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# Clay Mineral Precipitation and Transformation during Burial Diagenesis [and Discussion]

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# Clay mineral precipitation and transformation during burial diagenesis

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Detrital clay minerals alter systematically during burial diagenesis. Smectites evolve via intermediate 'illite–smectites' to illite. Trioctahedral 'smectite–chlorites' or 'vermiculite–chlorites' evolve towards true (polytype I b) chlorites. In other reactions, authigenic clays (kaolinite, illite, chlorite) precipitate directly from aqueous solution rather than by continuous modification of some precursor lattice. In yet others, one mineral replaces another.

Many of these reactions are influenced by organic matter and the various low molecular mass soluble products of its diagenetic and thermal maturation. Carbon dioxide and organic acids influence pore-water pH and this, in turn, affects the solubility of clay minerals. Trioctahedral phyllosilicates are particularly sensitive. In contrast, organic matter also acts as a reducing agent when iron (III) oxides are destabilized to produce $Fe^{2+}$ and a marked increase in alkalinity. This reaction stabilizes trioctahedral clays such as chamosite. The balance between these different reactions affects the course of clay mineral diagenesis and itself varies systematically with burial depth and temperature.

## INTRODUCTION

The increased costs of both exploitation of and exploration for petroleum have made the producing companies investigate more carefully the processes of its formation (where, when) and the properties of reservoirs in which it may reside (improved extraction efficiency). Clay minerals may be involved in the former as catalysts (Johns 1979) and certainly affect the latter by precipitating in pore space, thereby reducing permeability and porosity. Different clay minerals affect reservoirs in different ways and it is important to predict both the type and amount likely to be present. As more sophisticated methods of recovery come into practice, it is essential to understand the likely chemical reactions between clay minerals and drilling, completion and flood fluids.

To understand the precipitation of authigenic clay minerals it is necessary to identify 'reactant' phases that, because of inherent instability, break down to yield appropriate solutes. Links between this instability and temperature are obvious targets for further study. Another important issue is the 'transportability' of clay minerals in solution: to what extent is precipitation a strictly localized phenomenon and can reactions in one part of a burial sequence influence diagenesis tens or hundreds of metres away? Pore-water flow patterns during compaction are of immense importance if the answer to this is 'yes'.

## MINERALOGICAL COMPOSITION OF SEDIMENTS

Chemical changes within clay mineral assemblages cannot be attributed to reactions amongst clays alone and indeed all the available evidence suggests other minerals are involved. Clastic sediment sequences include shales, silts and sands. Shales start life as muds with upwards of

70 % pore water and relatively reactive, unstable minerals derived from soil profiles. As well as the clay minerals themselves, amorphous compounds of iron, aluminium and silicon are important, as is organic matter. Carbonate, reactive silica and more organic matter may be added from depositional waters.

Sands tend to be somewhat less reactive and are generally very rich in quartz. Varying amounts of feldspar and rock fragments (including clay minerals) are present. Reactivity may be enhanced by addition of volcanic components, especially glass.

In general, the sequence of reactions that has been observed within mudrocks and shales is somewhat different from that in sandstones within the same succession. It is useful, therefore, to consider one in detail and then to evaluate similarities and differences.

Shales typically consist of at least 50 % (by mass) clay material, as defined either on some arbitrary size basis (often less than 2 μm) or by the presence of identified phyllosilicate clay minerals. Bearing in mind the preponderance of fine-grained sediments in most clastic sedimentary sequences, it should be clear that clay mineral changes in shales are of major significance in the geochemical differentiation of shallow crustal material.

## Clay mineral composition and structure

The common clay minerals, smectite, illite, intermediates between these two (usually referred to as i/s clays), kaolinite and chlorite are all phyllosilicates with the sheet structure based on a largely covalent array of $SiO_4$ tetrahedra with three of the four oxygens shared, i.e. $|Si_4O_{10}^{4-}|_n$. Net negative charge is increased by $Al^{III}$ for $Si^{IV}$ substitution. Structurally, most clay minerals are closely related to the micas. The fundamental layer consists of two tetrahedral sheets bonded tightly together by a plane of metal atoms in octahedral coordination. The regular array of oxygens is completed by additional hydroxyl groups. Two varieties are found, one with divalent metals in all available sites (trioctahedral clays) and the other with two thirds occupied by trivalent metals. This terminology is not transparently logical:

$$|Al_4(OH)_4^{8+}|_n \text{ (dioctahedral)}; \; |Mg_6(OH)_4^{8+}|_n \text{ (trioctahedral)}.$$

Combinations of these sheet formulae give the simplest of all phyllosilicates, i.e.

$$Mg_6|Si_8O_{20}|(OH)_4 \quad \text{talc (trioctahedral)}$$

and

$$Al_4|Si_8O_{20}|(OH)_4 \quad \text{pyrophyllite (dioctahedral).}$$

Neither structure possesses net layer charge, so there are no interlayer cations. Bonding between layers is dispersive. Kaolinite is similar to pyrophyllite but has only one tetrahedral sheet per unit layer.

Most micaceous minerals (all clays except kaolinite) have significant net negative charge on the layer structure compensated by cations (usually $Na^+$, $K^+$ or $Ca^{2+}$) in interlayer sites. Clays with low interlayer charge tend to hydrate and swell and are referred to as smectites. The common clays of shales and mudrocks seem to be dioctahedral and can be thought of as substituted pyrophyllites. Table 1 lists somewhat simplified formulae for iron-poor and iron-rich varieties to illustrate the link between substitution, interlayer charge and nomenclature. It should be noted that the oxidation state of iron is III and that, in general, these structures would all be expected to be more resistant to hydrolysis than trioctahedral clays (divalent $Fe^{2+}$ and $Mg^{2+}$), on account of the significantly more covalent nature of the bonding within the layer.

Table 1. Simplified structural formulae for mica-like clay minerals. The dioctahedral clays occur commonly in detrital sediments

| | |
|---|---|
| dioctahedral sedimentary clay minerals (mica-like $d_{001} \approx 1.0$ nm) | |
| beidellite<br>$X_{0.5}(Al_4) \vert Si_{7.5}Al_{0.5}O_{20} \vert (OH)_4$ | nontronite<br>$X_{0.5}(Fe^{III}_4) \vert Si_{7.5}Al_{0.5}O_{20} \vert (OH)_4$ |
| mixed layer i/s clays<br>$X_{1.0}(Al_4) \vert Si_{7.0}Al_{1.0}O_{20} \vert (OH)_4$ | (intermediates) |
| ‘illite’<br>$K_{1.5}(Al_4) \vert Si_{6.5}Al_{1.5}O_{20} \vert (OH)_4$ | glauconite<br>$K_{1.5}(Fe^{III}_4) \vert Si_{6.5}Al_{1.5}O_{20} \vert (OH)_4$ |
| trioctahedral smectite (hydrothermal) | |
| saponite<br>$X_{0.5}(Mg_6) \vert Si_{7.5}Al_{0.5}O_{20} \vert (OH)_4$ | |

Chlorite minerals differ from mica-like clays in that interlayer space is occupied by a second octahedrally coordinated sheet, this time entirely as hydroxide. The simplest formulation is for a talc-like trioctahedral chlorite with an uncharged interlayer sheet, $Mg_{12} | Si_8O_{20} | (OH)_{16}$. Sedimentary chlorites invariably contain a considerable amount of Al in both tetrahedral and octahedral sites. A reasonable formulation might be $(Fe, Mg)_{10}Al_2 | Si_6Al_2O_{20} | (OH)_{16}$. It appears that both layers and interlayer sheets carry charges. In marked contrast to the shale clays in table 1, iron in chlorites (at least, in sandstones, from which the most precise data are obtained) is in the divalent state and the structure seems to be trioctahedral. Clays that are apparently intermediate between smectites and chlorites are also known and are usually presumed to be interstratifications.

## Broad compositional trend

The formulae given above are useful to illustrate links between structure and composition but are not sufficiently precise to use as a basis for evaluating diagenetic changes (see also Velde 1983). Accurate chemical data for the actual phases involved are needed but these are notoriously difficult to obtain, because it is virtually impossible to purify clays by either physical or chemical means (the latter may seriously modify composition). Historically, therefore, clay mineralogists tended to concentrate on relatively infrequent occurrences of monomineralic assemblages. More recently, microprobe and, especially, analytical transmission electron microscope (t.e.m.) methods are producing more reliable data (or, at least, single-phase data).

Weaver & Pollard (1973) compiled numerous ‘sound’ analyses for each different clay mineral group. For mudrock burial sequences, the dominant progression is from smectite at shallow burial through i/s intergrades to illite at depth, the latter retaining a small component of smectite. Figure 1 illustrates this progression with the use of simplified data ‘means’ from Weaver & Pollard (1973), together with more recent chemical data for marine nontronite (Malahoff *et al.* 1982) and analytical t.e.m. data for some illite and glauconite samples (Ireland *et al.* 1983). The beidellite–illite trend is one of increasing Al and K content with decreasing Si content and has been previously identified by many workers. At higher temperatures than those normally associated with diagenesis, the same trend is confirmed as white mica (phengite) replaces illite (McDowell & Elders 1981). No obvious change in iron content emerges although $Mg^{2+}$ seems to be lost during recrystallization.

The nontronite–glauconite progression (if progression it be) is less well documented. Two

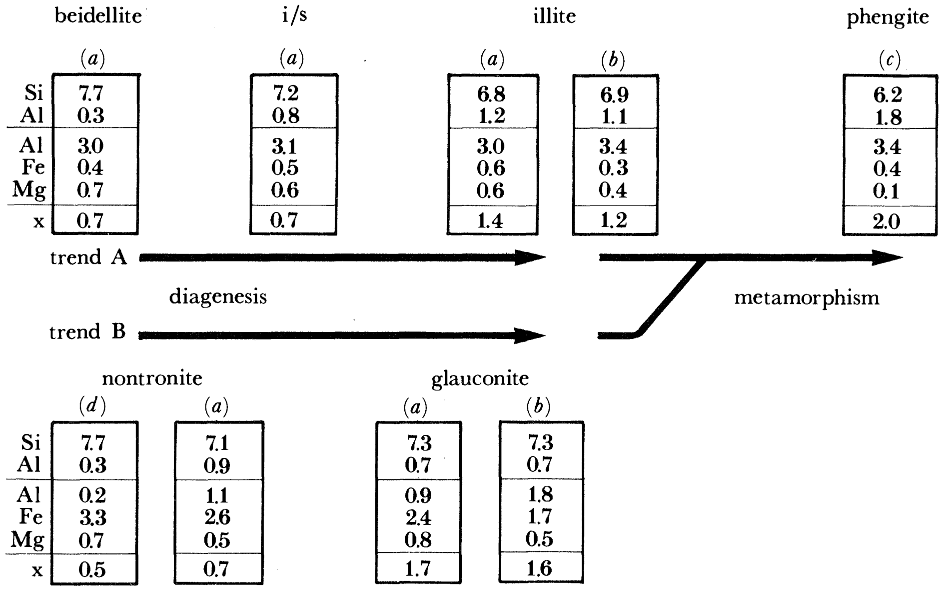

Figure 1. Compositional data (averages) for mica-like clay minerals from a variety of surface and sedimentary environments. (*a*) Weaver & Pollard (1973); (*b*) Ireland *et al.* (1983); (*c*) McDowell & Elders (1980); (*d*) Malahoff *et al.* (1982).

recent papers, Ireland *et al.* (1983) and Berg-Madsen (1983) demonstrate that a wide range of Al for $Fe^{III}$ substitution is possible in glauconites. Nontronite that forms today as submarine hydrothermal solutions mix with sea water and are oxidized (Malahoff *et al.* 1982) is very rich in octahedral iron(III). Because free oxygen is seldom, if ever, available in diagenetic environments it seems unlikely that the iron content of dioctahedral clays would increase with time; rather the reverse as suggested in figure 1. At temperatures characteristic of greenschist facies, octahedral iron is mostly eliminated, appearing as hematite in oxidized assemblages (as in the red–purple slates of the Cambrian Slate Belt of Gwynedd).

This broad comparison of data from many different sources confirms that, with increasing burial, the change from smectites to illites is one of increasing tetrahedral coordination of aluminium at the expense of silicon, with potassium incorporated in interlayer sites to compensate for the increased charge. The implication from studies of iron-rich dioctahedral clays is that octahedral iron(III) is replaced by aluminium.

## Soil clay minerals

As has already been mentioned, soils (and, by inference, sediments at deposition) contain substantial quantities of very finely divided (often X-ray amorphous) hydrated oxides of aluminium, iron and silicon. These are routinely separated (by selective dissolution) and analysed by soil scientists. Sedimentologists, however, seldom study this 'fraction', with the notable exceptions of the work of Drever (1971) and Foscolos & Powell (1980), who have demonstrated it to be present both in muds and deeply buried shales.

Soils, particularly acid soils, also contain chlorite-like minerals which are essentially dioctahedral i/s clays with incomplete interlayer hydroxide sheets. Weed & Nelson (1962) demonstrated that the interlayer sheet can be removed by leaching and that both $Fe^{III}$ and Al are present. Hsu & Bates (1964) were able to synthesize chlorite-like clays from vermiculite (high-charge smectite) and Al–OH polymers in solution.

These observations are important to the sedimentologist for two reasons. First, the weak 1.4 nm reflection commonly recorded on X-ray diffraction traces from shales may be from these hydroxy–interlayer clays rather than from true 'detrital' chlorites as is often assumed. If so, their composition would be very different from the authigenic chlorites reliably analysed from sandstones. Kirkland & Hajek (1972) estimated the composition of these clays, after first removing 'sesquioxides', to be

$$X_{0.8}(Al_{3.12}Fe_{0.48}Mg_{0.40})|Si_{6.48}Al_{1.42}O_{20}|(OH)_4,$$

with the interlayer sheet $Al_{2.9}(OH)_{7.58}$. Both octahedral sheets are presumably dioctahedral.

The second point is that soils clearly contain iron(III) in at least three distinct sites and these three types of iron react differently to acid leaching.

(*a*) As hydrated $Fe^{III}$ oxides (goethite, 'limonite' and amorphous sesquioxides).

(*b*) As interlayer Al–$Fe^{III}$ hydroxide sheets.

(*c*) As part of the more covalently bonded Al–$Fe^{III}$ dioctahedral layer.

This is a sequence of decreasing chemical reactivity. All types of iron would be destabilized by reducing conditions and inferences as to the sequence of involvement in diagenetic reactions are fairly obvious.

## SMECTITE TO ILLITE–PHENGITE TRANSFORMATION

Detailed investigations of shale diagenesis have been undertaken in many different sedimentary basins with remarkably consistent results. Most have relied on X-ray diffraction data with little or no reliable chemical information. Perhaps most complete have been studies of Gulf Coast Shale (Oligocene–Miocene) by Hower *et al.* (1976) and in the Sverdrup Basin (Tertiary–Triassic) by Foscolos & Powell (1980). Similar trends were noted for the Northern North Sea by Pearson *et al.* (1982). Boles (1981) made detailed comparisons of interbedded shale and sandstones (Eocene, Gulf Coast) at different burial depths.

The best estimates of changes in clay mineral composition come from Hower *et al.* (1976) and Foscolos & Powell (1980). Both separated very fine clay fractions (less than 0.1 μm and less than 0.2 μm respectively), which proved to be almost monomineralic on X-ray examination. Figure 2 documents data for shallowest and deepest samples from both studies, recalculated as '22 oxygen' mineral formulae. Figure 3 is a plot of iron content against depth for all samples. Both sequences perfectly parallel the beidellite–i/s–illite–phengite trend of figure 1, with gains in Al and K at the expense of lost Si. In these cases, however, loss of $Fe^{III}$ from octahedral layer sites is also systematic (see figure 3) and of the same magnitude. Neither of these two workers measured $Fe^{II}$ and $Fe^{III}$ separately but Pearson *et al.* (1982) documented a marked drop in the $Fe^{III}:Fe^{II}$ ratio over the same mineralogical transformations, although in somewhat coarser material.

On the basis of this analysis, the most important transformation affecting mudrocks during burial diagenesis would appear to be

$$\text{smectite} + Al + K \rightarrow \text{illite} + Si + Fe. \tag{1}$$

Magnesium may also be excluded, as at higher temperatures, but the evidence is not without ambiguity.

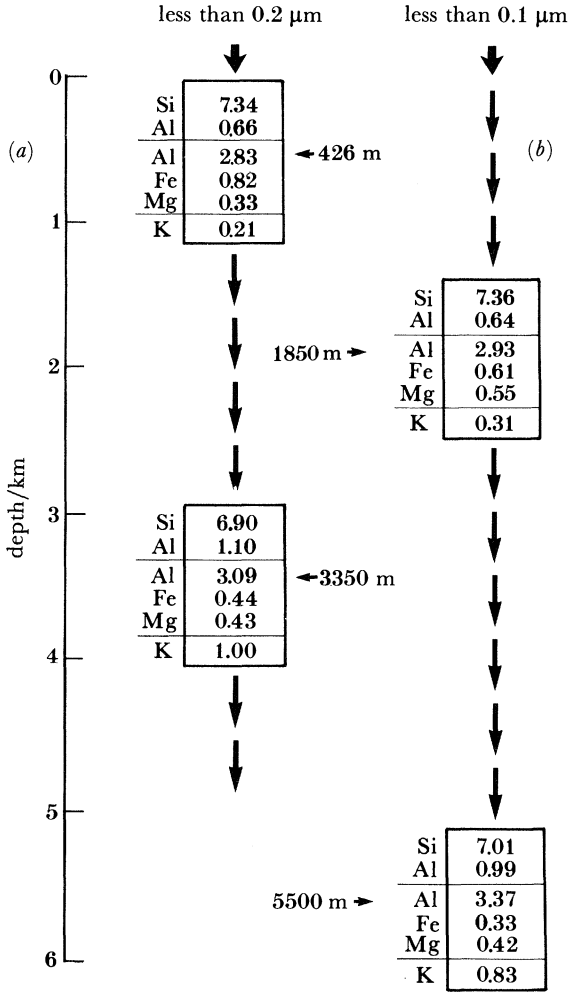

Figure 2. Progressive modification of fine sediment fractions (dominantly i/s clays) from (*a*) the Sverdrup Basin (Foscolos & Powell 1980) and (*b*) the Gulf Coast, U.S.A. (Hower *et al.* 1976).

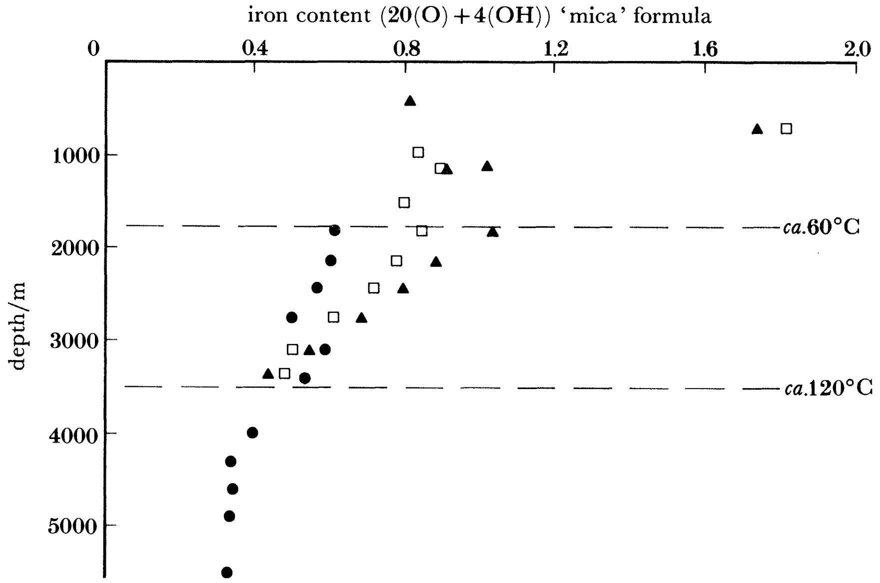

Figure 3. Elimination of iron from fine clay fractions in the Sverdrup Basin and Gulf Coast sequences; □, less than 0.2 μm fraction (Foscolos & Powell 1980); ▲, 0.2–2 μm fraction (Foscolos & Powell 1980); ●, less than 0.1 μm fraction (Hower *et al.* 1976). All data as mica formulae (22-oxygen basis).

At higher temperatures the same trend is continued. Recrystallization eventually produces phengitic mica, by which time virtually all octahedral magnesium is lost to trioctahedral chlorites of the quartz–albite–phengite–chlorite greenschist assemblage.

The research referred to above describes sediments draining largely temperate terrain. Source areas in humid sub-tropical or tropical climates would yield clay sediments relatively richer in kaolinite and soil sesquioxides (lateritic soils).

## Mineral dissolution–decomposition during mudrock diagenesis

Careful mineralogical analysis of a range of size separates enabled Hower *et al.* (1976) to demonstrate that the smectite–i/s–illite transition (maximum change between 2400 and 3700 m, approximately 65–95 °C) was accompanied by dissolution of calcite and potassium feldspar (virtually complete elimination). Chlorite increased in quantity over the same interval, suggesting authigenesis. Kaolinite decreased in the finest fractions but not in the coarser fractions. This implies dissolution or recrystallization. The quartz content appeared to increase slightly but it is difficult to attribute this to authigenesis because minor variations in original sediment composition cannot be ruled out.

These trends were confirmed by Boles & Franks (1979) in Eocene shales (and sandstones) in SW Texas. They were able to confirm a distinct decrease in kaolinite between 2700 and 4650 m (140–180 °C). An increase in chlorite was documented over the same interval, which led these authors to postulate a direct link between the two (involving $Mg^{2+}$ and $Fe^{2+}$ released in the smectite–illite transformation).

These studies demonstrate clearly that potassium feldspar and calcite (other carbonates too?) are destabilized within mudrocks at intermediate depths and temperatures (60–120 °C?). At somewhat higher temperatures kaolinite is definitely rendered unstable, perhaps also within the lower range.

Foscolos & Powell (1980) also noted a decrease in kaolinite from fine fractions with a parallel increase in chlorite (Sverdrup Basin). Their crucial contribution, however, was to demonstrate the presence and progressive elimination with depth of X-ray amorphous $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ from clay fractions. The bulk is lost at shallow depths (less than 1500 m present burial) before major smectite–illite transformation.

The sequence of destabilization (reactant contribution) listed above must therefore be prefaced by amorphous $SiO_2$ and $Al_2O_3$ as well as $Fe_2O_3$. Clearly these sediment constituents could play a very important part in early clay mineral reactions.

## Authigenic clay minerals: berthierine and chamosite

Berthierine (formerly referred to as chamosite) is the 0.7 nm phyllosilicate often found in iron-rich sediments. It is extremely fine-grained and commonly associated with iron oxides, making analysis difficult. Recent microprobe data by Iijima & Matsumoto (1982) and Curtis *et al.* (1984) confirm that it is aluminium-rich. In the former study, devoted to an investigation of berthierine formation, it was concluded that it was the mineral formed by reaction between siderite and kaolinite. This can be expressed thus:

$$9FeCO_3 + 3Al_2Si_2O_5(OH)_4 + 4H_2O \rightarrow Fe_9Al_3|Al_3Si_5O_{20}|(OH)_{16} + SiO_2 + 9CO_2. \qquad (2)$$

Replacement of kaolinite would thus acidify pore waters by raising $p_{CO_2}$. Iijima & Matsumoto (1982) suggested that this reaction occurred within the 65–150 °C temperature range; the same as that for smectite–illite transformation. At higher temperatures berthierine is replaced by 1.4 nm chlorite of similar composition, now referred to as chamosite.

## Authigenic precipitates

### (*a*) *Clays*

In sandstones, authigenic minerals precipitated from solution can usually be identified rather easily on the basis of crystal morphology. Numerous s.e.m. studies have shown that both kaolinite and illite form in this way as well as being derived from detrital material. Kaolinite often occurs as clusters of blocky crystals. Illite is fibrous to lath-like in appearance. Within burial sequences it tends to follow kaolinite and may replace it.

Iron-rich 1.4 nm chlorites (chamosites) commonly occur as well crystallized (polytype Ib) coatings (Hayes 1970). Microprobe and t.e.m. analyses (Boles & Franks 1979; McDowell & Elders 1981; Curtis *et al.* 1984) show them to be essentially trioctahedral, although the octahedral total often falls short of the theoretical 12 per formula unit (usually 11–11.5). Wet chemical analyses confirm that 1.4 as well as 0.7 nm authigenic clays are dominantly $Fe^{II}$.

More direct evidence of chlorite growing at the expense of kaolinite was obtained by Hutcheon *et al.* (1980). Kaolinite and dolomite are replaced by chlorite and calcite at temperatures estimated to be in the 180–250 °C range, i.e.

$$5CaMg(CO_3)_2+Al_2Si_2O_5(OH)_4+SiO_2+2H_2O \rightarrow Mg_5Al_2Si_3O_{10}(OH)_8+5CaCO_3+5CO_2. \tag{3}$$

This is not very different from the lower temperature reaction involving siderite to produce berthierine.

In sediments with significant volcaniclastic components, spontaneous hydration probably creates high (supersaturated) concentrations of Si, Al, Mg and $Fe^{II}$, which precipitate as trioctahedral smectites and intermediate smectite–chlorites (corrensite and swelling chlorites). It is possible that this is an evolutionary trend in which interlayer $Na^+$ and $Ca^{2+}$ ions are replaced by trioctahedral $Mg^{2+}$ and $Fe^{2+}$ hydroxide sheets (Curtis *et al.* 1984). At burial depths corresponding to temperatures of 150 °C or more, it seems likely that conversion is complete to true chlorite and some workers suggest that this is the most common pathway for extensive chlorite coating development. Certainly evidence can be found of remnant volcaniclastic grains.

### (*b*) *Other silicate reactions*

Systematic studies of sandstone diagenesis have shown clearly that both feldspar (albite) and quartz overgrowths on detrital framework grains are commonplace.

In addition to albite overgrowths, more calcic plagioclases are replaced progressively by nearly pure albite at temperatures above about 100 °C.

Boles (1981) calculated that as much as 16% by volume of the total quartz present had precipitated from solution. He noted a correlation between the quartz overgrowth content and the conversion of smectite to illite (i.e. at temperatures above about 70 °C) and, following others, attributed the overgrowths to silica liberated in that conversion (1).

This very brief survey suggests that in clastic sediments over an approximate temperature range of 60–150 °C, albite and quartz are stable together with (depending on bulk composition) kaolinite, illite (i/s at the lower end) or berthierine (iron-rich sediments). The 'chlorite' commonly recorded in fine-grained sediments on the basis of 1.4 nm X-ray reflections could either be detrital greenschist chlorite (polytype II b) or 'hydroxy–interlayer' vermiculite from soil systems. Strictly speaking, both are probably metastable.

At temperatures in excess of about 150 °C, it would appear that both kaolinite and berthierine are replaced by 1.4 nm trioctahedral chlorite (polytype I b, $\beta = 90$) (Hayes 1971). Dioctahedral clays become progressively phengitic as the assemblage evolves towards a typical quartz–chlorite–albite–muscovite assemblage.

### (*c*) *Non-silicates*

Mudrocks, shales and sandstones commonly contain pyrite $FeS_2$ and a wide range of carbonate cements: calcite, dolomite, ankerite and siderite. Many of these are very early (less than 1 km burial, and below 40 °C) and result in part from microbial processes. These early reactions have been extensively described in the literature and are referred to elsewhere in this volume.

At somewhat higher temperatures (*ca.* 60 °C), the smectite–illite conversion of (1) releases silica and calcium, which produce silica overgrowths and calcite cements in sandstones. In turn, this calcite is destabilized and replaced by ankerite at substantially higher temperatures still (approximately 120 °C according to Boles & Franks 1979; but possibly as low as 80 °C according to Muffler & White 1969):

$$4CaCO_3 + Fe^{2+} + Mg^{2+} \rightarrow 2CaMg_{0.5}Fe_{0.5}(CO_3)_2 + 2Ca^{2+}. \qquad (4)$$

It was also noted that these authigenic calcite and ankerite cements were more common in sandstones than adjacent shales, indicating, perhaps, both derivation from them and relatively more acidic environments at source.

## AN IMPORTANT DISTINCTION BETWEEN DETRITAL AND AUTHIGENIC CLAY MINERALS

Micaceous clays forming in surface environments (soils, sea-floor) are smectitic to illitic and have compositions ranging between beidellite, nontronite, illite and glauconite. All are dioctahedral with the more covalently bonded octahedral sheet consisting predominantly of Al or $Fe^{III}$. 'Hydroxy–interlayer' soil clays have incomplete Al–$Fe^{III}$ hydroxide sheets replacing cations in interlayer space. All are usually accompanied by amorphous hydrated oxides of Si, Al and $Fe^{III}$.

In sharp contrast, authigenic clays either contain little iron (kaolinite, illite) or are trioctahedral and rich in $Fe^{II}$ (berthierine, 1.4 nm chlorites). Other authigenic minerals also invariably contain iron as $Fe^{II}$ (pyrite, ferroan carbonates). The diagenetic process is thus characterized by the elimination of $Fe^{III}$ from detrital, dioctahedral clays and incorporation of $Fe^{II}$ in trioctahedral clays or non-silicates. The same pattern is seen in alteration of ocean-floor basalts (Kurnosov *et al.* 1982).

### IRON REDUCTION

One essential intermediate step must take place during redistribution of iron; the reduction from $Fe^{III}$ to $Fe^{II}$,

$$Fe_2O_3 \rightarrow 2FeO + |O|. \tag{5}$$

No oxide of iron(II) is stable in water, however, so spontaneous hydrolysis occurs with a marked increase in alkalinity and solution iron activity.

$$FeO + H_2O \rightarrow Fe^{2+} + 2OH^-.$$

At first sight, only one reducing agent is available in sediment systems. This is organic matter but virtually nothing is known about the reduction mechanism. Numerous possibilities exist, of which three might be:

(*a*) complete oxidation of 'carbohydrate' to $CO_2$,

$$2Fe_2O_3 + CH_2O + 4H_2O \rightarrow 4Fe^{2+} + 8OH^- + H_2CO_3; \tag{6}$$

(*b*) complete oxidation of 'methane' to $CO_2$,

$$4Fe_2O_3 + CH_4 + 7H_2O \rightarrow 8Fe^{2+} + 16OH^- + H_2CO_3; \tag{7}$$

(*c*) less than complete oxidation of methane,

$$4Fe_2O_3 + 2CH_4 + 6H_2O \rightarrow 8Fe^{2+} + 16OH^- + CH_3COOH. \tag{8}$$

In all cases, however, the reaction must cause a dramatic rise in pH and injection of relatively soluble $Fe^{2+}$ to the pore-water system. The possibility of generating organic acids is real and this would assist the mobilization of iron. On the other hand, the net result would be to increase pH. An increase from acid to neutral values favours precipitation of aluminosilicates and carbonates (Curtis 1983) but in more alkaline systems favours carbonates relative to both aluminosilicates and quartz. This is simply a result of the amphoteric nature of aluminosilicates, all of which have solubility minima in the pH6 region.

At very shallow burial depths and again at very deep burial, hydrogen sulphide is generated within sediments. The former case is the result of bacterial sulphate reduction and the latter from high-temperature (*ca.* 200 °C?) cracking. M. L. Coleman (personal communication, 1983) has pointed out that another reduction mechanism is offered that might have particular significance here. Pyrite, $FeS_2$, is particularly insoluble. Sulphur is present as the $S_2^{2-}$ polysulphide species. Reaction of $Fe^{III}$ with hydrogen sulphide would also generate 'excess' $Fe^{II}$ and increase alkalinity, although excess sulphide would presumably precipitate iron monosulphide:

$$Fe_2O_3 + 2H_2S \rightarrow FeS_2 + H_2O + Fe^{2+} + 2OH^-. \tag{9}$$

Similar reactions could be written for hydroxy–interlayer $Fe^{III}$ and dioctahedral $Fe^{III}$. In each case, alkalinity and $Fe^{2+}$ activity would rise, with conditions favouring ferroan carbonate or trioctahedral clay mineral precipitation. Drever (1971) and Foscolos & Powell (1980) have clearly demonstrated the progressive elimination of 'chemically leachable' and illitic $Fe^{III}$ in sediment sequences. It thus seems that iron reduction could be a key step in many of the reactions which characterize burial diagenesis. What we urgently need to know is something more about the reduction mechanisms and the reducing agents. It should then be possible to make better predictions of the time and scale of authigenic ferroan cements, both aluminosilicate and carbonate.

## CLOSED SYSTEMS OR OPEN SYSTEMS?

The relatively small amount of organic matter needed to reduce $Fe^{III}$ and change alkalinity suggests some alternatives to the 'chloritization' reactions where kaolinite and carbonate minerals react and liberate $CO_2$ as one product (see, for example, equations (2) and (3)). The assemblage kaolinite plus hematite plus organic matter is typical of lateritic soils and sediments derived from them. This assemblage, according to observations described above, would be unstable relative to berthierine at temperatures of *ca.* 50 °C and 1.4 nm chamosite at temperatures above about 120 °C, i.e.

$$Al_4Si_4O_{10}(OH)_8 + 4H_2O + 2SiO_2 + 5Fe_2O_3 + 2.5C \rightarrow 2Fe_5Al_2Si_3O_{10}(OH)_8 + 2.5CO_2. \quad (10)$$

A slight excess of iron reduction would compensate for the acidity entirely and precipitate siderite, $FeCO_3$. The Si (also Al) could be available in reactive form as soil sesquioxides. It is extremely tempting to look upon this type of reaction as being responsible for fine-grained 'chamositic' iron-ores. Siderite and iron oxides are often components of the assemblage and low organic carbon levels would not be unexpected after reaction.

The question of iron and, particularly, aluminium mobility is a vexed one. Many observations are consistent with migration of solutes from mudrocks into (through) sandstones. Other evidence (Tissot *et al.* 1974; Laplante 1974) suggests significant generation of $CO_2$ during the earliest stages (50 °C upwards) of kerogen maturation. Carothers & Kharaka (1978) have argued that short-chain aliphatic acids may be generated in the same way; to be degraded subsequently to methane and bicarbonate. It is conceivable that, over certain temperature intervals and in particular sediment compositions, pore-water acidification more than compensates for increased alkalinity by mineral hydration and dissolution reactions. Acid solutions certainly could then transport metals in solution which would then precipitate once removed from the site of acid generation. This would be in accordance with certain sandstone diagenetic patterns.

Once again, the main uncertainty lies with the behaviour of organic matter. And the answers must come from studies (experimental and field-based) of organic matter maturation by organic geochemists. The most important pyrolysis products as far as the mineralogist is concerned are relatively low molecular mass polar compounds. The properties of interest are effectiveness as reducing agents for $Fe^{III}$ and strength and complexing ability as acids. More information along these lines would not enable better predictions of hydrocarbon yield from source rocks but it certainly might on hydrocarbon yield from reservoirs.

## SUMMARY

This review of clay mineral transformation, precipitation and replacement reactions during burial diagenesis has attempted to gather together evidence that identifies iron as a particularly significant element. Detrital clays are dioctahedral and contain $Fe^{III}$. Authigenic clays are trioctahedral and contain $Fe^{II}$. Diagenesis amounts to elimination of $Fe^{III}$ from the former and precipitation of $Fe^{II}$ in the latter and in ferroan carbonate cements.

Reduction of $Fe^{III}$ to $Fe^{II}$ is the critical step because solubility (potential mobility) and alkalinity are markedly affected. Organic matter pyrolysis seems to offer the only possibility as a source of both reducing agents and acids to effect transport in the zone of maximum clay mineral diagenesis. Relatively little seems to be known about low molecular mass polar pyrolysis products but their systematic investigation would seem to be eminently worthwhile. One of the reasons for holding this meeting, however, was the hope and expectation that answers to some at least of these questions would emerge.

This paper is a consequence of a programme to obtain 'more reliable' clay mineral analyses by analytical transmission electron microscopy of single crystals. Many people in Sheffield have been involved; J. A. Whiteman, B. J. Ireland, R. Mulvaney, C. R. Hughes, C. K. Whittle, M. Vesey and S. Curtis. The programme was funded by the Science and Engineering Research Council, the Natural Environment Research Council and the Amoco Production Company, Tulsa Research Center.

M. L. Coleman and D. A. Spears contributed in a more general geochemical way and the manuscript was prepared by S. Forster.

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## *Discussion*

D. G. Murchison (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). Some of the sandstones Professor Curtis discussed had a porosity of 20 % at depths of as much as 5 km. How is this high porosity maintained?

C. D. Curtis. This is a well known anomaly and appears to be caused by a chlorite layer that coats the quartz grains completely, stopping them from producing quartz overgrowths.

R. A. Berner (*Department of Geology and Geophysics, Yale University, U.S.A.*). Hower *et al.* (1976) have argued that the addition of interlayers of illite to smectite generates hydrogen ions and that these then react with calcite. They argued that this reaction can account for the calcite loss during diagenesis. I noticed that Professor Curtis did not include the hydrogen-ion generation in his reaction scheme. Is this because he disagrees with their suggestion?

### *Reference*

Hower, J., Eslinger, E. V., Hower, M. E. & Perry, E. A. 1976 Mechanism of burial metamorphism in argillaceous sediment: 1. Mineralogical and chemical evidence. *Bull. Am. geol. Soc.* **87**, 725–737.

C. D. Curtis. There are a number of ways in which the mass and charge balances can be satisfied in these reactions and the suggestion of Hower *et al.* is one of these. I have no reason to favour their particular choice.

H. Shaw (*Department of Geology, Imperial College, London*). How did Professor Curtis determine the $Fe^{2+}/Fe^{3+}$ ratios which he presented?

C. D. Curtis. We tried to separate the clay minerals from the matrix by ‘gently’ crushing and rolling sandstones in water. In many cases we were able to isolate fairly pure chlorite, which gave good X-ray diffraction patterns. We then performed wet chemical analysis on these samples. Our t.e.m. work on the sandstones shows the presence of fine-grained hematite, the origin of which is unclear. If it is a contaminant then the ratios we determine will be too low. The ratios we determined were between 7:1 and 10:1 in the chlorites. The glauconites were harder to separate but where this was possible we found they were predominantly ferric. We then used the average ratios for each mineral in the probe analyses.

H. Shaw. Both Foscolos & Powell and Hower used bulk chemical analyses of crystals whose size was less than 0.1 μm to study the variation of the ferrous:ferric ratio during diagenesis. Does Professor Curtis suspect that their results also suffer from contamination from other phases containing iron? What is required are probe analyses of individual grains if chemical variations in clay minerals during diagenesis are to be firmly established.

C. D. Curtis. It would certainly be worthwhile to redetermine the ferrous: ferric ratios in these rocks with the use of modern techniques. Nonetheless, both groups used the same method of analysis throughout the sequence and it is therefore probable that the trends they observed were real. Foscolos & Powell also examined the leachable iron content of the rocks and found that they could remove more iron from the shallow samples than they could from the deeper ones.

M. Sarnthein (*Geolisches Palaontisches Institut*, *Universität Olshausenstrasse*, *F.R.G.*). How does Professor Curtis distinguish variations in the composition of detrital clay supply from variations produced by authigenic processes? It is straightforward to separate these sources only for minerals such as chlorite, which have a characteristic structure when they are produced by authigenic reactions.

C. D. Curtis. The principal argument in favour of an authigenic, rather than a detrital, origin for the variations observed in the deep sea is that the same variation with depth is found at a number of widely separated sites. We have tended to work on those minerals whose authigenic structure is distinctive, to avoid such problems of interpretation.

B. Durand (*Institut Français du Pétrole*, *Rueil Malmaison*, *France*). It is no longer fashionable to argue that oil migration is driven by the dehydration of smectite, because oil is not soluble in water. Therefore the generation of free water produces an obstacle to oil migration, because it decreases the relative permeability to oil. But maybe this idea will become fashionable again!

G. Eglinton (*Organic Geochemistry Unit*, *School of Chemistry*, *University of Bristol*). The equations Professor Curtis has presented which involve methane are presumably meant to describe the general nature of the reaction, rather than a specific interaction. The redox reactions with which you are concerned probably involve kerogen and its degradation products rather than methane.

C. D. Curtis. I showed these equations to demonstrate that the minerals require that some form of reduction has occurred. I have no information concerning the nature of the organic matter involved.

A. S. Mackenzie (*BP Geochemistry Branch*, *Sunbury-on-Thames*). Have the volume increases associated with clay diagenesis been calculated? These are important for deciding if the dewatering of clay is an important mechanism for producing overpressured zones, and for promoting the expulsion of petroleum from shale source rocks.

C. D. Curtis. It is not straightforward to measure the volume changes involved. Some berthierine-rich ironstones contain chlorite that has probably been produced by reaction of iron oxide with organic matter in the presence of kaolinite and not by the reaction of iron carbonate with kaolinite. This reaction should be associated with a considerable volume increase of 10–15%.

R. C. Surdam (*Department of Geology, University of Wyoming, U.S.A.*). The Cretaceous shales in the Big Horn Basin show the same transition in one horizon between depths of 700 m and 4 km as described by Hower *et al.* (1976). In this case the changes are not produced by crossing lithological boundaries.

In the Gulf Coast Eslinger (1979) has used Mössbauer spectroscopy to suggest that the $Fe^{2+}$ : $Fe^{3+}$ ratio in the clay increases with depth. This behaviour could be associated with catalytic effects, because Almon (1974) has suggested that the catalytic effect of clays may be produced by accepting electrons. The change in the ferrous:ferric ratio is probably also associated with the creation of ordered structures in the clay minerals.

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