clays by reaction with interlayer cations other than potassium (Eberl 1978). For example, montmorillonites that contain potassium yield the following series on hydrothermal treatment with increasing reaction time and temperature: K-montmorillonite → I–S (random) → I–S (ordered) → illite; whereas montmorillonites with lithium as the interlayer cation yield: Li-montmorillonite → Li-tosudite → cookeite (?). These differences in reaction products probably reflect differences in an interplay between growth of layer charge and interlayer cation hydration energies. Other interlayer cations give other reaction series; therefore, the origin of several geologically diverse clay minerals can be traced to hydrothermal reaction of precursor montmorillonites having different interlayer compositions.

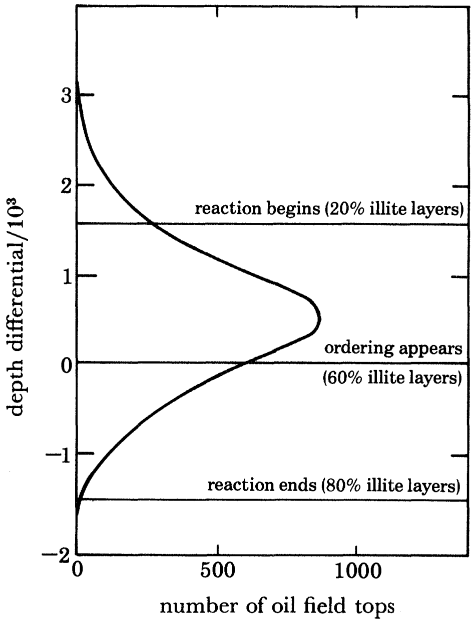


FIGURE 9. Relation between the beginning and end of the reaction of smectite to illite–smectite and the number of producing oil fields 'tops' in the U.S. Gulf Coast Tertiary (after Weaver 1979). The zero line refers to the depth at which the 1.7 nm X-ray peak can no longer be observed. This depth usually corresponds to the first appearance of ordered I–S.

Hydrothermal experiments also have shown that trioctahedral smectites react very differently than do dioctahedral smectites commonly found in burial diagenetic sequences. Trioctahedral smectites such as saponite and stevensite can be much less reactive than their dioctahedral counterparts. They can remain highly expanded even after hydrothermal treatment at 400 °C for 200 d, although eventually they may react to form mixed-layer talc–smectites or chlorite–smectites (Whitney 1983). Evidently, these trioctahedral systems contain insufficient aluminium to build the layer charge needed to form a mixed-layer mica–smectite structure (Eberl *et al.* 1978). Thus, aluminium, one of the least reactive elements in the weathering environment, plays a central role in reactions that occur in the diagenetic–hydrothermal environment.

Synthesis experiments also show that clays in hydrothermal systems frequently react according to Ostwald's step rule. This rule states that the first phase to form in a system held at constant temperature, pressure and composition may not be the thermodynamically stable phase; and that the initial phase may disappear with time yielding new phases as equilibrium is gradually approached in a series of steps. I–S formed in U.S. Gulf Coast sediments (figure 8*a*) may be a natural example of this rule, as indicated by hydrothermal experiments on similar systems (Eberl & Hower 1976). A clear example of Ostwald's rule in a synthetic system was demonstrated by Whitney (1979) and Whitney & Eberl (1982). Starting with a gel of composition similar to that of talc, the first phase to form at all temperatures in these experiments was talc. At 450 °C and below, however, the talc structure became more disordered with increasing reaction time, eventually yielding kerolite. Kerolite then dissolved, forming trioctahedral smectite (stevensite), and then this smectite reacted to form corrensite (figure 11). At 500 °C and above, only talc was synthesized throughout the time of the experiments. These experiments show that metastable clays may persist for many months even in relatively high temperature hydrothermal systems. The experiments suggest that may clays in nature also could be metastable, forming in response to Ostwald's step rule rather than in response to equilibrium conditions. It remains to be demonstrated whether or not reaction pathways followed in an Ostwald sequence can be described by irreversible thermodynamics (Helgeson 1968; Helgeson *et al.* 1969), by nucleation kinetics (Fyfe *et al.* 1958), or by some other model.

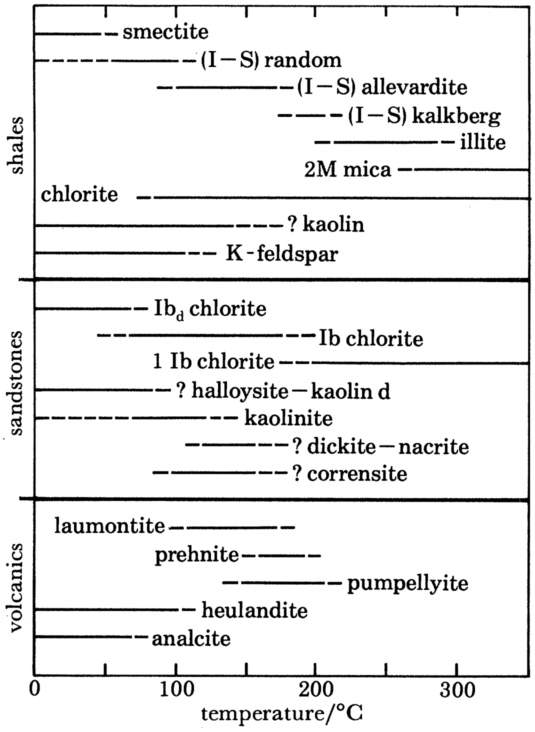


Figure 10. Comparison of temperature-dependent mineral assemblages in shales, sandstones and volcanic rocks. Temperatures do not represent equilibrium, but are applicable (with caution) to lower Tertiary and Mesozoic pre-greenschist facies rocks (from Hoffman & Hower 1979).

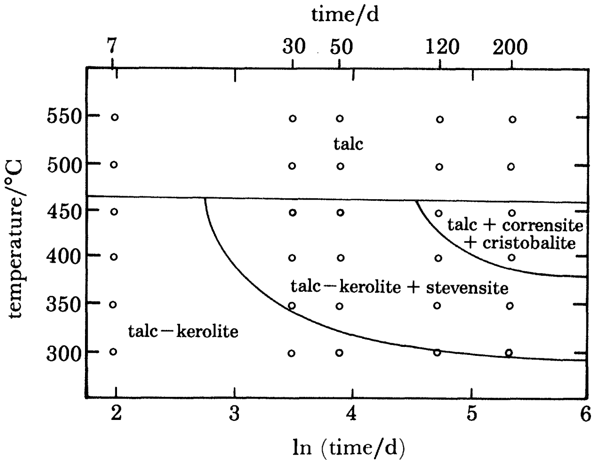


Figure 11. Synthesis diagram for the reaction of gel having the Mg/Si ratio of talc in an hydrothermal system held at 1 kilobar pressure. The circles are hydrothermal runs (from Whitney 1979).

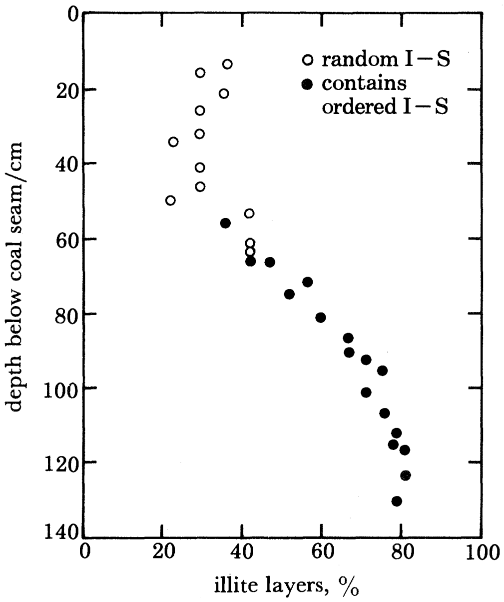


Figure 12. Relation between depth below coal, percentage illite layers in illite–smectite and type of interlayering for the under 2 μm size fraction of an Illinois underclay (after Rimmer & Eberl 1982).

TRANSFORMATION IN THE WEATHERING ENVIRONMENT

Clays transformed or neoformed in the diagenetic–hydrothermal environment may be buried deeper, or subjected to igneous intrusion, and eventually may recrystallize to coarser grained micas and chlorites as they enter the metamorphic environment at the greenschist facies (figures 2 and 10). Rather than trace this cycle any further, let shales containing illite be exposed to the weathering environment once again by uplift and erosion.

An interesting weathering pattern develops for such shales that have undergone acid leaching. The profile in figure 12 shows a gradual increase in percentage illite in I–S with depth in an Illinois underclay. (An underclay is a non-bedded, light coloured argillaceous rock that is commonly found beneath beds of coal.) Over a depth of 140 cm, the Illinois clays appear to duplicate trends observed for I–S over depth intervals of thousands of metres in burial diagenetic sequences (figure 8*a*). The clays in the underclay, however, have responded to a chemical rather than to a temperature gradient, and the reaction is different. Illite layers were transformed to smectite by a reaction in response to removal of interlayer potassium by acid leaching. Transformation was greatest at the top of the profile where leaching was most intense (Rimmer & Eberl 1982). The leaching sequence is: illite → I–S (ordered) → I–S (random) with increasing intensity. This series encompasses the plastic underclays. With more intense leaching, these transformed minerals will disappear, giving rise to neoformed kaolinite and aluminium hydroxide-bearing underclays (Huddle & Patterson 1961). Thus, all three mechanisms for clay formation may operate simultaneously, a situation commonly found in nature. In fact, all three mechanisms may operate to yield a single species of mixed-layer clay. Data from Jones & Weir (1983) suggest that clay minerals from alkaline, saline Lake Abert may originate from an interlayering of inherited montmorillonite, neoformed kerolite and stevensite, and transformed or neoformed illite and chlorite. An intimate mixture of these layers may diffract X-rays as a single mixed-layer clay mineral through the process of interparticle diffraction (Nadeau *et al.* 1984).

Conclusion

Clay minerals are nearly ubiquitous in the Earth's upper crust, and they offer a unique record of Earth processes and Earth history. Thus, clay mineral petrology forms an important branch of the science of geology. Clay minerals may be very responsive to environmental changes; yet they are not so responsive that all previous history is lost. For example, clays may react almost instantaneously to environmental changes through ion exchange and neoformation reactions; they may respond more slowly by layer transformation and by neoformation in an Ostwald step series; or they may remain unreactive. Different clays in a given deposit may react in a different manner and at different rates, thereby offering the potential for a unique solution to the problem of determining environmental conditions, past and present.

In order to read this complex record, it first is necessary to identify the clays precisely and then to determine their mechanisms of formation. Evidence for the occurrence of a transformation reaction would be the discovery of serial relationships in which one clay is seen to alter gradually into another clay over a temperature, pressure, compositional or time gradient (for example, figures 8*a* and 12). The sudden disappearance of one clay and the appearance of another, with no transitional phases, suggests neoformation (for example, figure 8*b*), or a change in source area. Radiometric age dates and textural information obtained from scanning electron microscopy are useful in distinguishing neoformation from inheritance (for example, Hower *et al.* 1963; Wilson & Pittman 1977).

The formation of clay minerals has been presented as a cyclic process (figure 2), but clay minerals in shales have changed through geological time. Young shales and recent sediments are relatively enriched in kaolinite and smectite-rich mixed-layer clay, whereas older, pre-Mesozoic shales are depleted in these phases and are enriched in chlorite and illite (Weaver 1967; Hower *et al.* 1976). It has been suggested that these differences in mineralogy are due to differences in chemical composition between recent and ancient weathering environments (Weaver 1967), or to a greater degree of diagenesis for older rocks (Grim 1968; Weaver & Beck 1971; Hower *et al.* 1976). The latter explanation is favoured by remarkable parallels found between trends in mineralogy and composition of shales with increasing geological age, and of shales subjected to increasing diagenetic grade (Garrels & Mackenzie 1975; Hower *et al.* 1976).

Finally, it is emphasized that clay mineral petrology is a young science that is still inexact and incomplete. For example, mixed-layer clays are among the most abundant of the clay minerals, but only recently has it been possible to characterize them with confidence (Reynolds & Hower 1970; Reynolds 1980; Srodon 1980). Mixed-layer clays may prove to be sensitive indicators of Earth history once their mechanisms and environments of formation are understood.

The author thanks C. Clemency, C. Farmer, D. Horton, W. Keller, B. Kimball, P. Nadeau, J. Russell, L. Schultz, J. Srodon, C. Weaver, A. Weir, and G. Whitney for their reviews of this manuscript. This paper is dedicated to the memory of G. W. Brindley and John Hower.

REFERENCES

Barshad, I. 1966 The effect of variation in precipitation on the nature of clay mineral formation in soils from acid and basic igneous rocks. *Proc. int. Clay Conf.* (Jerusalem) **1**, 167–173.

Bates, T. 1962 Halloysite and gibbsite formation in Hawaii. *Clays Clay Miner.* **9**, 315–328.

Biscaye, P. E. 1965 Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Bull. geol. Soc. Am.* **76**, 803–832.

Boles, J. R. & Franks, S. G. 1979 Clay diagenesis in Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. *J. sedim. Petrol.* **49**, 55–70.

Brindley, G. W. & Brown, G. 1980 *Crystal structures of clay minerals and their X-ray identification.* London: Mineralogical Society.

Clemency, C. V. 1975 Simultaneous weathering of a granitic gneiss and an intrusive amphibolite dike near São Paulo, Brazil, and the origin of clay minerals. *Proc. int. Clay Conf.* (Mexico), 157–172.

Drever, J. I. 1982 *The geochemistry of natural waters.* Englewood Cliffs, N.J.: Prentice-Hall.

Eberl, D. 1978 Reaction series for dioctahedral smectites. *Clays Clay Miner.* **26**, 327–340.

Eberl, D. D. 1980 Alkali cation selectivity and fixation by clay minerals. *Clays Clay Miner.* **28**, 161–172.

Eberl, D. & Hower, J. 1976 Kinetics of illite formation. *Bull. geol. Soc. Am.* **87**, 1326–1330.

Eberl, D., Whitney, G. & Khoury, H. 1978 Hydrothermal reactivity of smectite. *Am. Miner.* **63**, 401–409.

Esquevin, J. 1958 Les silicates de zinc. Etude de produits de synthèse et des minèraux naturels. *Theèse Sci. Paris.*

Fyfe, W. S., Turner, F. J. & Verhoogen, J. 1958 *Metamorphic reactions and metamorphic facies.* Geological Society of America Memoir 73.

Garrels, R. M. & Christ, C. L. 1965 *Solutions, minerals and equilibria.* San Francisco: Freeman Cooper & Company.

Garrels, R. M. & Mackenzie, F. T. 1975 Chemical history of the oceans deduced from post-depositional changes in sedimentary rocks. In *Studies in paleo-oceanography* (ed. W. W. Hay). Soc. Econ. Paleontologists & Mineralogists Spec. Pub. **20**, 193–204.

Griffin, J. J. Windom, H. & Goldberg, E. D. 1968 The distribution of clay minerals in the World Ocean. *Deep-Sea Res.* **15**, 433–459.

Grim, R. E. 1968 *Clay mineralogy.* New York: McGraw-Hill Book Co.

Hein, J. R. Yeh, H.-W. & Alexander, E. 1979 Origin of iron-rich montmorillonite from the manganese nodule belt of the north equatorial Pacific. *Clays Clay Miner.* **27**, 185–194.

Helgeson, H. C. 1968 Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions. I. Thermodynamic relations. *Geochim. cosmochim. Acta* **32**, 853–877.

Helgeson, H. C., Garrels, R. M. & Mackenzie, F. T. 1969 Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solution. II. Applications. *Geochim. cosmochim. Acta* **33**, 455–481.

Hoffman, J. & Hower, J. 1979 Clay mineral assemblages as low grade metamorphic geothermometers: application to the thrust faulted disturbed belt of Montana, U.S.A. In *Aspects of diagenesis* (ed. P. A. Scholle & P. R. Schluger). Soc. Econ. Paleontologists & Mineralogists Spec. Pub. **26**, 55–79.

Hower, J. 1981 Shale diagenesis. In *Clays and the resource geologist* (ed. F. J. Longstaffe). *Short course handbook* **7**, 60–80. Toronto: Mineralogical Association of Canada.

Hower, J., Hurley, P. M., Pinson, W. H. & Fairbairn, H. W. 1963 The dependence of K-Ar age on the mineralogy of various particle size ranges in a shale. *Geochim. cosmochim. Acta* **27**, 405–410.

Hower, J., Eslinger, E. V., Hower, M. E. & Perry, E. A. 1976 Mechanism of burial metamorphism of argillaceous sediment. I. Mineralogical and chemical evidence. *Bull. geol. Soc. Am.* **87**, 725–737.

Huang, W. H. & Keller, W. D. 1970 Dissolution of rock forming minerals in organic acids. Simulated first stage weathering of fresh mineral surfaces. *Am. Miner.* **55**, 2076–2094.

Huddle, J. W. & Patterson, S. H. 1961 Origin of Pennsylvanian underclay and related seat rocks. *Bull. geol. Soc. Am.* **72**, 1643–1660.

Hurley, P. M., Heezen, B. C., Pinson, W. H. & Fairbairn, H. W. 1963 K-Ar age values in pelagic sediments of the North Atlantic. *Geochim. cosmochim. Acta* **27**, 393–399.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Johns, W. D. 1979 Clay mineral catalysis and petroleum generation. *Am. Rev. Earth Planet Sci.* **7**, 183–198.

Jones, B. F. & Weir, A. H. 1983 Clay minerals of Lake Abert, an alkaline, saline lake. *Clays Clay Miner.* **31**, 161–172.

Kristmannsdottir, H. 1979 Alteration of basaltic rocks by hydrothermal activity at 100–300 °C. *Proc. int. Clay Conf.* (Oxford), 359–367.

Lisitzin, A. P. 1972 In *Sedimentation in the world ocean* (ed. K. S. Rodolfo). Soc. Econ. Paleontologists & Mineralogists Spec. Pub. **17**.

Millot, G. 1970 *Geology of clays* (trans. W. R. Farrand & H. Paquet). New York: Springer-Verlag.

Nadeau, P. H., Tait, J. M., McHardy, W. J. & Wilson, M. J. 1984 Interstratified XRD characteristics of physical mixtures of elementary clay particles (In the press.)

Odin, G. S. & Matter, A. 1981 De glauconiarum origine. *Sedimentology* **28**, 611–641.

Parham, W. E. 1966 Lateral variations of clay mineral assemblages in modern and ancient sediments. *Proc. int. Clay Conf.* (Jerusalem) **1**, 135–145.

Perry, E. A. & Hower, J. 1970 Burial diagenesis in Gulf Coast pelitic sediments. *Clays Clay Miner.* **18**, 165–177.

Perry, E. A. & Hower, J. 1972 Late-stage dehydration in deeply buried pelitic sediments. *Bull. Am. Ass. Petrol. Geol.* **56**, 2013–2021.

Porrenga, D. H. 1966 Clay minerals in recent sediments of the Niger delta. *Clays Clay Miner*, **14**, 221–233.

Reynolds, R. C. 1971 Clay mineral formation in an alpine environment. *Clays Clay Miner.* **19**, 361–374.

Reynolds, R. C. 1980 Interstratified clay minerals. In *Crystal structures of clay minerals and their X-ray identification* (ed. G. W. Brindley & G. Brown), pp. 249–303. London: Mineralogical Society.

Reynolds, R. C. & Hower, J. 1970 The nature of interlayering in mixed-layer illite–montmorillonite. *Clays Clay Miner.* **18**, 25–36.

Rich, C. I. 1968 Hydroxyl interlayers in expansible layer silicates. *Clays Clay Miner.* **16**, 15–30.

Rimmer, S. M. & Eberl, D. D. 1982 Origin of an underclay as revealed by vertical variations in mineralogy and chemistry. *Clays Clay Miner.* **30**, 422–430.

Sawhney, B. L. & Frink, C. R. 1978 Clay minerals as indicators of sediment source in tidal estuaries of Long Island Sound. *Clays Clay Miner.* **26**, 227–230.

Sayles, F. L. & Mangelsdorf, P. C. Jr. 1979 Cation-exchange characteristics of Amazon River suspended sediment and its reaction with seawater. *Geochim. cosmochim. Acta* **43**, 767–779.

Środoń, J. 1980 Precise identification of illite–smectite interstratifications by X-ray powder diffraction. *Clays Clay Miner.* **28**, 401–411.

Thompson, G. R., Fields, R. W. & Alt, D. 1982 Land-based evidence for Tertiary climatic variations: Northern Rockies. *Geology* **10**, 413–417.

Weaver, C. E. 1958 The effects and geologic significance of potassium ‘fixation’ by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material. *Am. Miner.* **43**, 839–861.

Weaver, C. E. 1959 The clay petrology of sediments. *Clays Clay Miner.* **6**, 154–187.

Weaver, C. E. 1960 Possible uses of clay minerals in the search for oil. *Bull. Am. Ass. Petrol. Geol.* **44**, 1505–1518.

Weaver, C. E. 1967 Potassium, illite, and the ocean. *Geochim. cosmochim. Acta* **31**, 2181–2196.

Weaver, C. E. 1979 Geothermal alteration of clay minerals and shales: Diagenesis. Technical Report UC-70. Office of Nuclear Waste Isolation, Battelle.

Weaver, C. E. & Beck, K. C. 1971 Clay water diagenesis during burial: How mud becomes gneiss. *Geol. Soc. Am. Spec. Paper* **134**, 1–96.

Whitehouse, U. G., Jeffrey, L. M. & Debbrecht, J. D. 1960 Differential settling tendencies of clay minerals in saline waters. *Clays Clay Miner.* **7**, 1–79.

Whitney, G. 1979 The paragenesis of synthetic phyllosilicates on the talc–phlogopite join. Ph.D. Thesis. University of Illinois, Urbana.

Whitney, G. & Eberl, D. D. 1982 Mineral paragenesis in a talc–water experimental hydrothermal system. *Am. Miner.* **67**,^{2}944–949.

Whitney, G. 1983 Hydrothermal reactivity of saponite. *Clays Clay Miner.* **31**, 1–8.

Wilson, M. D. & Pittman, E. D. 1977 Authigenic clays in sandstones: recognition and influence on reservoir properties and paleoenvironmental analysis. *J. sedim. Petrol.* **47**, 3–31.

Wilson, M. J. & Jones, D. 1983 Lichen weathering of minerals: implications for pedogenesis. *Spec. Publ. Geol. Soc. London* **11**, 5–12.

Discussion

V. C. Farmer. (*Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen AB*9 2*QJ, U.K.*). It seems unlikely that the diagenetic alteration of montmorillonite to illite is a transformation which preserves the layer structure of the parent montmorillonite, because (see Tchoubar, this meeting) (i) successive layers in montmorillonite are randomly oriented and randomly displaced relative to each other, whereas in illite the hexagonal holes in the tetrahedral layer are directly superimposed in successive layers; (ii) The structures of the octahedral sheets differ, as in illite only *cis* sites are occupied, whereas in montmorillonite, a *cis* and *trans* site are occupied by octahedral cations.

Thus the formation of illite from smectite involves major restructuring, and is best considered a neoformation, consistent with the larger and more regular crystals of illite and interstratified illite–smectites, compared with montmorillonite. The widespread occurrence of regularly interstratified illite–smectites can be understood if the restructuring largely involves adjacent smectite sheets. In the process, tetrahedral aluminium will be concentrated in the inner tetrahedral sheets, adjacent to potassium ions, and the outer tetrahedral sheet will be depleted in aluminium, compared with the original smectite. Thus a third mica layer is unlikely to build onto the initial two, so interstratification results.

D. D. Eberl. Whether illite forms from smectite during burial diagenesis by neoformation or by transformation is an open question. There is, however, no problem in making holes in adjacent 2:1 layers line up. K-smectite can be converted readily into an illite-like structure in the laboratory by dry heating or by wetting and drying. Also, the collapse of an expanded Na-vermiculite structure to an illite-like structure can be made to occur spontaneously in suspension by adding potassium. Rearrangements in the octahedral sheet also could occur during transformation. In fact, magnesium needed to form chlorite (figure 8*b*) may come from smectite's octahedral sheet.

Regularly shaped illite crystals have been observed in sandstones, thereby suggesting neoformation. But transmission electron microscopy studies of shales that initially contain detrital smectite suggest that both neoformation and transformation take place.

I agree with Dr Farmer's view of the illite crystals as having asymmetrical layer charges, but illite packets must be thicker than two 2:1 layers, otherwise there could never be a 20% expandable clay (see figure 8*a*). Only 50% expandable K-rectorite and clays of higher expandabilities could exist. When a two-layer thick illite crystal is converted into a three-layer thick illite, does the two-layer crystal completely dissolve and reprecipitate as a thicker crystal, or does it grow by increasing layer charge on its edges? This question could be resolved by careful K–Ar studies of an appropriate illite–smectite sequence. In the dissolution–reprecipitation mechanism, all radiogenic argon should be lost as a gas at each increase in illite content.

R. M. Barrer, F.R.S. (*Chemistry Department, Imperial College, London SW7, U.K.*). You mentioned the hydrothermal régime for clay mineral synthesis as beginning above about 60 °C. This low temperature is not strictly in the hydrothermal region which one usually associates with temperatures above 100 °C. Can you comment further on the temperature ranges over which smectites and kandites have been synthesized or have formed in Nature? Are there approximate upper limits?

D. D. Eberl. The conversion of montmorillonite into illite is detectable in U.S. Gulf Coast sediments when the burial temperature has reached approximately 60 °C. This temperature is in the realm of 'diagenesis'. Some authors distinguish between 'early' and 'late' diagenesis. Early diagenesis refers to changes that occur in the first few hundred metres of sediment where elevated temperatures are not encountered. In the present paper, these reactions are considered to occur in the sedimentary environment. Late stage diagenesis is synonymous with burial metamorphism. Precise temperature boundaries between 'early diagenesis', 'late diagenesis', 'hydrothermal', and 'metamorphic' are arbitrary.

Smectite has been synthesized at temperatures ranging from below 25 °C to 850 °C. In fact, an expanding phase has been synthesized at 1000 °C at 5 kilobar pressure. High pressures favour the development of expandable phases in systems of appropriate chemistries, thereby suggesting (from the Le Chatelier principle) that interlayer water is denser than pore water in hydrothermal systems. Smectite synthesis at low temperatures is favoured by the presence of magnesium. It is difficult to synthesize aluminium-rich smectites such as beidellite from gel at temperatures less than 200 °C.

Kaolinite, like beidellite, is difficult to synthesize at low temperatures. We were able to obtain a good yield of kaolinite starting with gel at 150 °C after 80 d, but were unsuccessful at 100 °C. The problem appears to be kinetic. Using organic catalysts, however, kaolinite has been synthesized at 25° C. The upper stability limit of kaolinite is about 405 °C where it reacts to form pyrophyllite. It can react to form pyrophyllite at a lower temperature if the Si/Al atomic ratio of the system is greater than one.