

# The influence of individual clay minerals on formation damage of reservoir sandstones: a critical review with some new insights

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**ABSTRACT:** The influence of individual clay minerals on formation damage of reservoir sandstones is reviewed, mainly through the mechanism of fine particle dispersion and migration leading to the accumulation and blockage of pore throats and significant reduction of permeability. The minerals discussed belong to the smectite, kaolinite, illite and chlorite groups respectively. These minerals usually occur in an aggregate form in reservoir sandstones and the physicochemical properties of these aggregates are reviewed in order to reach a better understanding of the factors that lead to their dispersion in aqueous pore fluids. Particularly significant properties include the surface charge on both basal and edge faces of the clay minerals and how this varies with pH, external surface area of both swelling and non-swelling clays, porosity and pore size distribution in the micro- and meso-pore size range and overall aggregate morphology. For non-swelling clays, and perhaps even for swelling clays, dispersion is thought to be initiated at the micro- or meso-pore level, where the interaction between the pore solution and the charged clay surfaces exposed on adjacent sides of slit- or wedge-shaped pores brings about expansion of the diffuse double electric layer (DDL) and an increase in hydration pressure. Such expansion occurs only in dilute electrolyte solutions in contrast to the effect of concentrated solutions which would shrink the thickness of the DDL and so inhibit dispersion. Stable dispersions are formed, particularly where the solution pH exceeds the isoelectric pH of the mineral, which is often at alkali pH values, so that both basal face and edge surfaces are negatively charged and the particles repel each other. The osmotic swelling of smectitic clays to a gel-like form, so effectively blocking pores *in situ*, is often invoked as an explanation of formation damage in reservoir sandstones. Such swelling certainly occurs in dilute aqueous solutions under earth surface conditions but it is uncertain that stable smectitic gels could form at the temperatures and pressures associated with deeply buried reservoir sandstones.

**KEYWORDS:** formation damage, reservoir sandstones, kaolinite, smectite, illite, chlorite, mixed-layer minerals, glauconite.

Formation damage may be defined as “a decline in the initial permeability of the reservoir rock following various wellbore operations, which may

be irreversible and which may have a serious economic impact upon the productivity of the reservoir”. An alternative definition is “a reduction in the initial permeability of the reservoir rock around the well bore following various operations such as drilling, completion, injection, attempted stimulation or production of the well”. These definitions relate to formation damage as a

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dynamic and progressive process and not to damage described as “incipient” where the poro-perm properties of a reservoir rock are adversely affected by the nature and distribution of authigenic clay minerals found in the original rock.

Formation damage is a problem of increasing significance as the cost of oil extraction rises, it being more important than ever to maximize productivity both in conventional well productivity and during enhanced oil recovery operations. Krueger (1986) gave a broad and comprehensive overview of the many factors that cause formation damage, as well as the operational procedures that may be used to control or mitigate these deleterious effects. He observed that, although there may be any number of reasons for the decline of well productivity, in most instances the transport of fine particles, usually clay minerals, and the chemical reactions of these particles with formation fluids are most often involved. It is of course well known that the physicochemical properties of the clay minerals are extremely variable, particularly with regard to basic attributes like particle size, morphology, swelling characteristics, hydration, cation exchange, dispersion, aggregation properties, etc., and there is also much diversity in the ways in which these fine particles interact with fluids, either native to the formation or introduced during exploration and production operations.

An early and prescient paper on formation damage caused by clay minerals in sandstones is that of Gray & Rex (1966). This paper, which predated the development of scanning electron microscopy, showed that in non-smectitic sandstones, loss of permeability was associated with the migrating and pore-plugging characteristics of euhedral illite and kaolinite particles following water movement within the formation. Similar observations have been made in reservoir sandstones many times since, but at the time it was widely believed that the main mechanism for formation damage was to be found in the swelling of smectitic clays. A particularly interesting observation was that analysis of the effluent from the cores of the sandstones examined showed that illite was more abundant than kaolinite, whereas in the untreated sandstones kaolinite was described as an abundant component and illite as a minor one. A possible implication of this finding was that the illitic clays were more mobile than kaolinite and preferentially migrated within the rock in response to water movement.

## MECHANISMS INVOLVED IN FORMATION DAMAGE

Various processes involving clay minerals are thought to be responsible for formation damage in sandstones. In brief, these include (a) swelling of smectitic clays, (b) dispersion and migration of a variety of clay minerals, including smectites but principally involving kaolinite and illite, and (c) transformation of clay minerals to other mineral phases. Each of these processes will be reviewed in turn with emphasis on the basic mechanisms involved.

### *Swelling of smectitic clays*

The well known ability of smectitic clays to adsorb water between their constituent silicate layers and to swell to many times their original volume suggests that it is highly likely that similar responses must occur in smectitic sandstones under appropriate chemical conditions. Smectite swelling can be directly related to the negative layer charge on the 2:1 layer which varies between 0.2 to 0.6 charges per  $O_{10}(OH)_2$  of the formula unit and which is compensated for by various interlayer cations. In the natural environment, these interlayer cations are normally hydrated and freely exchangeable with cations in external solutions, so that the distance between the silicate sheets is variable depending on the nature of the interlayer cation and on its hydration status. The seminal paper of Norrish (1954) showed that montmorillonite exhibited two types of swelling, depending on the nature of the exchangeable cation and on the salt concentration of the external solution. The first type, sometimes referred to as “crystalline swelling”, may be illustrated where the interlayer space of montmorillonite is occupied by divalent cations such as  $Ca^{2+}$  or  $Mg^{2+}$ . In these circumstances, the smectite maintains a basal spacing of  $\sim 15 \text{ \AA}$  through a wide range of relative humidities, indicative of a two-layer water structure in the interlayer space, but swells to a limit of 19–20  $\text{ \AA}$  when immersed in water (MacEwan & Wilson, 1980). The second type of swelling is usually described as “osmotic” and is best illustrated where the interlayer space of montmorillonite is occupied by a monovalent cation such as  $Na^+$  or  $Li^+$ . Norrish (1954) showed that at low salt concentrations of an external solution the individual silicate layers of a Na-montmorillonite will

delaminate and will be separated by distances of tens or even by hundreds of Ångströms. This phenomenon finds a general explanation on the basis of the electrical double-layer theory, where the diffuse double layers exert a repulsive force which is far greater than the attractive van der Waals forces between the unit layers. Osmotic swelling may lead to the formation of a gel which it is thought could lead to severe formation damage through the reduction of permeability, either directly through *in situ* swelling within pores or indirectly through the breakdown of the gel thus leading to the release and migration of fine particles (Zhou *et al.*, 1996). The formation of a gel through the osmotic swelling of a highly smectitic (80–90%) mixed-layer illite-smectite clay in response to immersion in fresh water of a reservoir sandstone was directly observed by Baker *et al.* (1993) using an Environmental Scanning Electron Microscope (ESEM). However, whether such gel formation could take place under the elevated temperature and pressure conditions characteristic of hydrocarbon basins is at present unknown.

Mohan & Fogler (1997) presented evidence to show that the change from the crystalline to osmotic swelling regimes of smectitic clays at certain critical salt concentrations was implicated in the release and migration of fines, so causing formation damage through the constriction of pore throats. The initiation of osmotic swelling, involving expansion of the basal spacing from ~20 Å to ~40 Å, was considered to occur relatively suddenly and was referred to as a “microquake”. This was thought to bring about either the breakdown of a gel structure, or at least prevention of its formation, leading to the release of the fine smectite particles involved in the incipient gel formation. A mathematical model was developed by Mohan & Fogler (1997) that was consistent with the experimental observations of Norrish (1954), showing that the transition from crystalline to osmotic swelling occurred at salt concentrations of 0.25 M NaCl and below.

#### *Dispersion and migration of clay minerals*

Amongst the most obvious of the factors affecting the dispersion and migration of clays are the ways in which they occur in sandstones, particularly their spatial arrangement in relation to the fabric and structural features of the rock, their

micro-aggregate structure, morphology, surface area, porosity and particle size distribution. These factors are all highly variable and will be reviewed on an individual clay mineral basis later. It may be noted, however, that generally the clay minerals of most interest with regard to fines migration have formed during diagenesis. Detrital clays could also be involved in dispersion and migration, although they are unlikely to be significant in clean, well sorted sandstones typical of many reservoir rocks. Such clays occur largely in shales and if shaly intercalations occur in reservoir sandstones then they could be significant in forming intra-formational permeability barriers.

Dispersion of clay minerals will also relate to their structure, composition and particularly the nature of the exposed outer surfaces, because it is these surfaces which interact with the formation fluids. For example, in comparing the nature of the outer surfaces of the non-swelling minerals kaolinite and illite it is evident that marked differences may be anticipated. Thus, the asymmetric 1:1 layer structure of kaolinite indicates that exposed basal surfaces of the mineral will consist of both silica tetrahedra and alumina octahedra, whilst the chemical composition of the clay mineral shows it to have a minor permanent negative charge with no fixed interlayer cations and a small cation exchange capacity (CEC). In contrast, the symmetric 2:1 layer structure of illite indicates that its exposed basal surfaces will consist only of silica tetrahedra, whilst its chemical composition shows it to have a high permanent negative charge which is compensated for by fixed interlayer cations, as well as a CEC distinctly higher than that of kaolinite.

In analysing, the interactions between the clay mineral surfaces of non-swelling minerals and formation fluids, the use of the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory seems to be particularly appropriate, as illustrated by Tchistiakov (2000). This theory quantifies the attractive and repulsive forces between charged particles and postulates that around such particles there exists a diffuse double layer (DDL) of cations and anions. The DDL consists of a compact layer of cations (the so-called Stern layer) closely adsorbed to the negatively charged outer surface of the mineral particle, followed by a broader more diffuse layer where the concentration and distribution of ions differs but gradually becomes the same as that of the bulk solution with increasing distance from

the charged surface. Tchistiakov (2000) analysed the stability of clays in sandstone formations in terms of zeta ( $\zeta$ ) potential, which is equivalent to the electrokinetic potential at the particle/fluid shear plane when there is motion between the particle and fluid. This shear plane is thought to exist close to, but not at, the boundary between the Stern and diffuse layers. The potential of the clay mineral surface, which will clearly be different when comparing kaolinite and illite for example, will control the  $\zeta$  potential and thickness of the DDL, which will also be influenced by the predominant exchangeable cations, the salt concentration and composition of the pore fluids, as well as their dielectric constants and pH. According to Tchistiakov (2000), the electrokinetic potential is one of the main factors which determine the dispersibility and migration of clay minerals in sandstone reservoirs. Other factors that need to be considered here include the temperature/pressure conditions in the reservoir as well as the hydrodynamic force resulting from the flow rate of the pore solutions.

#### *Transformation of clay minerals to other phases*

This mechanism has been implicated in some reports of formation damage. For example, Hayatdavoudi & Ghalambor (1996, 1998) investigated a highly kaolinitic sandstone from Tuscaloosa, Louisiana, that had been subjected to sodium hydroxide treatment at pH 10–12. This treatment brought about a considerable decrease in permeability which was attributed to the *in situ* conversion of kaolinite booklets to dickite and halloysite, resulting in the disintegration, fragmentation and volume increase of the kaolin mineral within the same pore space. Fines migration was ruled out as a cause of formation damage in this instance. Where formations have been subjected to more elevated temperatures for longer periods of time, as for example during steam injection, then there is a possibility that damage may occur following fines migration, dissolution, and precipitation of new phases. Bauer *et al.* (1998) showed that treatment of kaolinite with highly alkaline KOH solutions (pH >11) at 35°C and 80°C could produce illite after only 75 and 15 days respectively. Such a transformation could be envisaged under the conditions described by Hayatdavoudi & Ghalambor (1996, 1998), although the use of

NaOH solutions would likely bring about formation of a Na-rich illite, namely brammallite. However, such highly alkaline pH values as those mentioned above are unlikely to exist during well production.

## PHYSICOCHEMICAL PROPERTIES AND ROLE OF INDIVIDUAL CLAY MINERALS

### *Smectitic clays*

Montmorillonite in sandstones usually occurs in lamellar aggregates, often showing a rough honeycomb, cellular arrangement (Fig. 1) in the dried state under the SEM, although several aggregate structures are possible. Thus, Schultz (1969) showed that some montmorillonites were made up of “mossy” type aggregates formed by association of thin, curled films into acicular or lath-like strips, whereas others yielded aggregates consisting largely of tiny globular or granular units. It may be noted, however, that the micromorphological structure of authigenic clays in sandstones as observed by SEM in dried unpreserved core samples may not correspond with the *in situ* morphology of the clays in preserved cores after critical point drying, a technique which avoids the surface tension effects of air-drying (McHardy *et al.*, 1982). This applies particularly to clays of delicate morphology which after air drying may shrink back against the core walls to give the

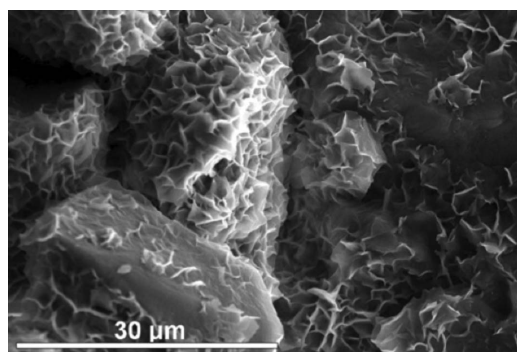


FIG. 1. Montmorillonite coating detrital grains in a Miocene arkose, Madrid Basin, Spain. (Image reproduced from the ‘Images of Clay Archive’ of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=118>]).

impression of a pore-lining habit. Such clays when observed after critical point drying may be found to be essentially pore-filling, as was observed for the authigenic illitic clays in the Magnus sandstone of the North Sea (McHardy *et al.*, 1982) and synthesized smectitic clays in reservoir sands (Nadeau, 1998).

When dispersed in an aqueous medium, smectitic aggregates yield particles of indeterminate shape with poorly defined outlines and of variable size, but usually in the 1–2  $\mu\text{m}$  range. These particles may be further dispersed into yet finer fractions, again of variable size and shape but usually  $<0.2 \mu\text{m}$  in diameter. The thickness of these particles is also variable, depending to a considerable extent on the nature of the saturating cation. Thus,  $\text{Na}^+$ -montmorillonite may disperse into its elementary 10 Å silicate units in aqueous suspensions of dilute ionic concentration, whereas in similar conditions  $\text{Ca}^{2+}$ - and  $\text{Mg}^{2+}$ -saturated montmorillonite forms tactoids consisting of 4 to 7 silicate units (Schramm & Kwak, 1982). These differences in dispersibility relate to the fact that Na-montmorillonite has the capacity to swell and form gels from such aqueous suspensions, where the individual silicate units delaminate from thicker aggregates and become separated by tens and even hundreds of Ångströms, at the same time retaining a rough parallelism between the layer units. In contrast,  $\text{Ca}^{2+}$ - and  $\text{Mg}^{2+}$ -montmorillonites show swelling to a much more limited extent, yielding a stable basal spacing of  $\sim 19 \text{ Å}$  in distilled water (MacEwan & Wilson, 1980), indicative of only three to four water layers between the silicate units, and having little or no capacity to form gels.

Swelling of montmorillonite can result in physical changes to the clay mineral. For example, Katti & Katti (2006) using a controlled cell to monitor swelling and swelling pressure of Wyoming montmorillonite found a decrease in “particle” (aggregate?) size from 3.25  $\mu\text{m}$  at 0% swelling to 0.75  $\mu\text{m}$  at 75% swelling, as well as a change from a well ordered lamellar arrangement to a randomly-oriented one. Thus, swelling was considered to have brought about particle breakdown and rearrangement.

However, the dispersion behaviour of montmorillonites may not always be the same as observed by Méring & Oberlin (1971). They compared the dispersibility in water of the previously separated fine fractions of montmorillonites from Wyoming and Camp Berteaux after they had been dried down.

It was found that the latter remained in an aggregated state even when finely pulverised before being immersed in water, whereas Wyoming montmorillonite re-dispersed quite easily. These findings were attributed to differences in particle size and mode of aggregation between the two smectites, with Wyoming montmorillonite occurring in relatively large particles (0.2 to 0.5  $\mu\text{m}$  in diameter) aggregated in a laminar face-to-face manner, whereas the Camp Berteaux montmorillonite was made up of very small particles of  $\sim 0.01 \mu\text{m}$  in diameter associated in an edge-to-edge fashion.

Such differences between individual montmorillonite samples are revealed by surface area and porosity measurements. External surface area appears to be particularly variable and, for example, Dogan *et al.* (2006) found values of 22.7  $\text{m}^2 \text{g}^{-1}$  for unfractionated Wyoming montmorillonite compared with 65.2  $\text{m}^2 \text{g}^{-1}$  for an unfractionated montmorillonite from California. Again, Aylmore *et al.* (1970) recorded a nitrogen adsorption surface area for the  $<2 \mu\text{m}$  fraction (dried and compressed into small cores) of  $\text{Na}^+$ -Wyoming montmorillonite and  $\text{Na}^+$ -Redhill montmorillonite of 39.8 and 147  $\text{m}^2 \text{g}^{-1}$  respectively. Such differences may be accounted for in terms of particle size, aggregate structure and porosity. Thus, the Redhill montmorillonite is made up of much smaller particles than Wyoming montmorillonite, has a greater pore volume and a higher proportion of mesopores of  $<100 \text{ Å}$  in diameter.

Montmorillonite disperses most easily under alkaline conditions and low salt concentrations, and tends to flocculate at acidic pH values and high salt concentrations. The point of zero charge for the edge sites of montmorillonite has been found to be at  $\sim \text{pH } 6.5$  (Tombác *et al.*, 2004) and flocculation occurs below this pH value because edge(+)/face(−) associations enable a card-house type structure to be formed in salt solutions. In dense suspensions above pH 6.5, however, montmorillonite occurred in well ordered lamellar packages. The critical coagulation concentration (CCC) for montmorillonite in chloride solutions of Ca, Na and K was in the range 0.01 to 0.05 N (Zheng, 1988).

Another factor to be taken into account with regard to the dispersion and flocculation behaviour of smectitic clays is their layer charge, both the amount and localization in the structure. Thus, Christidis *et al.* (2006) found that low-charge montmorillonitic bentonites tended not to flocculate



because they were fully swelling and formed thin quasi-crystals and viscous suspensions. With high-charge montmorillonites, however, non-swelling layers occurred, resulting in the formation of thicker quasi-crystals and suspensions of lower viscosity. The proportion of tetrahedral charge in the 2:1 silicate unit layer was thought to be an important factor in accounting for these observations. This suggestion is certainly consistent with the finding that saponite, a Mg-rich trioctahedral smectite which is predominantly tetrahedrally charged, has a lower swelling capacity than montmorillonite, particularly after  $\text{Na}^+$  saturation where it maintains a two-layer water structure (Suquet *et al.*, 1975, 1977) and indicating that it is probably less easily dispersible. Saponites may occur in detrital grains in reservoir sandstones, especially when there is a volcanogenic contribution to the sediment, or may form authigenically through reaction between quartz, dolomite and kaolinite at somewhat elevated temperatures (Nadeau, 1998). Like other 2:1 clay minerals, saponite will disperse most easily under alkaline conditions and low salt concentrations.

### Kaolinite

The kaolinite that occurs in sandstones is nearly always of the well crystallized variety, often occurring in booklets and vermicules, and as discrete aggregates rather than as pore-lining or pore-bridging clays (Fig. 2). The euhedral nature of these forms of kaolinite and their textural relation-

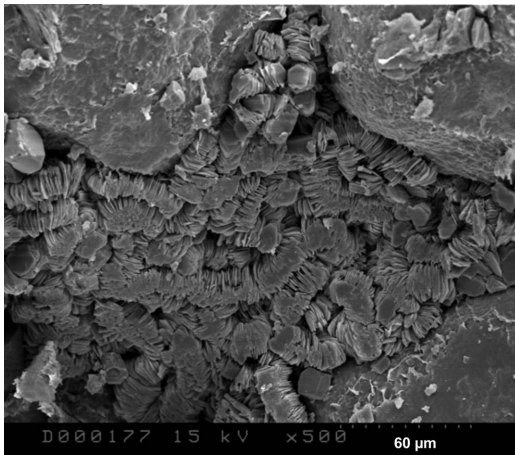


FIG. 2. SEM of vermicular diagenetic kaolinite infilling pore of reservoir sandstone.

ships with other sandstone components indicate that they are authigenic (Fig. 3). Individual kaolinite occurrences may show considerable variation in terms of morphology and particle size. Thus, particles may be distinctly elongated or have an irregular outline.

The specific surface area (SSA) and porosity of sandstone kaolinites are parameters of evident importance in terms of interactions with pore fluids. Murray & Lyons (1959) were amongst the first to suggest that there was a general relationship between decreasing crystallinity of kaolinite and its SSA, with well crystallized kaolinite ranging from 8 to 12  $\text{m}^2 \text{g}^{-1}$ , kaolinite of medium crystallinity from 12 to 15  $\text{m}^2 \text{g}^{-1}$  and poorly crystalline kaolinite from  $\sim 16$  to 26  $\text{m}^2 \text{g}^{-1}$ . The porosity of discrete sandstone kaolinite aggregates was investigated by Sardini *et al.* (2009) using a novel technique involving image analysis following impregnation of the rock with radioactive resin. Values of 42% porosity for kaolinite aggregates were found, in accordance with previous estimates of the microporosity of these aggregates by Hurst & Nadeau (1995). Jozefaciuk (2009) showed that the porosity parameters of kaolinite aggregates depend on their size, with large aggregates (0.25 to 4 mm) having dominant pore sizes of  $\sim 0.09 \mu\text{m}$  and smaller ones ( $< 0.25 \text{ mm}$ ) having pore sizes in the range 0.56 to 1.8  $\mu\text{m}$ . Diamond (1970) found that pore sizes for well crystallized Georgia kaolinite ranged from 30 to 200 nm, the larger pores being interpreted as representing the spaces between the

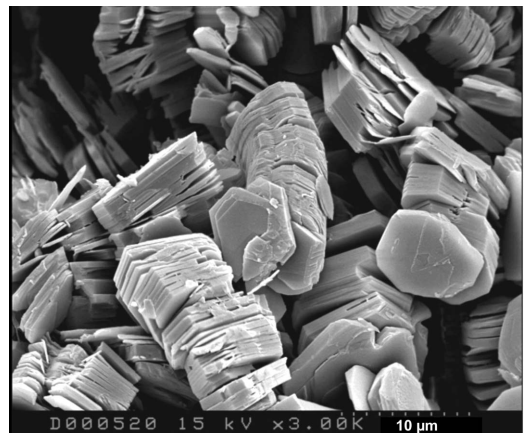


FIG. 3. SEM image of well crystallized kaolinite from sandstone. Note hexagonal morphology, smooth basal surfaces and abundance of slit- and wedge-shaped pores.

book-like aggregates in which the clay mineral occurred.

### *Dickite*

Dickite is relatively uncommon when compared to kaolinite and characteristically occurs in much larger crystals, although usually with the same euhedral, hexagonal morphology. The dickite that occurs in sandstones as a diagenetic phase is frequently described as having a characteristic blocky appearance under the SEM when compared to the vermicular and book-like kaolinite found at more shallow depths of the stratigraphic sequence (Ehrenberg *et al.*, 1993). Crystals from the type locality in Anglesey had a width up to  $\sim 8 \mu\text{m}$  and thicknesses ranging from 0.07 to 0.25  $\mu\text{m}$  (Davis *et al.*, 1950). The more coarse-grained nature of dickite is evident from Fig. 4, where many crystals exceed 10  $\mu\text{m}$  in size and may even approach 20  $\mu\text{m}$ . In view of their similarities in chemistry and structure, it may be anticipated that the dispersion behaviour of dickite is similar to that of coarse-grained kaolinite as described above.

### *Illite and mixed-layer illite/smectite (I/S)*

Illitic clay is of common occurrence in reservoir sandstones, as is I/S of a highly illitic nature. The most common authigenic morphology is in the form of laths which may be exceedingly thin. Weaver (1953) early recorded illite laths of 40 to 60  $\text{\AA}$

thickness in some Ordovician greywackes in Pennsylvania. Illite particles separated from the Permian Rotliegend sandstone of the North Sea were found to be only 90  $\text{\AA}$  thick, 0.5 to 1.0  $\mu\text{m}$  long and 0.1 to 0.2  $\mu\text{m}$  wide (Nadeau *et al.*, 1985). Under the SEM, lath-shaped illite in sandstone pores often appears as a distinctive tangled mass of fibres or hairs that may completely fill the pore space (Fig. 5). Even thinner illitic laths (20 to 40  $\text{\AA}$  thick) were found in the Magnus Sandstone of the North Sea (Fig. 6) but these yielded mixed-layer I/S diffraction patterns (McHardy *et al.*, 1982). Sandstones may also contain authigenic illite of a platy morphology and in such occurrences lath-like or fibrous forms may be seen growing from the edges of the plates (Fig. 7). These examples illustrate that illite may occur in a variety of morphological forms as well as the manner in which these forms may evolve during crystal growth.

Various studies have confirmed that thin, lath-like forms represent the earliest stages of illite formation and that further growth leads to increases in particle thickness as well as transformation to an irregular platy morphology and finally to well developed hexagonal forms (Inoue *et al.*, 1988; Inoue & Kitigawa, 1994; Środoń *et al.*, 2000). It is important to bear in mind, therefore, that the nature of illite, particularly with respect to its crystallinity, particle size and thickness, in addition to associated chemical and physical properties such as cation exchange capacity, surface area and porosity, can

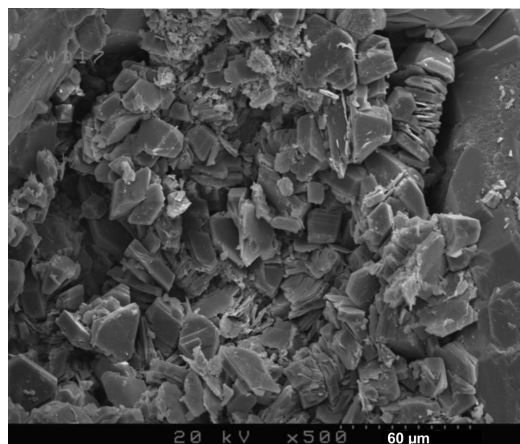


FIG. 4. SEM of a dickite in sandstone showing the coarse nature of dickite crystals, both in terms of particle size and thickness.

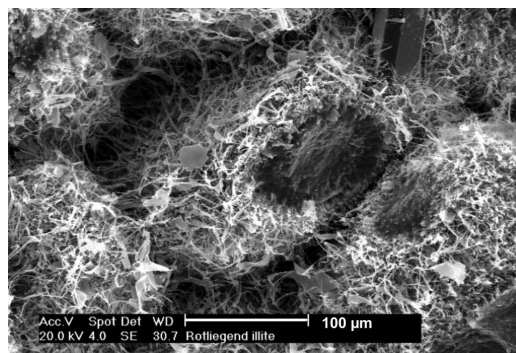


FIG. 5. SEM of fibrous illite, critical point-dried from methanol, Rotliegend Sandstone, North Sea. (Image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=91>]).

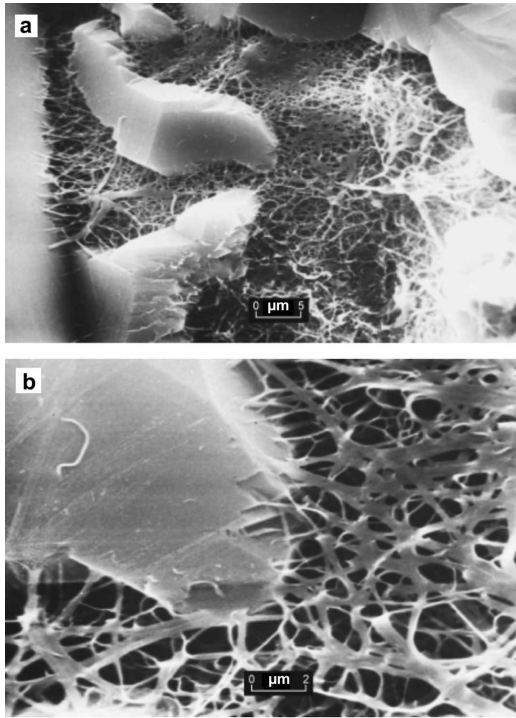


FIG. 6. SEMs showing (a) authigenic pore-filling illite from the Magnus Sandstone, North Sea which is (b) anchored in a later quartz overgrowth. Samples were prepared from preserved core after critical point drying and yielded XRD patterns characteristic of I/S (McHardy *et al.*, 1982).

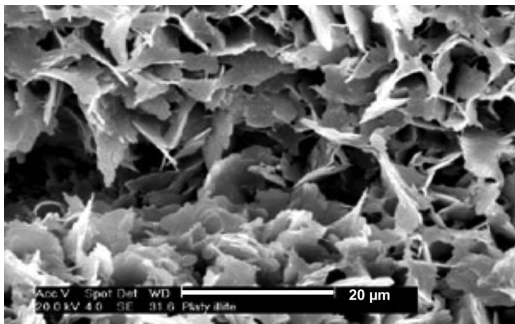


FIG. 7. Network of platy authigenic illite from sandstone with incipient lath-like or fibrous forms growing from the peripheries of the platy particles. (Image reproduced from the ‘Images of Clay Archive’ of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=93>]).

be extremely variable. Indeed, XRD traces of illitic material from sandstones are frequently characterized by a broad 10 Å basal reflection which may respond to ethylene glycol treatment by further narrowing towards the low-angle side of the diffraction peak. Decomposition of such a basal reflection, according to the procedure of Lanson (1997), strongly suggests that the diffraction maximum is the product of three separate components, which have been generally interpreted as representing a mixture of well crystallized illite, poorly-crystallized illite and mixed-layer I/S. With regard to the latter phase, computer simulations such as those of Reynolds (1980) indicate that the peak profile following ethylene glycol solvation is very often consistent with a specific type of ordering in a crystal structure where every three illite layers is followed by a smectite layer. Thus, an IIIS structure is formed which, using an ordering parameter from the German literature termed “Reichweite”, is referred to as R3.

There is at present no consensus as to the explanation of this R3 I/S ordering in terms of crystal growth mechanisms. Where R3 I/S occurs in pelitic sequences, it was initially suggested that this type of ordering developed directly by a solid state transformation in a layer-by-layer manner from an R1 I/S precursor, which had itself developed from smectite (Hower *et al.*, 1976). The apparent absence of R2 I/S was thought to be evidence consistent with this hypothesis. Since this time, however, there have been many reported occurrences of R2 I/S and other intermediate states of ordering of I/S in pelitic sediments (Wilson, 2013, and references therein) and in any case the distinctive filamentous morphology of illite and I/S in reservoir sandstones clearly indicate *de novo* crystallization rather than layer-by-layer transformation of a smectitic precursor. A rational explanation for the development of R3 I/S in reservoir sandstones was advanced by Nadeau *et al.* (1984a,b) building on the observations of McHardy *et al.* (1982) with respect to the filamentous illite in sandstones in the Magnus Field in the North Sea. In brief, it was shown that thin illite particles dried down onto a glass slide and glycolated will diffract as though they contain smectite layers, because glycol is adsorbed between the thin illite particles. In these circumstances, diffraction is an inter-particle effect and does not necessarily denote the existence of smectite layers *per se*. TEM determinations of particle thickness showed that samples of R3 I/S are



dominated by thin illites 30 to 50 Å in thickness and that the response to ethylene glycol disappeared as the illite particles increased in thickness (Nadeau *et al.*, 1985). The apparent R3 ordering is therefore interpreted as an indication of exceedingly thin illite particles with an average thickness of 30 to 50 Å, rather than being indicative of a special and rather mysterious type of ordering involving two separate phases. In the present paper we regard the broad 10 Å reflection that is often characteristic of authigenic illites in sandstones, as representing mixtures of illites of different thicknesses and particle sizes in various stages of development. So-called R3 I/S is here regarded as being representative of very thin illite in the earliest stages of development.

Many of the physical properties of authigenic illite in sandstones will reflect the stage to which illite has evolved. Nadeau (1985) suggested that there was a useful approximate relationship between total surface area (S) in  $\text{m}^2 \text{g}^{-1}$  and mean particle thickness (T) in nm, namely  $S = 800/T$ . Using this relationship, an illite consisting of five unit layers would have a total surface area of  $160 \text{ m}^2 \text{g}^{-1}$  whilst for thicker crystals consisting of, for example, fifty unit layers, the total surface area would be only  $16 \text{ m}^2 \text{g}^{-1}$ . These figures are reasonably consistent with experimental observations. For a Ca-saturated illite separated from a South Australian soil, Aylmore & Quirk (1967) determined by nitrogen adsorption external surface areas of 163 and  $227 \text{ m}^2 \text{g}^{-1}$  for the <2 µm and 0.1 µm fractions respectively, values which exceeded the surface areas for Ca-saturated Wyoming bentonite ( $38.1 \text{ m}^2 \text{g}^{-1}$ ) and Redhill montmorillonite ( $99.4 \text{ m}^2 \text{g}^{-1}$ ) calculated by the same method. The porosity of illite in sandstones must also be highly variable. Quite clearly, illite occurring in the lath-like form shown in Figs 5 and 6 would have enormous and easily accessible pore space, but the situation would be different where the predominant morphology was platy. Aylmore *et al.* (1970) compared the porosity of compacted illite with that of compacted montmorillonite and found that the illite had the greater porosity and a higher predominance of meso- and micro-pores. This porosity was thought to be largely due to slit- or wedge-shaped voids between platy particles aligned roughly parallel to one another. Although these findings refer to soil illites, it is probable that a similar picture exists in sediments during the early stages of diagenesis.

#### *Glaucanite and mixed-layer glauconite/smectite (G/S)*

Hydrocarbon reservoirs are sometimes found in glauconitic sandstones so the question arises as to whether the glauconite mineral may possibly give rise to formation damage problems. Although glauconite is a true mica-type clay mineral, yielding XRD profiles similar to illite and SEM images similar to smectite (Fig. 8), its mode of occurrence as granular, coarse sand-size, coherent rounded pellets, usually described as lobate or vermiform, as well as its ability to replace various types of rock fragments or carbonate material and to fill confined spaces in microfossils, suggests that it would not normally be susceptible to dispersion and migration. On the other hand, many glauconites appear to enter a mixed-layer structure with varying proportions of smectite and when dispersed may consist of exceedingly small and thin lath-like particles, concentrated in the <0.2 µm fraction (Vali & Köster, 1986; Buatier *et al.*, 1989). Furthermore, although glauconite appears to be able to retain its granular coherence for long periods of time, it can break down in soils to finely dispersed particles forming a green plasma (Courbe *et al.*, 1981) or may be selectively translocated down soil profiles to form a distinct clay-rich horizon (Van Ranst & De Coninck, 1983).

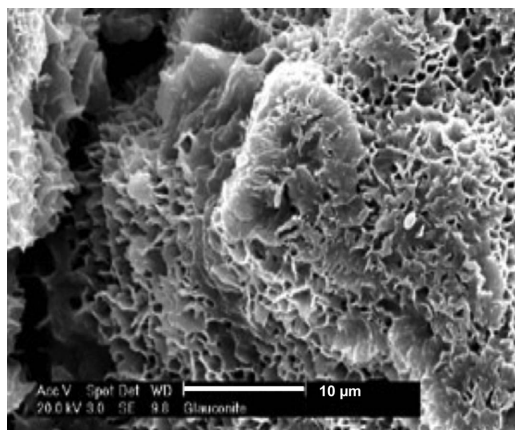


FIG. 8. Internal structure of glauconite grain from the Isle of Wight showing honeycomb “smectitic” texture. (Image reproduced from the ‘Images of Clay Archive’ of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=81>]).

The dispersion and migration of glauconite particles cannot therefore be altogether discounted as a possibility in hydrocarbon reservoirs. Problems encountered during the construction of the Westerschelde tunnel in glauconitic sands in the Netherlands are believed to have been caused by the engineering behaviour of the glauconite itself (Verhoef & Snijders, 1999). In particular, mechanical damage to the granular glauconite was thought to have released fine particles, resulting in an increase in adsorbed water and increased swelling and plasticity of the glauconitic sands. This may be a reflection of the maturity of the glauconite, the immature soft forms tending to break down and disperse whereas the mature indurated forms tend to resist such dispersion and may even be reworked.

Finally, it should be noted that, unlike illite, glauconite will readily decompose in strong mineral acids ultimately to yield an amorphous form of silica which is highly reactive (Yadav *et al.*, 2000). Possible deleterious effects resulting from the use of acidic fluids during production operations might therefore follow in glauconitic sandstones.

#### *Chlorite and mixed-layer chlorite/smectite (C/S)*

In reservoir sandstones, authigenic chlorite is often observed to be coating detrital grains of quartz, thus acting as a pore-lining clay. In this form, chlorite appears to have inhibited the formation of quartz overgrowths and has thus been responsible for the preservation of porosity even in deeply buried sandstones (Hillier, 1994; Billault *et al.*, 2003). Both iron-rich (chamosite) and Mg-rich (clinochlore) types of chlorite occur as clay coatings, and SEM studies suggest the possibility of systematic morphological differences. Fe-rich chlorite may occur in randomly arranged, euhedral, bladed crystals between 1–2  $\mu\text{m}$  in diameter and showing an abundance of edge-to-face contacts. Crystals of authigenic Mg-rich chlorites tend to be less-well developed and occur in thin subhedral plates between 1–5  $\mu\text{m}$  in diameter, with occasional euhedral hexagonal particles, and again showing an abundance of edge-to-face contacts (Figs 9 and 10). Hillier (1994) observed that Mg-rich chlorites in a variety of reservoir sandstones occurred in a cellular, honeycomb arrangement, reminiscent of that found in smectitic clays. Chlorite may also occur in reservoir sandstones as a pore-filling clay. Humphreys *et al.* (1989) showed that in this form

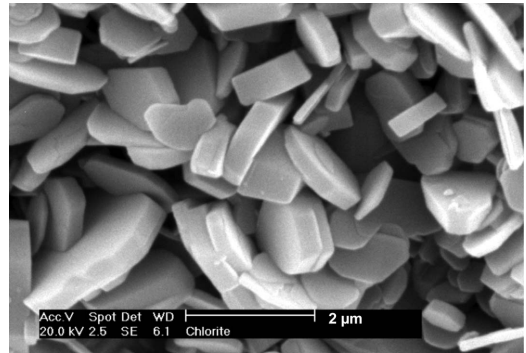


FIG. 9. Fe-rich chlorite, Spiro Sandstone, Arkoma Basin, Oklahoma, USA, showing well developed crystalline form and interlocking edge-to-face contacts. (Image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=72>]).

the chlorite consisted of randomly arranged subhedral plates in the 3 to 8  $\mu\text{m}$  size range, occasionally in rosette-shaped clusters. Edge-to-face contacts were again predominant. Tomkins (1981) showed that a regularly interstratified chlorite-smectite mineral (corrensite), with a smectite-like honeycomb morphology (Fig. 11), occurred in a Permian reservoir sandstone in

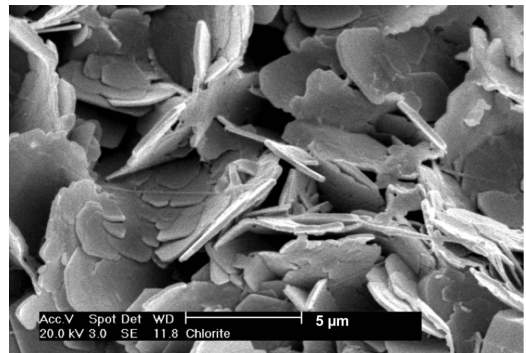


FIG. 10. Aggregate of Mg-rich chlorite, Rotliegend sandstone, Northern Germany, showing less well developed crystalline form than Fe-rich chlorite, and with an abundance of edge-to-face, face-to-face and edge-to-edge contacts, as well as a relatively open, porous structure. (Image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [<http://www.minersoc.org/photo.php?id=71>]).

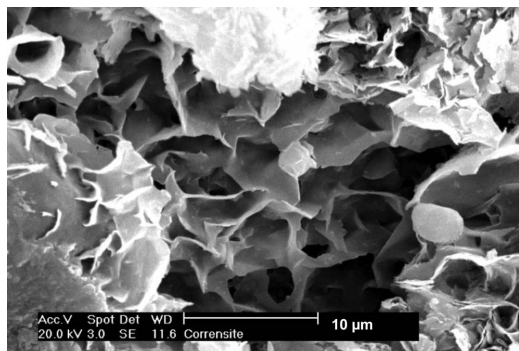


FIG. 11. Corrensite (R1 ordered mixed-layer trioctahedral chlorite-trioctahedral smectite) from the Yates Formation sandstone showing well developed cellular structure similar to that of smectite. (Image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society [http://www.minersoc.org/photo.php?id=75]).

Texas. It was suggested that this type of clay could be water-sensitive.

## DISCUSSION

### *Smectitic clays*

As previously discussed, the ability of smectitic clays to swell in aqueous fluids was long considered to be a major causative factor leading to formation damage in hydrocarbon reservoirs, the mineral involved in most instances being montmorillonite. It was envisaged that the formation of *in situ* swollen smectitic gels could be responsible for directly blocking pore throats, or alternatively there was an indirect effect where the gels dispersed and the fine particles migrated to accumulate in pore throats at a distance. It is a moot point, however, as to which of these two mechanisms is the more important.

Zhou *et al.* (1996) considered that osmotic swelling of smectite clays was of primary importance in causing formation damage and developed a novel X-ray method to determine the exact conditions in which such swelling took place. Diagrams were developed to determine the compatibility between smectitic clays and various fluids used in drilling, completion and flooding operations, insofar as they caused or inhibited osmotic swelling. In general it was confirmed that osmotic

swelling occurred in dilute salt solutions as found in the pioneer work of Norrish (1954). The critical NaCl concentration at which osmotic swelling occurs was found to be 0.5 M for montmorillonite and 0.3 M for saponite. Mohan & Fogler (1997) also studied the impact of osmotic swelling of montmorillonite on the permeability reduction of reservoir sandstones but concluded that this was due mainly to fines migration. It was envisaged that the sudden transition from crystalline to osmotic swelling at the critical salt concentration (0.25–0.5 M) caused a "microquake", thus initiating fines migration and leading to pore blockage.

The physical reality of gel formation from smectitic clays in sandstones was revealed by the Environmental SEM study of Baker *et al.* (1993) in which the same area of clay could be imaged before and after immersion in fresh water. In the dried state, the clay was made up of aggregates in the irregular cellular form typical of many montmorillonites (Fig. 1). Following fresh water treatment, however, there was a dramatic morphological transformation to an amorphous-looking gel which largely replaced the original cellular structure seen in the untreated state. It is of interest that Baker *et al.* (1993) noted that another sandstone that was even more smectitic (90% S in an I/S mixed-layer structure) showed little or no morphological or volume change after fresh water immersion for up to six weeks, retaining also its visible porosity characteristics. The swelling behaviour of smectites in sandstones can be variable, therefore, for reasons that are not yet clear.

The various factors associated with clay-induced formation damage have been reviewed by Tchistiakov (2000) with particular emphasis on DLVO theory and the role of the diffuse double electric layer (DDL) in promoting the dispersion of clay minerals from their aggregate form or their detachment from the quartz surfaces of the sandstone pores. The electrokinetic or zeta ( $\zeta$ ) potential existing between a clay surface and a surrounding fluid, when there is relative motion between them, was considered to be particularly significant with respect to clay dispersion or detachment from detrital grains. The value of the  $\zeta$  potential can be approximated by electrophoresis or electroosmosis methods, an increase in value leading to clay release. Many factors contribute to  $\zeta$  potential, the most important ones for the smectites connected with their structure and chemistry being layer charge (both amount and localization), nature

of exchangeable and adsorbed cations (valency and hydrated radius), and isoelectric pH value. The interaction between layer charge and exchangeable cation shows that smectites saturated with monovalent cations have a higher  $\zeta$  potential and are thus more dispersible than when saturated with di- or trivalent cations. The effect of an increase in the salt concentration in the external solution is to shrink the DDL and to decrease the  $\zeta$  potential. Increasing temperature tends to increase the  $\zeta$  potential and can thus enhance the release of smectites and other clays in sandstones.

Although it is evident from laboratory studies that Na-saturated smectites will swell and/or disperse most readily at alkaline pH values and low salt concentrations, it is not at all certain that such smectites will behave in exactly the same way under basin conditions. Uncertainty arises from the Monte Carlo and molecular dynamics computer simulations of Na-montmorillonite under such conditions (Odrizola & Guevara-Rodríguez, 2004; de Pablo *et al.*, 2005), from which it was concluded that the one-layer hydrate was stable at temperatures up to  $\sim 200^\circ\text{C}$  and pressures up to  $\sim 100$  MPa, corresponding to depths of  $\sim 6.7$  km assuming normal geothermal and lithostatic gradients. These studies suggest that osmotically swollen Na-montmorillonite gels may not form at these elevated temperatures and pressures in the same way as they do under surface conditions. Even if it was possible for such a gel to form in deeply buried sandstones it is uncertain that it would be stable under the hydrodynamic conditions consequent on the fluid flow through the rock pores.

Another factor that should be considered in accounting for different swelling and dispersion behaviours of smectites may be found in the different pore structures and micromorphology of the smectitic aggregates. As indicated above, there is considerable variability in the external surface areas and porosity of individual smectite samples and this could well influence their swelling characteristics. For example, as noted above, the Redhill montmorillonite has a greater pore volume, a higher proportion of mesopores of  $<100$  Å in diameter and is made up of much smaller particles than Wyoming montmorillonite. The importance of the microstructure of smectitic clays was emphasized by Likos & Lu (2006) in their comparative study of the bulk volume changes of  $\text{Na}^+$ - and  $\text{Ca}^{2+}$ -montmorillonite. They found that in the  $\text{Na}^+$  fabric system, the volume of interparticle voids was such as to negate

the effect of swelling at the interlamellar level, whereas this was not true of the  $\text{Ca}^{2+}$  system. Salles *et al.* (2008) later showed that swelling of solid Na-montmorillonite material in a hydration sequence occurs not only at a structural level in the interlamellar space, but also in mesopores corresponding to interparticle voids in the 2–50 nm range. Furthermore, interparticle osmotic swelling begins at a lower relative humidity than that in the interlamellar space (54% and 80% respectively) and shows expansion ranging from 22.5 Å to 40 Å when there is only a single layer of water in the structural interlayers. It was concluded that interparticle osmotic swelling plays a dominant role in the overall swelling process of montmorillonite over a broad range of relative humidities.

The swelling and shrinkage reactions in interparticle voids in smectites, rather than at the interlamellar level, may possibly be important in the understanding of some anomalous examples of formation damage of smectitic sandstones. Thus, Bishop (1997) described formation damage in such sandstones from South America and the North Sea following invasion of high salinity brines and Mohan *et al.* (1999) described a similar effect in a smectitic sandstone from California. These examples of formation damage were attributed to flocculation damage (Bishop, 1997) or to fines movement consequent upon crystalline swelling of smectite (Mohan *et al.*, 1999). The latter interpretation appears to contradict the accepted wisdom that increasing the salt concentration should decrease the  $\zeta$  potential of a clay and therefore enhance its stability against dispersion. However, Bishop (1997) surmised that the high salinity brine had brought about a flocculation reaction that effectively disrupted that micro-structure of the smectitic clay, thus releasing fines that were able to migrate. This mechanism is feasible assuming that heterogeneous flocculation and shrinkage occur firstly in pores of different sizes at the interparticle level, bringing about a much greater volume change than would occur from contraction of the interlamellar space, and leads to increased strain and aggregate disruption. The fines so released would be able to migrate and reflocculate under the saline conditions, eventually to plug pore throats as suggested by Bishop (1997).

#### *Kaolinitic clays*

Given that dispersion of clays is usually brought about because electrostatic repulsion between



particulate surfaces predominates over attractive forces, then the dispersion of kaolinite can be rationalized in terms of concepts based on the DDL and the way in which the DDL changes in response to the chemistry of the pore fluids. It is, however, first necessary to review recent information on the nature of the charge on the different surfaces of kaolinite so as to better understand the implications that this information may have for dispersion and aggregation of the clay particles.

Brady *et al.* (1996) examined the pH-dependent surface charge on well crystallized Georgia kaolinite, assuming the absence of permanent negative charge, and concluded that edge sites contributed more to charge development than previously thought. Scanning force microscopy (SFM) showed that the percent edge surface area ranges from 10 to 50% of the total surface area and molecular electrostatic potential (MEP) calculations indicated significant differences between edge and basal surfaces, with edge sites having a greater potential for surface reactions. Gupta & Miller (2010) used atomic force microscopy (AFM) to show that there were charge differences between the silica tetrahedral and alumina octahedral faces of kaolinite at pH values ranging from 4 to 10. The silica face is negatively charged at pH >4 whereas the alumina face only becomes negatively charged at pH >8. The iso-electric point of the silica face was found to be at pH <4 and for the alumina face between pH 6 and 8. The pH-dependent charge shown by the basal surfaces of kaolinite in this study contrast with the conclusion of Brady *et al.* (1996) that no basal plane participation was required in order to explain site densities determined from proton adsorption isotherms. Gupta *et al.* (2011) explored the implications of their AFM study with respect to the interactions of the different kaolinite surfaces and their conclusions may be used to estimate the likely effect of changing pH on the stability of kaolinite aggregates as they occur in sandstones.

As illustrated in Figs 2 and 3, authigenic kaolinite in sandstones typically occurs in forms where there is an almost total dominance of face-to-face contacts, so that it is disruption of these contacts which will control the dispersion of the clay mineral. The kaolinite aggregates are highly porous and, in addition to the large pores that are clearly evident under the SEM, there may well be a significant proportion of pores in the mesopore size range (2–50 nm) or even in the micropore size

range (<2 nm). In considering the effect of changing pH on the net interaction energy of the basal surfaces of kaolinite, Gupta *et al.* (2011) showed that this depends on the nature of the adjacent surfaces. The asymmetric nature of the kaolinite structure means that there are three possibilities, namely silica face-silica face, alumina face-alumina face and silica face-alumina face. Interaction between negatively charged silica faces is strongly repulsive in the pH range of 4–10, whereas the alumina faces show only a slight repulsion at pH 6. The silica face-alumina face interaction is attractive below pH 7.5, reaching a maximum at pH 5, and is slightly repulsive at pH >7.5. The combined effect of these interactions is that above pH 8 face-face contacts of kaolinite are uniformly negatively charged and repulsive and are at a maximum where separation distances between the opposing basal surfaces are at ~5 nm. As noted above, pores in the mesopore size range (2–50 nm) do occur in well crystallized kaolinite so that increased hydration pressures would occur at such points within the aggregate structure under the appropriate pH conditions. It may be concluded, therefore, that kaolinite occurring in booklets and vermicules will tend to disperse at pH values >8 due to the repulsive effects between face-to-face contacts, and especially when these basal faces are exposed in the opposing surfaces of slit- and wedge-shaped micro- and mesopores. The dispersion will tend to be stable at these pH values as the interaction forces between face-face, face-edge, and edge-edge contacts will all be negatively charged and repulsive. Thus, following dispersion from its aggregate form and given sufficient hydrodynamic force, the kaolinite particles will tend to migrate from their point of origin within the sandstone until physically trapped in pore throats of smaller dimensions than the particle size of the dispersed clay.

As noted by Gupta *et al.* (2011), however, the effect of the thickness of the DDL is significant. Where the pore fluid is of high ionic strength then the thickness of the DDL will be compressed and there will be smaller repulsive force in the micro- and mesopores than if the pore fluid was of low ionic concentration. The effect of high salt concentration would be generally to decrease the  $\zeta$  potential associated with a kaolinite clay whereas the effect of low salt concentration would be to increase it. The effect of an increase in temperature would also usually lead to an increase in  $\zeta$  potential

and stabilization of dispersion, as well as to an enhancement of particle mobility.

#### *Illite and mixed-layer illite/smectite (I/S)*

The external surfaces of authigenic illite in reservoir sandstones, whether the clay mineral occurs in filamentous or platy aggregate form, will have a high permanent negative charge. These surfaces will thus have a cation exchange capacity and will be characterized by a diffuse double layer that is susceptible to change according to the nature of the exchangeable cation, the salt concentration of the external solution, its pH and temperature in the same way as described above. The dispersion properties of fine-grained (<0.1  $\mu\text{m}$ ) and coarse-grained (1–2  $\mu\text{m}$ ) illites were investigated by Emerson & Chi (1977) from the dried state and from the wet remoulded state. Complete dispersion from both the dried and remoulded states was achieved for the fine-grained illites when only a small percentage (4–8%) of the exchange sites was occupied by Na, whereas the coarse-grained illite dispersed less readily. The latter dispersed more easily when Mg-saturated, especially when compared with the Ca-saturated form which only dispersed partially from the dried state but more extensively after wet remoulding. Similar findings regarding the difficulty of dispersing dried Ca-illite in fresh water were recorded by Rengasamy (1982) who proposed that aggregates were formed, linked by hydrogen bonds between the Ca ion, water molecules and oxygens on the basal and edge surfaces of the illite crystallites. Similar bonds would be possible with Na-illite but they would be weaker because of the lower charge of the Na ion.

The dispersibility of illite, as with smectite and kaolinite, is also affected by pH (Chorom & Rengasamy, 1995). In the Na-form, illite tends not to disperse at pH <4 in deionized water, in contrast to smectite which was 86% dispersible at pH 3.5. At pH values > 7, however, 85 to 97% of Na-illite became dispersible and it was concluded that this behaviour was due primarily to changes in the net negative charge on the clay with change of pH and electrolyte concentration. Ca-illite exhibited different behaviour in that dispersibility in deionized water increased steadily between pH 2 to 7, after which the clay tended to flocculate from pH 7 to 10. This behaviour was considered to be due to the aggregating effect of precipitated calcite following adjustment of the pH with  $\text{Ca}(\text{OH})_2$ . In

general, the point of zero net charge (PZNC) for illite varies with the ionic strength of the background electrolyte solution, shifting to higher values with decreasing concentration. Thus, the PZNC of Fithian illite ranges between pH 6.0 and 7.5 (Gu & Evans, 2007), whereas PZNC values for the illites studied by Du *et al.* (1997) and Lackovic *et al.* (2003) were at pH 3.5 and 8.5 respectively. From the SEMs of authigenic illite shown in Figs 5 to 7, it is evident that there is a predominance of edge-to-face contacts, irrespective of whether the illite is in a filamentous, lath-like form (Fig. 5) or a platy form (Fig. 7). Such an arrangement suggests that authigenic illite grows at pH values below the PZNC through the aggregation of negatively charged basal surfaces and positively charged edge surfaces.

The dispersion and migration of illite particles in sandstones will evidently depend to a large extent on their mode of occurrence. Where exceedingly fine lath-like particles are anchored within quartz overgrowths as is evident in Fig. 6, then it is clear that particle migration would be severely inhibited, if not totally prevented, whatever the hydrodynamic conditions. Moreover, it is also clear from the arrangement of individual particles that the illitic clay is already dispersed to a high degree. Where such illite has grown within the pores and is not attached to the pore walls, then such fine particles could very easily be swept through the sandstone by fluid movement, especially if the fluid pH is above the PZNC of illite so that both basal and edge surfaces are negatively charged. In these circumstances, preferential migration of fine illite over the more coarse-grained kaolinite could readily occur. Where illite occurs in the form of platy aggregates, then it would be anticipated that the external surfaces of the clay mineral exposed in the micropores of the aggregates will have a high negative charge. Thus, these surfaces will have a cation exchange capacity and will be characterized by a diffuse double layer that is susceptible to change according to the nature of the exchangeable cation, the salt concentration of the external solution, its pH and temperature in the same way as previously described.

#### *Chlorite and mixed-layer chlorite/smectite (C/S)*

There is not much evidence that migration of fine particles of chlorite is a significant factor in causing formation damage in reservoir sandstones. Chlorite

itself is usually regarded as a relatively non-reactive clay mineral with a small CEC and a low layer charge where the negative charge on the 2:1 layer is compensated by the positive charge on the interlayer hydroxide sheet. In addition, the mineral occurs in relatively large platy crystals in an arrangement consisting of interlocking particles containing a predominance of edge-to-face contacts (Figs 9 and 10). These features suggest that the clay mineral would not be generally reactive to aqueous fluids and would be resistant to dispersion. It should be noted, however, that both Fe-rich and Mg-rich chlorites are susceptible to acid dissolution, and decompose to yield siliceous or ferruginous gelatinous masses which have been known to cause formation damage in the event of acid treatment of the reservoir rock.

Although chlorite itself may be considered to be resistant to dispersion and migration compared with other authigenic clay minerals, X-ray diffraction examination of what appears to be chlorite may reveal the presence of swelling layers when solvated with ethylene glycol, thus indicating a mixed-layer chlorite/smectite structure. The question arises, therefore, as to whether an authigenic chloritic mineral in this form may possibly give rise to formation damage. The mineral corrensite, which is a regular interstratification of chlorite and smectite layers in a 1:1 ratio, occurs in reservoir sandstones and, in the same way as chlorite, forms pore lining aggregates where there are an abundance of edge-to-face contacts between individual platy particles, thus forming a cellular, honeycomb-type morphology (Fig. 11). The individual plates, however, appear to be very much thinner than those consisting of chlorite, resulting in an overall appearance not unlike that of smectitic clays. Bearing in mind that corrensite has a CEC approximately half that of smectite, indicating that it is a reactive mineral, it is evidently a possibility that the mineral could be involved in causing formation damage.

As yet, the dispersibility of corrensite in the form in which it occurs in sandstones has not been systematically investigated. It is known, however, that formations such as the Mercia Mudstone Group of Triassic age in the UK contain substantial amounts of corrensite (Jeans, 2006) and are notoriously difficult to disperse to a  $<2 \mu\text{m}$  grain size. These rocks show a total clay content of 50 to 90% as determined by X-ray diffraction analysis of the bulk rock compared with a clay ( $<2 \mu\text{m}$ )

content of 20 to 40% when determined by sedimentation after aqueous dispersion (Sherwood & Hollis, 1966). Initially, it was considered that the clays were cemented into silt-size aggregates by a combination of organic matter, carbonates and aluminium and iron oxides, but removal by chemical means of all these constituents made no difference to the amount of clay dispersed. A similar resistance to aqueous dispersion is implied by the results of Baker *et al* (1994) in a study of corrensite reservoir sandstones using an ESEM to observe the response of the clays *in situ* to soaking in fresh water. Such treatment for up to three months resulted in no visible swelling or change in morphology, and it was concluded that the presence of corrensite or mixed-layer chlorite/smectite may not necessarily indicate that reservoirs containing these clays are freshwater-sensitive.

## CONCLUSIONS

This review has focused solely on the role of individual clay minerals in causing formation damage in reservoir sandstones, mainly considering the factors influencing their propensity to disperse and migrate as aqueous suspensions in pore fluids varying in salinity and pH. For smectitic clays, however, the possibility that *in situ* gel formation following osmotic swelling of  $\text{Na}^+$ -clay causes a blockage in the pore structure of the sandstone is also considered. Although such swelling can certainly occur under earth surface conditions, it is not at all clear that stable gel formation from smectites could occur under the elevated temperatures and pressures encountered at depth. Computer simulation studies suggest it does not, as the one layer hydrate of  $\text{Na}^+$ -montmorillonite appears to be the stable form at temperatures up to  $\sim 200^\circ\text{C}$  and pressures up to  $\sim 100 \text{ MPa}$ . Dispersion and fine particle migration therefore seems to be a more generally applicable mechanism, particularly at alkaline pH values and low salt concentrations, although formation damage problems are also encountered following invasion of high salinity brines into smectitic sandstones. It is emphasized, however, that the physical and chemical properties of individual smectites show considerable variability with respect to external surface area, porosity, microstructure, layer charge and cation exchange capacity, all of which will impact upon the dispersibility of the clay.

Authigenic kaolinite in sandstones usually occurs in aggregates of a vermicular or book-like aspect with a predominance of face-to-face contacts. Recent investigations indicate that both the silica and alumina basal surfaces become negatively charged at alkaline pH values as do edge sites. At alkaline pH values, therefore, all charged sites become uniformly negative thus resulting in stable dispersions. It is suggested that dispersion will take place most readily where the basal faces of kaolinite are exposed in the opposing surfaces of slit- and wedge-shaped micro- and mesopores.

Authigenic illitic clays in sandstones occur in aggregate form showing both a filamentous and platy morphology. Both forms show a high degree of edge-to-face contacts, suggesting that the clay mineral has formed at pH values below the isoelectric point, where edge surfaces are positively charged and face surfaces are negatively charged, thus leading to an open network structure when particle morphology is lath-like. If such illite is not attached to pore walls through subsequent quartz overgrowths, then the fine particles could be easily dispersed where the pore fluids are at alkaline pH values and face and edge surfaces become uniformly negatively charged. It can be readily envisaged that preferential migration of such fine-grained illite could occur over the larger crystalline particles of kaolinite.

There is not much evidence that authigenic chlorite is susceptible to dispersion and migration within reservoir sandstones in same way as the other clay minerals just described. This could be due to its aggregate morphology which consists of an interlocking arrangement of comparatively large and thick crystals (Fig. 9) and in some instances a greater degree of face-to-face contacts (Fig. 10) similar to kaolinite (Fig. 3), combined with weakly charged surfaces as reflected by a low overall CEC. On the other hand, mixed-layer chlorite/smectite has a relatively high CEC and a micromorphology similar to that of smectite (Figs 1 and 11) so that particle dispersion and migration remain a possibility. The susceptibility of the chlorite minerals in general to acid dissolution, leading to the formation of gelatinous masses, could also lead to damage following acid treatment of the reservoir rock.

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