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See table of contents

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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 pores 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.

Dunoyer de Sezoncze (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 isomorphic 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](image_url)  
*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 isomorphic 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 northeastern 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, 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 CO₂. The latter can be released from the decarboxylation of the concomitant organic matter (Tisot and Welte, 1978). This reaction yields amorphous silica as follows:

$$3KAlSi_3O_8 + H_2CO_3 + 12H_2O = K_2Al[Si_3O_8](OH)_2 + 6H_2SiO_3 + K_2CO_3$$

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:

$$K^+ + \text{smectite} = \text{illite}/\text{smectite} + \text{silica} + \text{other products}$$

Indeed, equation 2 yields Ca²⁺, Mg²⁺, Fe⁺, and H₂O (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. δ¹⁸O values for SiO₂ 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 δ¹⁸O values, or if one peels off the successive layers of SiO₂ by HF, then δ¹⁸O 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.
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 H₂O sloughs off from smectites. These changes are recognized by the reduction of the d₀₀₁ 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⁺⁺ by Al⁺³ in the crystal lattice of smectite not taken place, the d₀₀₁ 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 Å² where a and b are the unit cell dimensions for smectite.

The specific planar surface in m²/g, is

\[
\text{Molecular weight of smectite: } 6.02 \times 10^{23} \text{ mole}^{-1}
\]

\[
96.6 \text{ Å}^2 \times 6.02 \times 10^{23} \text{ mole}^{-1} = 0.02 \text{ m}^2/\text{g}
\]

where 720 g is the atomic weight of smectite in grams, 10⁻²³ is a conversion factor from Å² to m² and 6.02 × 10²³ mole⁻¹ is Avogadro's number.

Since there is a reduction of the d₀₀₁ spacing from 1.54 nm to 1.18 nm, that is, 0.36 nm, then the water loss per m²/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 1 g/cm³, this water loss converts to 290.88 mg. per gram of clay. This result is comparable to the experimental result of Moorey et al. (1952) who reported a loss of 270 mg of H₂O per gram of Ca smectite when the d₀₀₁ 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 d₀₀₁ 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:

\[
\pi = -\frac{R \times T}{v \times M} \ln \left( \frac{P}{Po} \right)
\]

where \( \pi \) = osmotic pressure in atmospheres \( R \) = gas constant in litre-atmospheres/mole degree \( T \) = absolute temperature (25°C = 298 K) \( v \times M \) = molar volume of water = 0.01802 litre/mole \( P/\text{Po} \) = relative humidity at which the d₀₀₁ spacing is observed

At 50 percent relative humidity, or at \( P/\text{Po} = 0.5 \), the d₀₀₁ spacing of Ca smectite is 15.6 Å or 1.56 nm (Brown, 1961). Therefore, at \( P/\text{Po} = 0.5 \) the d₀₀₁ spacing of Ca smectite is

\[
\pi = \frac{0.821 \times 298}{0.1802} \times 2.303 \times \log 0.5 = 941.02 \text{ atm. or;}
\]

\[
941.02 \text{ atm. } \times 1.013 \text{ bar/atm. } = 953.25 \text{ bars.}
\]

At 4 percent relative humidity, \( P/\text{Po} = 0.04 \), the d₀₀₁ spacing of Ca vermiculite is 12.0 Å or 1.2 nm, therefore:

\[
\pi = \frac{0.821 \times 298}{0.1802} \times 2.303 \times \log 0.04 = 4,066.92 \text{ atm.}
\]

As a result, to remove the second layer of water 4,066.92 atm. or 4,119.79 bars (4,086.92 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, \( \Delta f \), we can measure the work in ergs/g of H₂O, which is required to free the second layer of water from the clay surface. This is given by

\[
\Delta f = -\frac{R \times T}{M} \times 2.303 \log P/\text{Po}
\]

where \( R \) is the gas constant 8.316 × 10⁷ erg/mole/K
\( T \) is the temperature in K
\( M \) is the molecular weight of water 18.02 gm/mole
\( P/\text{Po} \) is the relative humidity

**Figure 3** d₀₀₁ 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 absorbed on the clay surface is 

\[ -4.12 \times 10^{-6} \text{ ergs} \cdot \text{g} \]. Since one calorie is 

\[ 4.184 \times 10^{-4} \text{ ergs} \], the partial free energy 

can be calculated as \(-98.48 \text{ cal/g}\). From this 

calculation, it is obvious that the second 

clay water layer process requires much more energy, especially if the mineral is 

vermiculite.

To remove the last monolayers of water which is absorbed 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 size 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:Po 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:Po value at which the \( d_{100} \) spacing of 
vermiculites becomes 9.6 Å, or .96 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 Kittick (1969a, b). Work by 
Fosco and Kodama (1974), Fosco and 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 smectic 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 

absorbed 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°C, while in the Sverdrup and Beaufort- 
Mackenzie Basins the second dehydration 
step was not encountered at temperatures 
below 150°C. The author believes that 
the difference is probably due to the type of 
smectites encountered in the different 
basins.

It is possible that triocahedral smectites 
behave differently than dioctahedral smectites, 
the latter being closer to a vermiculite 
structure (Kish, 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 absorbed 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 
\( d_{100} \) spacing can define the kind of 
expandable layer silicates, the components 
and their weight percentages (Brown, 
1961). Under given physical conditions, 
a binary mixture of illite-smectite with Ca²⁺ 
absorbed on its surface will show specific 
\( d_{100} \) spacings. K⁺-saturated illite-smectite 
will achieve similar \( d_{100} \) spacings under 
the same physical conditions. However, 
a ternary system of clays consisting of illite-
smectite-vermiculite with Ca²⁺ absorbed 
on its surface will show \( d_{100} \) spacings, similar 
to a binary system, but when saturated 
with K⁺ will show different \( d_{100} \) spacings 
(Fig. 4). Chemical analysis of the calcium-
saturated clays can be used to confirm 
the results of the X-ray analysis. The 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 
K₂O contents measure the illicic 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. 
Illest exist in 1M, 1Md, 2M, and 3T forms. 
The latter is a rare type. 1Md illite, the 

Figure 4 \( d_{100} \) spacings of calcium and potas-

sium saturated \(< 0.2 \mu m \) oriented specimen 
under various x-ray conditions from a North Sa-
dine H-49 well sample.
in the pore solution increases, kaolinite is illitized (Hemley, 1959). For a $[K^+] / [H^+]$ equal to $10^7$, kaolinite is transformed to illite at 100°C while, at a ratio of $[K^+] / [H^+]$ equal to $10^3$, a temperature of 200°C is needed to achieve the same conversion. Durnoyer de Seconzac (1969) demonstrated the instability of kaolinite in sea water above 200°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 CO$_2$. However, if Fe (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 CO$_2$ derived from the decarboxylation 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°C-100°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, aluminium, iron and magnesium are available, chlorite can be formed from the aluminium, silica, iron and magnesium, as proposed by Aimon and Davies (1979), where

$$2\text{Al(OH)}_4^- + 3\text{H}_2\text{SiO}_4 + 4\text{Mg}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} \cdot \text{Mg}_2 \cdot \text{Al}_2 \cdot \text{Si}_3 \cdot \text{O}_10 \cdot \text{(OH)}_8 + 2\text{H}_2\text{O}$$

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

$$5\text{Ca} \cdot \text{Mg} \cdot (\text{CO}_3)_2 + \text{Al}_2 \cdot \text{Si}_3 \cdot \text{O}_10 \cdot \text{SiO}_2 + 2\text{H}_2\text{O}$$

orite + kaolinite + quartz = Mg$_2$Al$_2$Si$_3$O$_10$ (OH)$_2$ + 5CaCO$_3$ + 5CO$_2$

chlorite + calcite

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

$$3.5\text{Fe}^{3+} + 3.5\text{Mg}^{2+} + 9\text{H}_2\text{O} + 3\text{Al}_2\text{Si}_3\text{O}_10\cdot\text{(OH)}_2$$

= Fe$_{3.5}$Mg$_3$Al$_2$Si$_3$O$_10$ (OH)$_2$ + 14H$^+$

chlorite

However, in most cases chlorite in the late stages of diagenesis of pelitic sediments seems to derive from amorphous aluminium, 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:

$$\text{H}^- + \text{expandable clays} \xrightarrow{\text{reaction}} \text{interchange}$$

$$\left[\text{Al}^{3+}, \text{Fe}^{3+}, \text{Ca}^{2+}\right] \cdot (\text{OH})_2 \cdot \text{Mg}^{2+} \cdot (\text{OH})_2$$

$$\text{expandable clays} \xrightarrow{\text{time}} \text{chloritization}$$

heat

$$\text{clay} \xrightarrow{\text{time}} \text{chlorites}$$

heat

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

Figure 5 X-ray diffraction patterns of oriented clay specimens from North Sabine H-39 well after heating at 550°C for 1 hour. A 0.2 to 2.0 $\mu$m fraction, B < 0.2 $\mu$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 hydroxyaluminion 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 hydri 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 to 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 authogenesis 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, CO₂ favours the dissolution of calcite through the reaction
\[
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 = \text{Ca(HCO}_3\text{)}_2
\]

Once Ca(HCO₃)₂ has encountered a neutral pH, authigenic calcite is formed. This usually occurs in sandstones adjacent to shales. Calcite cement is also formed when K⁺ derived from feldspar dissolution substitutes absorbed Ca²⁺ or Mg²⁺ on the smectite surfaces, thus inducing the transformation of smectite to interstratified smectite-illite along with the expelled water (Foscoslos and Kodama, 1974). The exchanged calcium moves with HCO₃⁻, 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:
\[
2\text{CaCO}_3 + \text{Mg}^2⁺ = \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^2⁺
\]

When the concentration of iron in the expelled pore fluids increases, then ferroan dolomite and finally ankerite (CaMg₂Fe₂(OH)₆(CO₃)₃) 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)₃ 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 Co₂, 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 Foscoslos 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 of 1500 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 catagenesis, however, is the destruction of 2:1 layer silicates, as reported by Foscoslos and Powell.
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 absorbent 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 silicates 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 (Foscoslo 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; Foscoslo 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 may 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 dehydration 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 dehydration 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 dehydration of the clays, iron hydroxide precipitates on 2:1 layer silicates to form in the less than 2 μ fraction iron-rich chlorite and in the 2:1 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 catagenesis 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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