

## Diagenesis 7. Catagenesis of Argillaceous Sedimentary Rocks

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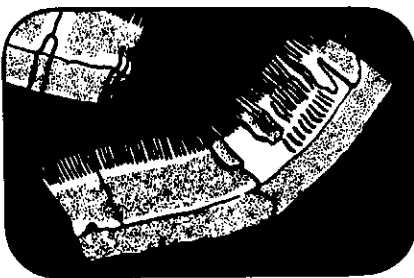
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# Articles



## Diagenesis 7. Catagenesis of Argillaceous Sedimentary Rocks

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### Introduction

Argillaceous sediments undergo progressive transformation upon burial beneath succeeding sediments. These transformations affect the water content and the mineralogical, inorganic and organic components of the pelitic rocks. Changes in organic or mineral matter resulting from pressure and temperature conditions that are much different from those at deposition are attributed to *catagenesis*.

Compaction and gravitational displacement of water was the first dewatering mechanism recognized (Hedberg, 1936). Power (1967) recognized that dewatering also occurred during the conversion of smectite to illite. He designated these two processes of dewatering as Stages I and II, respectively (Fig. 1).

In 1969, Burst used statistics to correlate clay dehydration with petroleum occurrences by plotting the difference between the depth of the first clay dehydration, which occurs when 25 percent of smectite is converted to illite, and the production

depth from 5,368 locations in the Gulf Coast area of the United States. He found it significant that although dehydration depths of the sediments ranged from 4,000 to 10,000 feet, the hydrocarbon production depths were distributed about a mean of 1,500 feet above the theoretical first clay dehydration level. Finally, the same investigator correlated his three stages of sediment dehydration with the flushing of hydrocarbons from the source rocks, which he called the "Gulf Coast Fluid Redistribution Model" (Fig. 2).

Thus, gravitational displacement squeezes out water from the pore throats by the rearrangement of sedimentary grains while alteration of the 2:1 layer silicate promotes the sloughing of water layers from their surfaces. The latter was thought to be instrumental in the dissolution of hydrocarbons, thereby aiding primary oil migration.

Dunnoyer de Seconzac (1970) reviewed the mineral transformation that takes place during the stepwise burial of shales and concurred that smectite undergoes conversion to interstratified illite-smectite and finally to illite. Perry and Hower (1972) proposed a two-step dehydration model, instead of the one-step model suggested by

Burst. In the first step, there is water expulsion engendered by the relatively rapid collapse of the smectite layers, while the second step is marked by the transition from random to ordered interlayering. This promotes a second dehydration from the layered illites. The conversion of smectite to illite through the intermediary step of a binary mixed-layered silicate is discussed further by Hower *et al.* (1976) and Aronson and Hower (1976). They have suggested that smectite reacts with K-feldspar and sometimes with mica, in absence of K-feldspar, to produce illite, chlorite and quartz. Thus, the mineralogical components in pelitic sediments adjust to the prevailing physicochemical conditions.

In 1974 Foscolos and Kodama studied the transformation of smectite to illite in the Cretaceous shales of northeastern British Columbia and showed that in order to promote the dehydration of expandable layer silicates, the temperature must first reach a critical value and then aluminum must enter and substitute for silicon in the structure of the expandable clay. This isomorphous substitution upsets the crystal electroneutrality because an ion with a 3 valence, aluminum, substitutes for an ion with a 4 valence, silicon, thus increasing

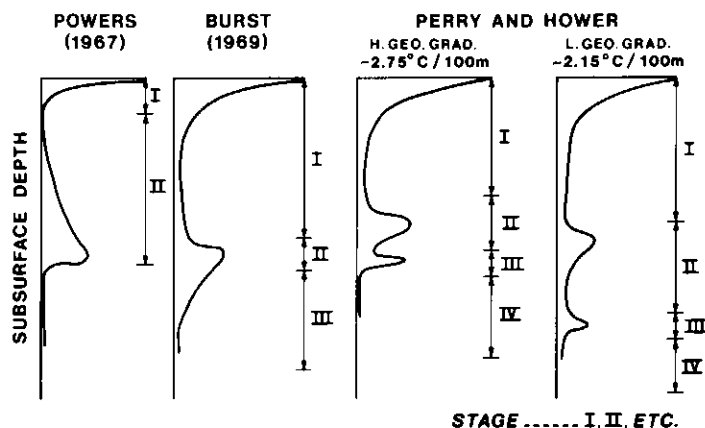


Figure 1 Dewatering process of argillaceous sedimentary rocks upon burial

the negative charge which originates from the oxygens and hydroxyls of the lattice. To counterbalance this negative charge, potassium must be absorbed on the clay surface. This process triggers the expulsion of calcium from the clay surface and the sloughing off of the absorbed water. Further isomorphous substitution of silicon by aluminum releases magnesium and iron into the solution. The same authors recognized also that the transformation of smectite to illite involves an intermediate stage. Smectite is transformed to vermiculite and then to illite.

Subsequent work by Foscolos *et al.* (1976) and Powell *et al.* (1978) in north-eastern British Columbia, the Canadian Arctic Islands and the Beaufort-Mackenzie Basin of the Canadian Northwest Territories has shown that though clay dehydration coincides with the onset of hydrocarbon generation at 0.5%  $R_o$  vitrinite reflectance, the main phase of hydrocarbon generation occurs at greater levels of burial. Quantitative mineralogical and geochemical studies showed systematic decreases in amorphous inorganic components and in the quantity of layer silicates with increasing depth (Foscolos and Powell, 1982).

Recent work in diagenesis of pelitic sediments indicates that diagenesis is a multifaceted process consisting of mineral alterations along with the dewatering processes. The latter comprises at least four mechanisms: 1) gravitational displacement; 2) water expulsion from the inorganic gels; 3) the sloughing of water from the hydrous layer silicates; and 4) the release of water from the destruction of the clay minerals. The primary objective of this review is to discuss the alterations and genesis of minerals in shales during diagenesis along with the generation of water from the last three processes and their relation to oil and gas generation and migration.

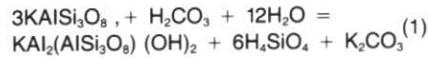
### Mineral Transformation in Pelitic Sediments During Burial

The most abundant minerals in shales are the silicates, while carbonates are minor components. Mineral identification in pelitic sediments reveals more or less the same components. However, quantitative estimation of individual minerals with burial depth indicates that some key components, such as smectite, kaolinite and chlorite, disappear or appear at certain depths, while others transform gradually.

The nature of the most commonly encountered constituents with burial depth is, therefore, discussed individually.

**Quartz.** Quartz is ubiquitous in shales and, apparently, its absolute amount increases with burial depth (unpublished data from the Beaufort-Mackenzie and Sverdrup

Basins). This implies that either the remaining minerals are removed from the system, thus increasing its relative abundance, or that quartz is added to the system during the destruction of other minerals. This is accomplished by removing the other cations either by forming new minerals *in situ* which are less rich in silica, or by transporting the products to adjacent sandstones, leaving silica gel behind. For example, K-feldspar can be transformed to a 2:1 layer silicate through the exposure to  $CO_2$ . The latter can be released from the decarbonization of the concomitant organic matter (Tissot and Welte, 1978). This reaction yields amorphous silica as follows:



Another reaction which also produces amorphous silica is the transformation of smectite to illite which in diagenesis usually follows the first equation. The reaction can be written in general terms:



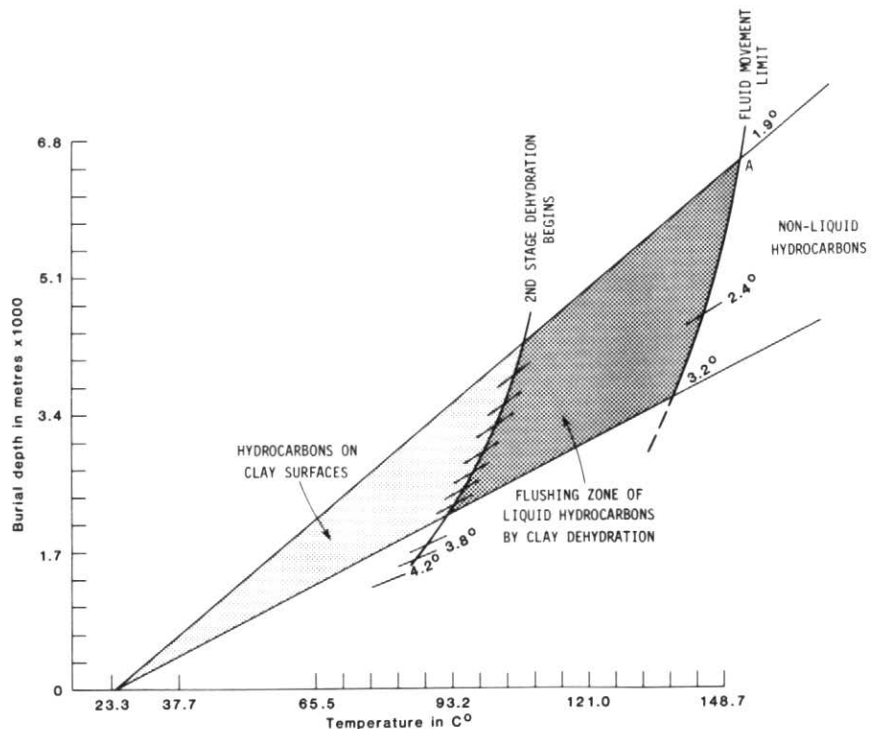
Indeed, equation 2 yields  $Ca^{2+}Mg^{2+}$ ,  $Fe^{2+}$  and  $H_2O$  (Foscolos and Kodama, 1974; Hoffman and Hower, 1979; Boles and Franks, 1979). Amorphous silica, generated from either or both reactions 1 and 2, can be reabsorbed on existing quartz grains, inducing crystal overgrowth (Longstaffe, 1983). Oxygen isotope work can verify this process.  $\delta^{18}O$  values for  $SiO_2$  derived from

igneous and metamorphic rocks must be lower than that derived from the conversion of amorphous silica gel to crystalline quartz. Thus silica gel absorbed on pre-existing quartz grains should have higher  $\delta^{18}O$  values, or if one peels off the successive layers of  $SiO_2$  by HF, then  $\delta^{18}O$  values of the remaining quartz crystal should decrease progressively.

**Feldspars.** The most common feldspar encountered in pelitic sediments is K-feldspar. Albite and anorthite are very seldom encountered because they are easily weathered (Birkeland, 1973). In the early stages of diagenesis K-feldspar also disappears when attacked by carbonic acid. The products of this reaction are used to enhance quartz overgrowth or to activate the transformation of smectite to illite through the intermediary step of mixed layer silicates.

**Layer Silicates.** Layer silicates are the second most abundant component of pelitic sediments after quartz and feldspars. They include smectite, illite, interstratified 2:1 layer kaolinite, and chlorite.

**Smectite.** Smectites are stable at temperatures much higher than those encountered during diagenesis. However, the chemical composition of the interstitial solutions is the most important factor in transforming smectites to illite via the mixed layer path. Discrete smectites are usually abundant



**Figure 2** Correlation between burial depth, geothermal gradients in  $^{\circ}C/100$  metres and oc-

currence of hydrocarbons (modified after Burst, 1969)

in the middle or late stages of diagenesis. Any occurrence of discrete smectite in deep zones of diagenesis should be considered as due to hydrothermal phenomena.

**Mixed Layered Silicates.** Mixed layered silicates appear in the early stages of diagenesis. Once potassium and aluminum are present in the interstitial pore water and the temperature is between 90°–100°C, smectite is converted to illite (Foscolos *et al.*, 1976; Powell *et al.*, 1978). Aluminum substitutes for silica in the tetrahedral positions, thus promoting a charge deficit within the crystal cell unit. To counterbalance the negative charge, a potassium ion is preferentially absorbed on the smectite surface by displacing absorbed calcium and/or magnesium. This implies that silicon from within the unit cell as well as calcium and magnesium from the surface are expelled into the solution. In addition, absorbed H<sub>2</sub>O sloughs off from smectites. These changes are recognized by the reduction of the d<sub>001</sub> spacing of a Ca-saturated smectite from 1.56 nm to 1.20 nm in the mixed layer (Fig. 3). One should notice the permanent imprint that these chemical changes impart on the smectite lattice in order to be identified by x-rays. Had the isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup> in the crystal lattice of smectite not taken place, the d<sub>001</sub> spacing of the clay mineral should have stayed the same, that is, 1.56 nm. As a result, the amount of water loss by dehydration for one gram of smectite converted to one gram of 50 percent illite–50 percent smectite is calculated as follows:

Two face areas of a unit cell = 2 × a × b  
 = 2 × 5.25 × 9.20 = 96.6 Å<sup>2</sup> where a and b are the unit cell dimensions for smectite.

The specific planar surface in m<sup>2</sup>/g, is

$$\frac{96.6 \text{ \AA}^2 \times 10^{-20} \text{ m}^2/\text{\AA}^2}{\text{Molecular weight of smectite } 6.02 \times 10^{23} \text{ mole}^{-1}} = \frac{96.6 \text{ m}^2 \times 6.02 \times 10^{23} \text{ mole}^{-1}}{720 \text{ g/mole} \times 10^{20}} = 808 \text{ m}^2/\text{g.}$$

where 720 g is the atomic weight of smectite in grams, 10<sup>-20</sup> is a conversion factor from Å<sup>2</sup> to m<sup>2</sup> and 6.02 × 10<sup>23</sup> mole<sup>-1</sup> is Avogadro's number.

Since there is a reduction of the d<sub>001</sub> spacing from 1.54 nm to 1.18 nm, that is 0.36 nm, then the water loss per m<sup>2</sup>/g of smectite when converted to 50 percent illite – 50 percent smectite is

$$808 \times 10^4 \text{ cm}^2/\text{g} \times 0.36 \times 10^{-7} \text{ cm} = 290.88 \times 10^{-3} \text{ cm}^3/\text{g}$$

Assuming a density of 1g/cm<sup>3</sup>, this water loss converts to 290.88 mg. per gram of clay. This result is comparable to the experimental result of Mooney *et al.* (1952) who reported a loss of 270 mg of H<sub>2</sub>O per gram of Ca smectite when the d<sub>001</sub> spacing is reduced from 1.56 nm to 1.20 nm, that is, by 0.36 nm.

By thermodynamic manipulation of the water vapour absorption and desorption isotherms of the clay and simultaneous layer distance measurements by x-ray diffraction of the d<sub>001</sub> spacings of smectites, Keenan *et al.* (1951) and Mooney *et al.* (1952) have calculated the required pressure to remove a monolayer of water of 0.36 nm (3.6 Å) thickness, as follows:

$$\pi = \frac{-R T}{v_1 M} \ln P/P_0$$

where π = osmotic pressure in atmospheres

R = gas constant in litre-atmospheres/mole degree

T = absolute temperature (25°C = 298°K)

v<sub>1</sub>M = molar volume of water = 0.01802 litre/mole

P/P<sub>0</sub> = relative humidity at which the d<sub>001</sub> spacing is observed

At 50 percent relative humidity, or at P/P<sub>0</sub> = .5, the d<sub>001</sub> spacing of Ca smectite is 15.6 Å or 1.56 nm (Brown, 1961). Therefore, at P/P<sub>0</sub> = .5 the d<sub>001</sub> spacing of Ca

smectite is

$$\pi = \frac{.0821 \times 298}{.01802} \times 2.303 \times \log. 5 = 941.02 \text{ atm. or;} \\ 941 \text{ atm.} \times 1.013 \text{ bar/atm.} = 953.25 \text{ bars.}$$

At 4 percent relative humidity, P/P<sub>0</sub> = .04, the d<sub>001</sub> spacing of Ca vermiculite is 12.0 Å or 1.2 nm, therefore:

$$\pi = \frac{.0821 \times 298}{.01802} \times 2.303 \times \log. 04 = 4,066.92 \text{ atm.}$$

As a result, to remove the second layer of water 4,066.92 atm. or 4,119.79 bars (4,066.92 atm. × 1.013 bar/atm.) of pressure is required. For 0.25 nm thickness, van Olphen (1977) has calculated the pressure of removal of the second layer of water at 4,000 bars.

Using the partial free energy difference, Δf, we can measure the work in ergs/g. of H<sub>2</sub>O, which is required to free the second layer of water from the clay surface. This is given by

$$\Delta f = \frac{-R T}{M} \times 2.303 \log P/P_0$$

where R is the gas constant 8.316 × 10<sup>7</sup> erg/mole/K°

T is the temperature in K°, (273°K C°)

M is the molecular weight of water 18.02 gm/mole

P/P<sub>0</sub> is the relative humidity

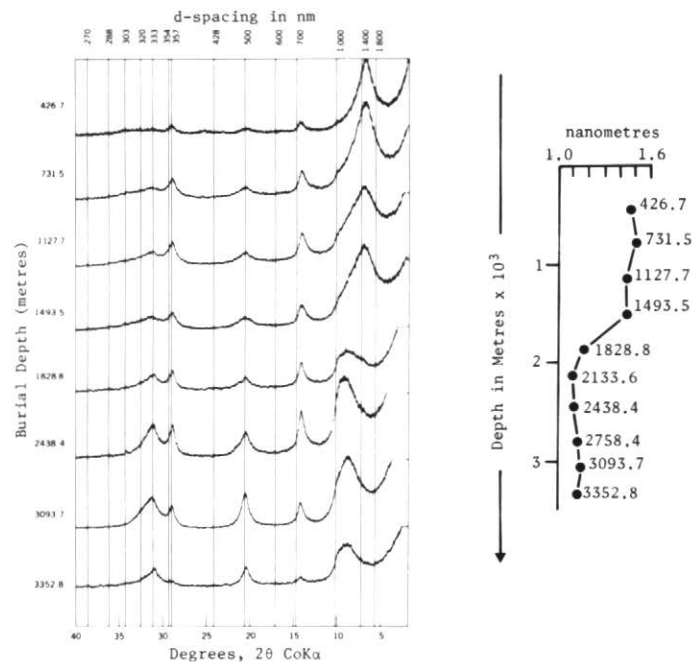


Figure 3 d<sub>001</sub> spacings of Ca saturated 0.2 μm specimen at 50 percent relative humidity versus

burial depth from a North Sabine H-49 well sample (Foscolos and Powell, 1980)

Thus, the respective free energy between free water and the second water layer which is adsorbed on the clay surface is  $-412.05 \times 10^7$  ergs/g. Since one calorie is  $4.184 \times 10^7$  ergs, the partial free energy can be calculated as  $-98.48$  cal/g. From this calculation, it is obvious that the second clay dewatering process requires much more energy, especially if the mineral is vermiculite.

To remove the last monolayers of water which is adsorbed on the clay surface, different free energies and pressures will be required, depending on the type of expandable 2:1 layer silicate and the ion adsorbed on its clay surface. If it is smectite, the required free energy to release the last monolayer of water is much less than that of vermiculite. The explanation lies in two factors: first, the amount of charge deficit originating from the clay mineral is larger in vermiculites than smectites, and secondly, the seat of the charge is in both octahedral and tetrahedral positions, the latter being very close to the clay surface. This renders very strong attractive forces on the last monolayer of water. The magnitude of the force can be calculated from Coulomb's law:

$$F = \frac{Q_1 Q_2}{D r^2}$$

where  $F$  is the force in dynes,  $Q$  is the charge of the particles in esu,  $D$  is the dielectric constant of water (80), and  $r$  is the distance between the origin of charges and the centre of water molecules in centimetres.

It is obvious that in vermiculites the  $Q$  value is large and the  $r$  value is small. As a result, even at extremely low  $P/P_0$  relative humidity values water is still adsorbed on the vermiculite surfaces, making the desorption of the last monolayer of water very difficult. The exact free energy or work requires a very precise knowledge of the  $P/P_0$  value at which the  $d_{001}$  spacing of vermiculites becomes  $9.6 \text{ \AA}$ , or  $.96 \text{ nm}$ . So far this value has not been determined, but it is in the order of tens of thousands of atmospheres. A good discussion on this subject is presented by van Olphen (1954, 1965) and Kittrick (1969a, b). Work by Foscolos and Kodama (1974), Foscolos *et al.* (1976) and Powell *et al.* (1978), encompassing research in northeastern British Columbia, the Beaufort-Mackenzie and the Sverdrup Basins in Canada, has shown that the transformation of smectite to 2:1 mixed-layer silicates passes through the vermiculitic step. Thus, the mixed-layered system consists of illite-smectite-vermiculite rather than the binary system observed by Perry and Hower (1972). The implication of having a ternary system with vermiculite as an intermediary in the transformation of smectite to illite is that the last layer of

adsorbed water on the clay surface is very difficult to expel within the range of oil generation and therefore it should not be considered in the oil migration mechanism, at least for the wells studied in Canada. Perry and Hower (1972) reported a second clay dehydration from the pelitic sediments of the Gulf Coast at temperatures around  $140^\circ\text{C}$ , while in the Sverdrup and Beaufort-Mackenzie Basins the second dehydration step was not encountered at temperatures close to  $150^\circ\text{C}$ . The author believes that the difference is probably due to the type of smectites encountered in the different basins.

It is possible that trioctahedral smectites behave differently than dioctahedral smectites, the latter being closer to a vermiculitic structure (Kishk, 1967). To date, dioctahedral expandable clays have been encountered in all samples from the Sverdrup and Beaufort-Mackenzie Basins. Illite-vermiculite-chlorite-smectite mixed layers are very often encountered at deeper burial depths (Powell *et al.*, 1978).

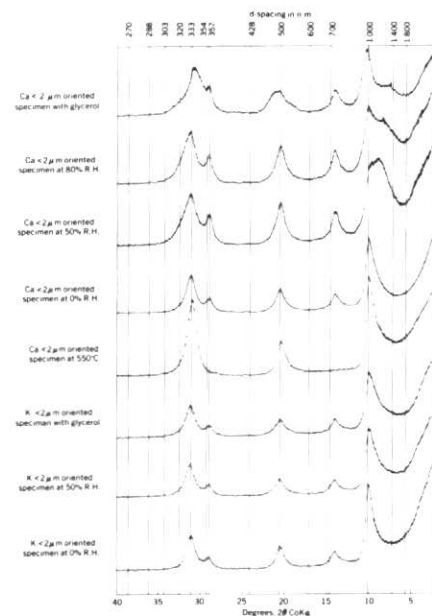
To identify a ternary or quaternary system of mixed layer silicates the clay fraction must be subjected to a series of treatments with two different cations adsorbed on the clay surfaces. By knowing the adsorbed cation on the clay surface and the physico-chemical conditions under which the sample is subjected during x-ray analysis, the  $d_{001}$  spacing can define the kind of expandable layer silicates, the components and their weighted percentages (Brown, 1961). Under given physical conditions, a binary mixture of illite-smectite with  $\text{Ca}^{2+}$  adsorbed on its surface will show specific  $d_{001}$  spacings.  $\text{K}^+$ -saturated illite-smectite will achieve similar  $d_{001}$  spacings under the same physical conditions. However, a ternary system of clays consisting of illite-smectite-vermiculite with  $\text{Ca}^{2+}$  adsorbed on its surface will show  $d_{001}$  spacings, similar to a binary system, but when saturated with  $\text{K}^+$  will show different  $d_{001}$  spacings (Fig. 4). Chemical analysis of the calcium-saturated clays can be used to confirm the results of the x-ray analysis. The  $\text{CaO}$  contents are used as a measure of the cation exchange capacity (C.E.C.) which is the charge of the clay surface, while the  $\text{K}_2\text{O}$  contents measure the illitic component of the mixed layers. From these two results an estimation of the expandable component can be made. Consequently, the chemical analysis can check the information obtained from the x-ray patterns concerning the composition of the mixed layers.

**Illite.** Illite is not a particular mineral. The term is used to designate a group of clay minerals having a mica-type structure. Illites exist in 1M, 1Md, 2M and 3T forms. The latter is a rare type. 1Md illite, the

disordered form, is the most common type in sedimentary basins, and as the temperature rises during catagenesis the reaction goes from 1Md to 2M. The methods for studying these transformations by x-ray techniques and their significance in sedimentary rocks are reported by Maxwell and Hower (1967) and Velde and Hower (1963).

The crystallinity of illite, that is, the morphology of the 1 nm peak, has been used by Weaver (1960, 1961) and by Kubler (1964) as a diagenetic indicator. This indicator, which is quantified by measuring the ratio of heights at 1.0 nm and 1.5 nm or the width of the 1 nm peak at half height, is valid only at the late stages of diagenesis or early metamorphism. In the early stages of diagenesis the rearrangement of ions in the interlayering spacing of the 2:1 layer silicates and the experimental condition under which the sample is x-rayed renders its value questionable. A comparative scheme using all these indicators for diagenesis is presented by Foscolos and Stott (1975) and Foscolos *et al.* (1976).

**Kaolinite.** Kaolinite is abundant in the early and middle stages of diagenesis, while usually absent in the last stages (Dunnoyer de Seconzac, 1970; Foscolos and Powell, 1980; Hower, 1981; Boles, 1981). It seems that once the chloride salt solutions have been expelled from pelitic sediments, the pH value of the system becomes more alkaline. With temperature rising above  $100^\circ\text{C}$ , kaolinite is dissolved or transformed to other minerals. As the ratio of  $[\text{K}^+]/[\text{H}^+]$

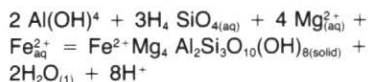


**Figure 4**  $d_{001}$  spacings of calcium and potassium saturated  $<0.2 \mu\text{m}$  oriented specimen under various x-ray conditions from a North Sabine H-49 well sample

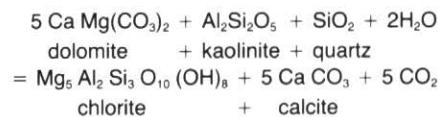
in the pore solution increases, kaolinite is illitized (Hemley, 1959). For a  $[K^+]/[H^+]$  equal to  $10^6$ , kaolinite is transformed to illite at  $100^\circ\text{C}$  while, at a ratio of  $[K^+]/[H^+]$  equal to  $10^3$ , a temperature of  $200^\circ\text{C}$  is needed to achieve the same conversion. Dunnyer de Seconzac (1969) demonstrated the instability of kaolinite in sea water above  $200^\circ\text{C}$ . Another reaction where kaolinite is transformed at elevated temperatures is reported by Hutcheon *et al.* (1980). At high temperatures kaolinite reacts with dolomite and silica to produce a magnesium chlorite, calcite and  $\text{CO}_2$ . However, if  $\text{Fe}(\text{OH})_3$  is present, an iron-magnesium chlorite can be produced, a product very often encountered in diagenesis.

**Chlorite.** Diagenetic chlorite is not detected in pelitic sediments in the early or middle stages of diagenesis in either the Sverdrup or the Beaufort-Mackenzie Basins or in northeastern British Columbia (Foscolos and Stott, 1975; Foscolos *et al.* 1976; Foscolos and Powell, 1980). The possible explanation lies in the presence of  $\text{CO}_2$  derived from the decarbonization of the organic matter, which renders the pore water acidic. Under low pH values chlorite is dissolved. Indeed, the instability of chlorite in acid media and temperatures around  $80^\circ\text{C}$ – $100^\circ\text{C}$  is used as a technique for removing it from samples where kaolinite and chlorite are present. This facilitates mineral identification by x-ray diffraction (Brown, 1960).

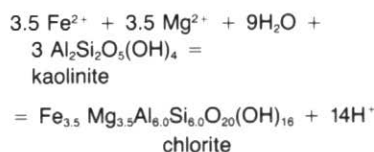
In late diagenesis, where amorphous silica, aluminum, iron and magnesium are available, chlorite can be formed from the aluminum, silica, iron and magnesium, as proposed by Almon and Davies (1979), where



or, as proposed by Hutcheon *et al.* (1980), where

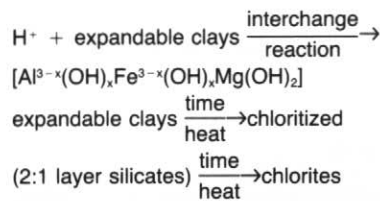


or, as proposed by Boles and Franks (1979), where



However, in most cases chlorite in the late stages of diagenesis of pelitic sediments

seems to derive from amorphous aluminum, iron and magnesium ions which are incorporated into the ternary system of 2:1 layer silicates. The conversion of chloritic intergrades to discrete chlorites with depth was documented in samples from Drake Point D-68 and Cape Norem A-80 wells in the Sverdrup Basin and in samples from Cretaceous shales of northeastern British Columbia (Fig. 5). Based upon the presence of carbonic acid, derived from the maturation of the organic matter at the early stages, the overall reaction can be summarized as follows:



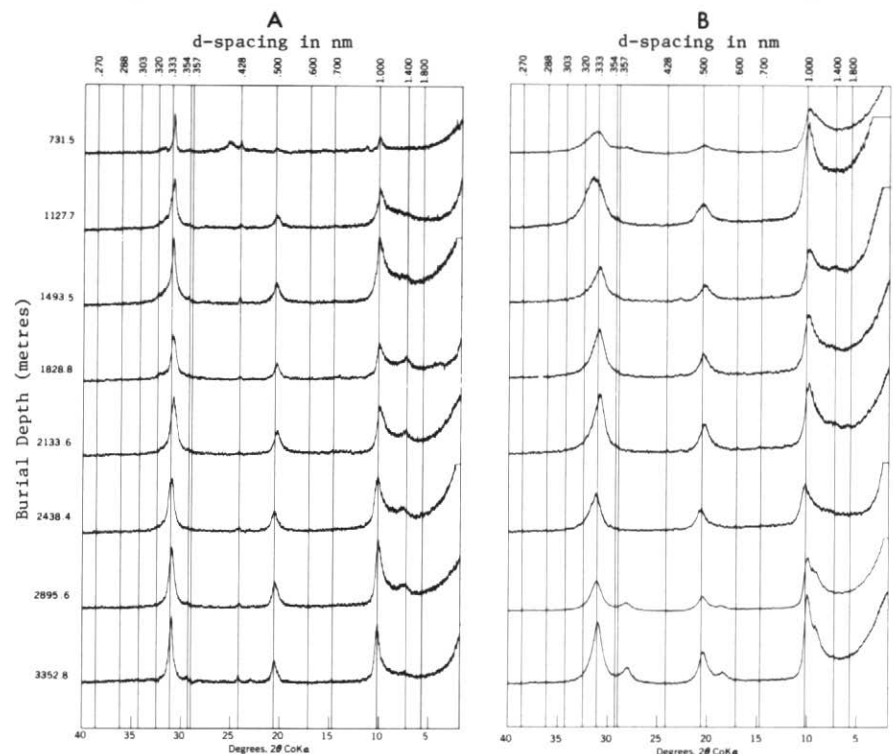
The absorption of protons by clays and their interchange with octahedral aluminum, iron and magnesium have been discussed by Foscolos (1964) and Foscolos and Barshad (1969).

**Amorphous Inorganic Gels**

Amorphous material, or gels, occur either by initial deposition or during the destruc-

tion of silicates such as feldspars, through the action of carbonic acid, or the transformation of smectite to illite. The colloidal portion of silica, aluminum and iron can be extracted and measured following the techniques of Aquillera and Jackson (1953) and that of Jackson (1965). Foscolos and Powell (1980) have determined free iron, silicon and aluminum in six wells and one formation in the Sverdrup and Beaufort-Mackenzie Basins of the Northwest Territories. The results indicate that amorphous material, which in some cases amounts to over 35 percent, decreases with burial depth.

If one accepts that the amorphous inorganic gels have a composition similar to allophane, as proposed by Ross and Kerr (1934), then the amount of water released between ambient temperature and  $100^\circ\text{C}$  is approximately 15 percent, while the water given off between  $100^\circ\text{C}$  and  $150^\circ\text{C}$  is 7 percent (Jackson, 1956). This implies that prior to first clay dehydration, 1.5 g of  $\text{H}_2\text{O}$  will be released from 10 g of amorphous material to the pore space, while 0.7 g will be released after the first clay dehydration. This amount of water is roughly equal to that given off from 10 g of smectite clay when it transformed to 50 percent illite and 50 percent smectite. On the basis of the previous calculations, this amounts to 1.35 g of  $\text{H}_2\text{O}$ . Thus the amount of pure



**Figure 5** X-ray diffraction patterns of oriented clay specimens from North Sabine H-39 well after heating at  $550^\circ\text{C}$  for 1/2 hour. A 0.2 to 2.0

$\mu\text{m}$  fraction. B < 0.2  $\mu\text{m}$  fraction (Foscolos and Powell, 1978)

or salt-free water released in the pore system prior and during the first dehydration of clays from both the amorphous material and the smectite transformation process creates an over-pressure zone. Statistical data indicate that there is a good correlation between the over-pressured zone and the sonic transit-time in shales (van Elsberg, 1978).

Amorphous inorganic gels, besides supplying water to the system, also provide cementing agents to either the pelitic sediments or the adjacent sandstones through the process of mineral formation. Under acid or neutral pH values amorphous silica probably is retained in shale, while amorphous aluminum migrates as hydroxyalu-

minium ion to form some kind of monomer with amorphous silica, which is available in sandstones during this diagenesis. These monomers, as proposed by Siffert (1967), can be considered as precursors of authigenic booklets of kaolinite and hairy illites encountered in the sandstones (Figs. 6 and 7). Such monomers can then link to similar monomers to form tetrahedral and octahedral sheets. The formation of an octahedral sheet involves the rearrangement of OH ions and Al ions, while a tetrahedral sheet requires the removal of water from the OH group linked to silica ions. From Figures 6 and 7, it is obvious that the ratio of silica/aluminum determines the kind of amorphous monomer gel to

be formed and, therefore, the kind of layer silicate. However, to precipitate clay minerals from solution, aluminum must be present in sixfold co-ordination in order to form a gibbsitic layer. Linares and Huertas (1970) have shown that organic matter (fulvic acid) complexes aluminum in sixfold co-ordination, and that with pH change, aluminum hydroxide is formed and oriented into a gibbsitic layer. The latter absorbs silica tetrahedra to form kaolinite. Therefore organic compounds derived from the diagenesis of organic matter in source rocks may act similarly to induce synthesis and authigenesis of many different clay minerals in either shales or sandstones.

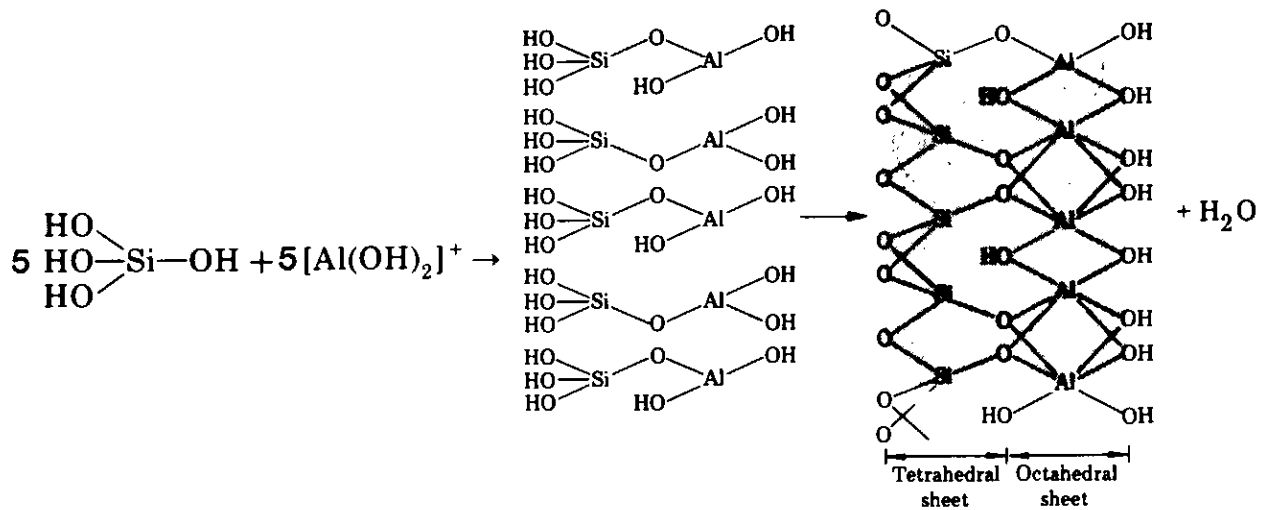


Figure 6 Formation of authigenic kaolinite (Siffert, 1967)

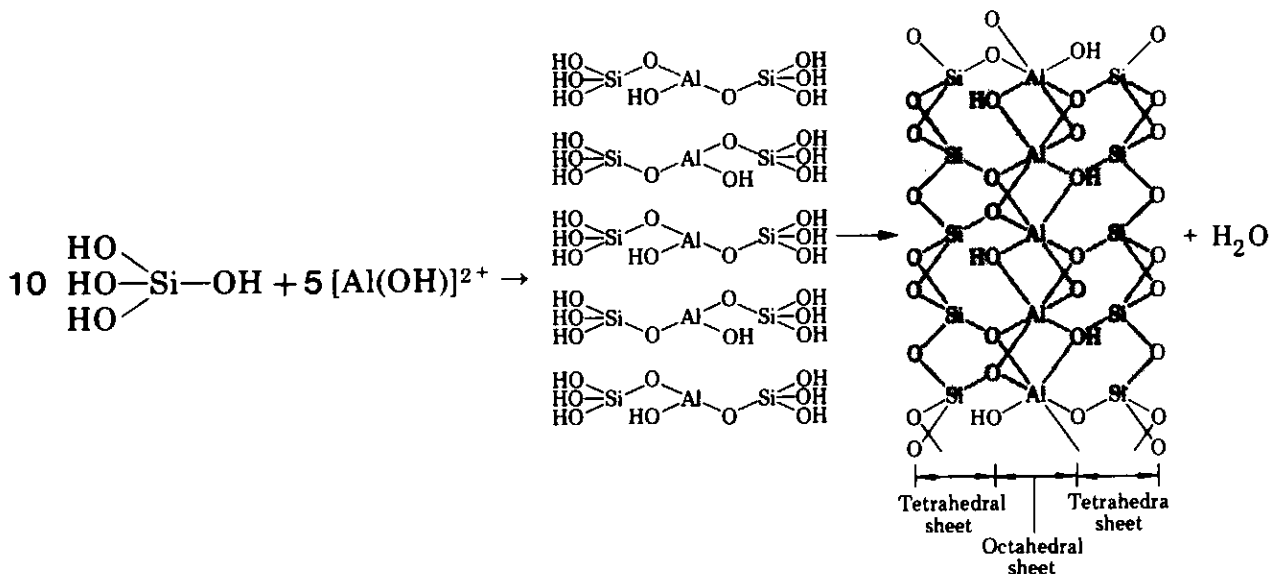
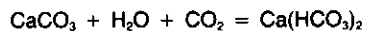


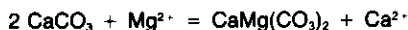
Figure 7 Formation of authigenic 2:1 layer silicate (Siffert, 1967)

**Carbonates.** Calcite is very seldom encountered in pelitic sediments as a product of diagenesis. In the early stages of diagenesis, CO<sub>2</sub> favours the dissolution of calcite through the reaction



Once Ca(HCO<sub>3</sub>)<sub>2</sub> has encountered a neutral pH, authigenic calcite is formed. This usually occurs in sandstones adjacent to shales. Calcite cement is also formed when K<sup>+</sup> derived from feldspar dissolution substitutes absorbed Ca<sup>2+</sup> or Mg<sup>2+</sup> on the smectite surfaces, thus inducing the transformation of smectite to interstratified smectite-illite along with the expelled water (Foscolos and Kodama, 1974). The exchanged calcium moves with HCO<sub>3</sub><sup>-</sup>, generated from the decarbonization process of the inherited organic matter, to the adjacent sandstones, precipitating authigenic calcite. Therefore calcite cement is encountered in sandstones during the early stages of diagenesis. As transformation of smectite to illite proceeds with burial depth, pore fluids are enriched mainly with magnesium, and to a lesser extent, with iron. These enriched pore fluids migrate to sandstones along with carbonic acid to

form dolomite cement or to react with calcite and form dolomite as follows:



When the concentration of iron in the expelled pore fluids increases, then ferroan dolomite and finally ankerite (CaMg<sub>0.5</sub>Fe<sub>0.5</sub>(CO<sub>3</sub>)<sub>2</sub>) is generated as an authigenic cement. Ankerite is very seldom encountered in shales. It seems that as diagenesis proceeds the pH of the pelitic sediment becomes alkaline because K clays, in the absence of buffering salts in the pore fluids, raise the pH of the rock. This induces iron to precipitate as Fe(OH)<sub>3</sub> on the 2:1 clay mineral surfaces (Tazaki *et al.*, 1983). This process eventually leads to chloritization of the 2:1 layer silicates and the formation of iron-rich sedimentary chlorites. If authigenic kaolinite and quartz are present, then iron, magnesium and/or ankerite may react to produce iron-rich chlorites (Boles and Franks, 1979), or chlorite, calcite and CO<sub>2</sub>, as documented by Muffler and White (1969) and Hutcheon *et al.* (1980).

**Relationship Between Clay Catagenesis, Organic Matter Diagenesis and Cementation**

The relationship between clay catagenesis and organic matter diagenesis has been put forward by Powell *et al.* (1978) and Foscolos and Powell (1979) in their study of the Sverdrup Basin. The results are illustrated in Figure 8 and show that amorphous inorganic matter loses water and decreases in concentration at a burial depth about 600 m above the first dehydration step of smectite. The first clay dehydration step coincides with 0.5 percent Ro vitrinite reflectance and occurs at about 1500 m above the main phase of oil generation. The second dehydration takes place below the depth of the oil-generating zone, since vermiculite is a major component in the mixed layers (Powell *et al.*, 1978). These results suggest that the depths of clay dehydration and the loss of water from the amorphous aluminosilicate gels are not coincident with the depths of oil generation, and it is difficult to envisage a role for water derived by this process in oil migration.

An important aspect of diagenesis, however, is the destruction of 2:1 layer silicates, as reported by Foscolos and Powell

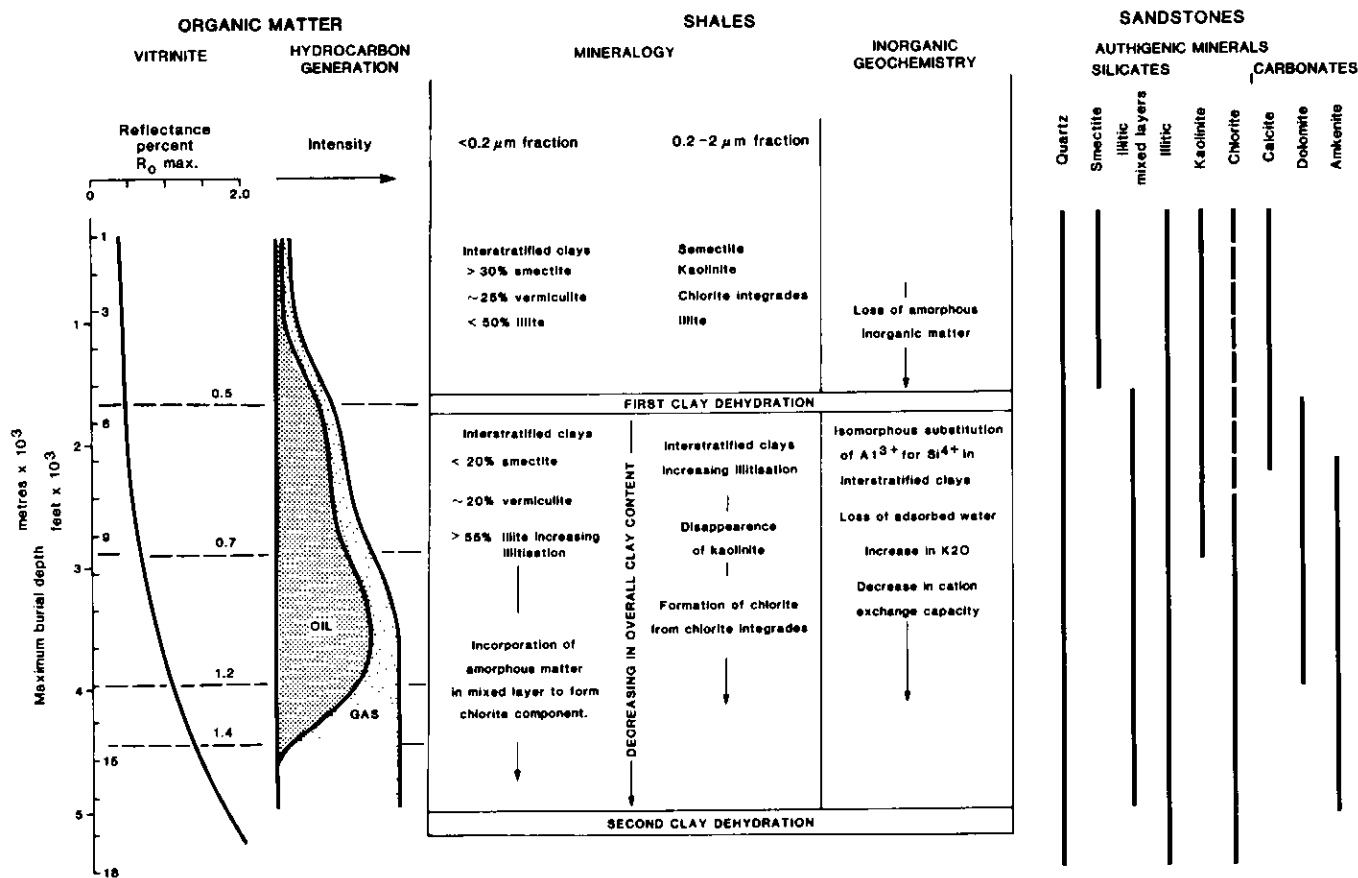


Figure 8 Relation between diagenesis (catagenesis) of shales and the occurrence of authi-

genic minerals in sandstones (Foscolos and Powell, 1979)



(1980). Although smectite is transformed to illite via vermiculitization, the absolute amount of 2:1 layer silicates decreases with burial depth. The destruction of silicates might have implications because absorption sites, where organic matter can be absorbed, are destroyed. Therefore hydrocarbons might be moving away from pelitic sediments because the seats of absorption are destroyed. There is also a distinct possibility that once the absorbed sites are reduced, that is, once the cation exchange capacity is lowered, the absorptive sites are reduced and polar organic liquids are released to the pore systems. The effects, if any, of the destruction of the 2:1 layer silicate with burial depth to the migration of hydrocarbons and to cementation of adjacent sandstones is a new area of research worth probing.

Crystal-lattice-water derived from the breakdown of the layer silicates ensures an ongoing sediment dehydration. For example, in the North Sabine H-49 well it was calculated that water derived prior to first clay dehydration from all reactions involving clay minerals (absorbed water, cavity water and crystal-lattice-water) amounts to 3.8 percent, while the water loss between the two dehydration steps, that is, within the hydrocarbon generating zone, amounts to 3.7 percent (Foscolos and Powell, 1980).

In addition to water, the dissolution of the amorphous inorganic matter and the destruction of the layer silicates releases silica, aluminum, iron, calcium, magnesium and potassium to the pore water. If these elements remain in place, they may precipitate to form part of the existing minerals, such as quartz, or form authigenic clays, such as chlorites. However, the net decrease of the layer silicates with depth suggests that some of these cations may migrate with compaction water into more porous and permeable horizons, forming authigenic clays in sandstone reservoirs (Curtis, 1978; Foscolos and Powell, 1979). In such cases both permeability and porosity of the shales and adjacent sandstones are affected by formation of authigenic cements both before and during hydrocarbon generation and migration.

### Conclusion

The following conclusions concerning the catagenesis of shales can be made:

1. The first stage in catagenesis is marked by the accumulation of amorphous inorganic components which occur either by initial deposition and/or during the destruction of silicates. This stage takes place prior to the onset of the first clay dehydration of the 2:1 layer silicates.
2. The first clay dehydration is attributed to the conversion of smectite to mixed layer silicates and occurs prior to the onset of hydrocarbon generation from the organic

matter. Dehydration is attributed to isomorphous substitution of silicon ions by aluminum ions in the clay structure and the ensuing absorption of potassium ions and displacement of calcium and magnesium ions from the clay surface.

3. The first dewatering of the clays marks the onset of the destruction of the 2:1 layer silicates, as well as kaolinite. Thus there is a net decrease in concentrations as the clays undergo structural transformations.
4. The mixed layered clays comprise a ternary system of smectite-vermiculite-illite. Vermiculite appears to be an intermediary mineral in the conversion of smectite to illite.
5. The second dewatering of the clays occurs after oil has become cracked to gas. The high temperature requirement is attributed to the presence of a Ca-vermiculite component in the mixed layer clays.
6. After the first dewatering of the clays, iron hydroxide precipitates on 2:1 layer silicates to form in the less than  $2 \mu$  fraction iron-rich chlorite intergrades and in the  $2-2 \mu$  fraction iron-rich chlorites.
7. With burial, pelitic sediments release water not only upon compaction but also from the crystallization of amorphous material, the dehydration of the expandable layer silicates and the destruction of the layer silicates.
8. The destruction of silicates, the transformation of the layer silicates and diagenesis of organic matter provide inorganic material which acts as cementing agents in adjacent sandstones.
9. The type of minerals in shales and adjacent sandstones is a function of temperature, the existing physicochemical conditions and the ions concentration of the pore fluids.

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