# Chapter 2 Subsurface Micro Structure

## Rock and Soil Minerals

If one is interested in the transport of more than a single component through porous media, it will soon be discovered that the relative rate of transport of components through the medium is strongly dependent on the minerals composing the medium. The flow of oil and water is strongly dependent on the wettability of these two phase on the pore surfaces. The wetting phase will be next to the pore surfaces and the nonwetting phase will occupy the interior portion of the pore space away from the surfaces. We will see later that the wettability is dependent on both the minerals and the composition of the fluids. Inorganic salts do not transport through rocks and soil without some retention compared to the water with which it is flowing. The surfaces of minerals have electrical charges which attract the ions of the opposite charge and repel the ions of the same charge. Solid organic minerals may adsorb or absorb organic components in the water.

The discussion of minerals will be divided into sandstone and carbonate facies [*definition*: (a) The aspect, appearance, and characteristics of a rock unit, usually reflecting the conditions of its origin; esp. as differentiating the unit from adjacent or associated units. (b) A mappable, areally restricted part of a lithostratigraphic body, differing in lithology or fossil content from other beds deposited at the same time and in lithologic continuity. (c) A distinctive rock type, e.g. “red-bed facies”, “black-shale facies”. (d) A body of rock distinguished on the basis of its fossil content. (e) The environment or area in which a rock was formed, e.g. “sandy-bottom facies”, “eolian facies”, “volcanic facies”.].

### Sandstone Minerals

We saw in the first chapter that sandstones were the result of deposition of minerals transported by the action of water, wind, and ice. The source of the minerals were mountains or erosion of sediments. The mountains are the result of the uplifting of the earth's crust and can consist of igneous, metamorphoric, or sedimentary rock. The minerals that will be found in a sediment will be a function of the source rock and the weathering or diagenesis that the minerals have undergone. Sediments near granite source (e.g. California-Nevada border) will consist of mostly quartz and feldspar. Sediments from sandstone source rock (e.g. Mississippi River delta) will be much more weathered and much if not all of the feldspar will be transformed to clay minerals. Sandstone are rocks composed primarily of silicate minerals, e.g., silica, feldspar, and clays.

### Silica

Silica (silicon dioxide) is the mineral generally most abundant in sandstone because the crystalline form of silica, **quartz**, is present in abundance in most non carbonate source rock (e.g., quartzite, granite, sandstone) and is the most durable of the common minerals. **Cryptocrystalline** silica is not as abundant but is equally durable as quartz. It can be of organic origin (e.g., **chert** or **flint** are metamorphic products of opal from diatoms) or from precipitation as **chalcedony** (e.g., agate, jasper). Cryptocrystalline silica is porous but the pores are so fine that it remains water saturated unless it is dried. **Opal** is a amorphous form of silica that can contain as much as 20% water as pore water and water of hydration. Opal formed by precipitation has been shown to consist of packed spheres which will diffract light in a "play of colors" if the conditions are right, i.e., precious opal. The opal of importance in petroleum reservoirs is diatomite, the sediment consisting of the skeletons of the single cell algae, diatoms. Diatomite has a porosity as high as 60% with most of the pore space within the body cavities. Billions of barrels of oil exist in diatomite formations in California in formations that may be one thousand feet thick. The challenge is that unfractured diatomite has a permeability that is much less than one millidarcy.

### Feldspar

Feldspar is a mineral that is abundant in igneous rocks such as granite. It constitutes 60% of the Earth's crust. Feldspar (as well as quartz) is a tectosilicate in which the silica tetrahedrons are linked in a three dimensional network. It has the general formula, $MAl(Al,Si)_3O_8$ ,where M = K, Na, Ca. The common feldspars are the potassium feldspars, **orthoclase** and **microcline,** the sodium feldspar, **albite**, and the sodium-calcium feldspar, **plagioclase**. Sandstone that contains abundant feldspar is called **feldspathic**. Feldspar is an abundant mineral that chemically decomposes in the presence of water to form clays. In some cases corroded feldspar grains have been observed with the clay mineral kaolinite replacing the feldspar grain.

### Clay

The clay minerals are layer silicate materials. The crystal lattice consists of two or three layers of silica ($SiO_2$) like or alumina ($Al_2O_3$) like layers. **Kaolinite** is a two layer (1:1 silica:alumina) clay that is often the first degradation product in the weathering of feldspar in an acidic environment. Common three layer (2:1 silica:alumina) clay minerals are **smectite**, and **illite**. These three layer clays have the crystal structure of the micas, muscovite and biotite. An example of a four layer clay is **chlorite**. It is sometimes found as the iron-rich chlorite, **chamosite**. A common feature of clays is that they are finely dispersed and thus have a large specific surface area.

### Iron Minerals

The most commonly observed iron mineral is **hematite** ($Fe_2O_3$, ferric oxide) and it hydrated forms, which are responsible for the red soils in parts of East Texas. Hematite exists in an oxidizing environment. In reducing environments the iron oxide commonly transforms to **siderite** ($FeCO_3$, ferrous carbonate) or **pyrite** ($FeS_2$).

### Carbonate Minerals

The common carbonate rock, **limestone**, is formed from marine animals. It is initially composed primarily of the mineral, **calcite** and **aragonite** ($CaCO_3$). Usually some magnesium is present and it will be called a low Mg calcite or low Mg aragonite. Magnesium containing brine (e.g., sea water) percolating through limestone will result in some of the calcium being replaced by magnesium and the resulting rock is called **dolostone** and the resulting mineral is called **dolomite** [$CaMg(CO_3)_2$] when it has equal amounts of calcium and magnesium. Iron (ferrous) carbonate is called **siderite**. When calcite has part of the calcium replaced with iron, it is called **ankerite** when it has equal amounts of calcium and iron. The green color in green marble is due to the solid solution of ferrous iron in calcite. When some the the calcium is replaced by manganese, a pink colored calcite will result. Pure $MnCO_3$ is the red minerial, **rhodochrosite**. If a deposit is associated with an **evaporite** from the drying of a sea, it may also contain calcium sulfate in form of **gypsum** ($CaSO_4 \cdot 2H_2O$) or **anhydrite (**without water).

## Diagenesis

Diagenesis is all the chemical, physical, and biologic changes undergone by a sediment after its initial deposition, and during and after its lithification, exclusive of superficial alteration (weathering) and metamorphism. **Lithification** is the conversion of a newly deposited sediment into a consolidated rock, involving processes such as cementation, compaction, desiccation, and crystallization.

### Compaction

Compaction begins immediately after deposition. If the sediment was deposited from a turbidite current, the sediment compacts as the solids settles and the water leaks out. As additional sediment accumulates the vertical stress on the sediment increases above that of the hydrostatic pressure because of the greater density of the solids (e.g., 2.65 $g/cm^3$) compared to the density of the water (e.g., 1.0 $g/cm^3$). Rearrangement and deformation of the load bearing mineral grains will occur as a result of this stress. If the grain mineral is quartz, there may be some rearrangement of the grains but only a small amount of deformation. If the grain mineral is a clay, there may be large rearrangement and deformation of the ductile clay platelets as in Figure 2.1. The pressure of the water in the pore space will increase above the hydrostatic pressure upon compaction unless the water is free to leak away, i.e., become **geopressured**. Upon deep burial depth additional compaction will occur through crushing and pressure dissolution at grain contact points. The porosity of a sand may decrease from 0.4 before compaction to 0.3 after compaction as a result of just mechanical compaction. Pressure dissolution can reduce the porosity to zero if given enough time.

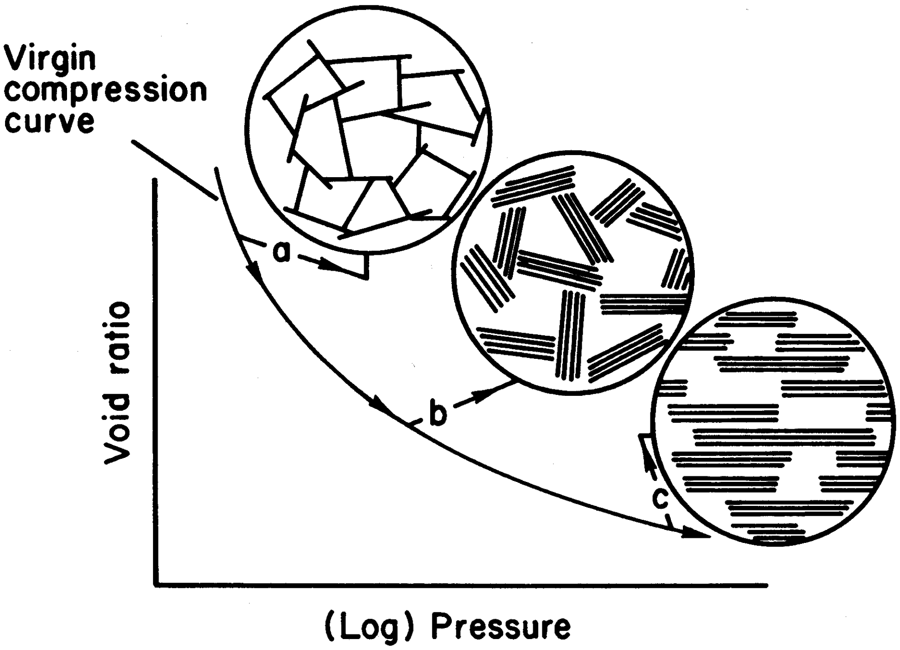


Fig. 2.1 Fabric changes during consolidation of a clay [Bennet and Hulbert 1986 (Ingles 1968)]

Figure 2.2 shows the change in porosity of clay/shale as a function of depth. The porosity of clay can be as high as 0.7 when first deposited. The curves showing high porosity at great depth is probably geopressured.

Figure 2.3 shows the porosity of sandstones as a function of depth. The data correlate with the geothermal gradient. Stress and burial time increase with depth but apparently the kinetics of pressure dissolution, which is a function of temperature, is also a factor.

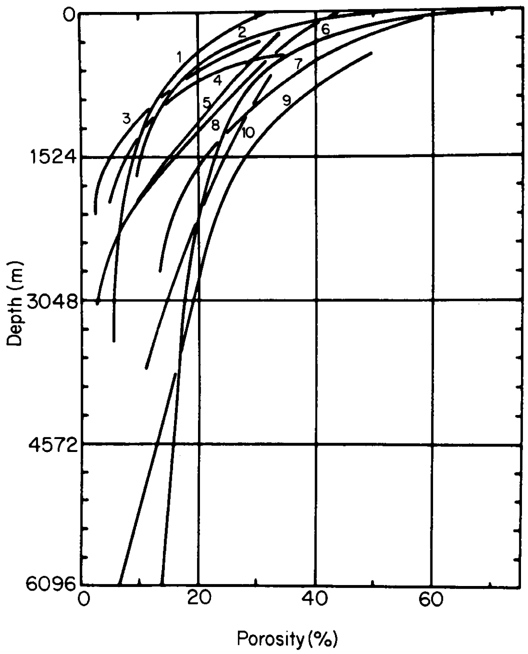


Fig 2.2 Porosity of clay/shale as a function of depth [Jenyon 1990 (Magara 1980)]

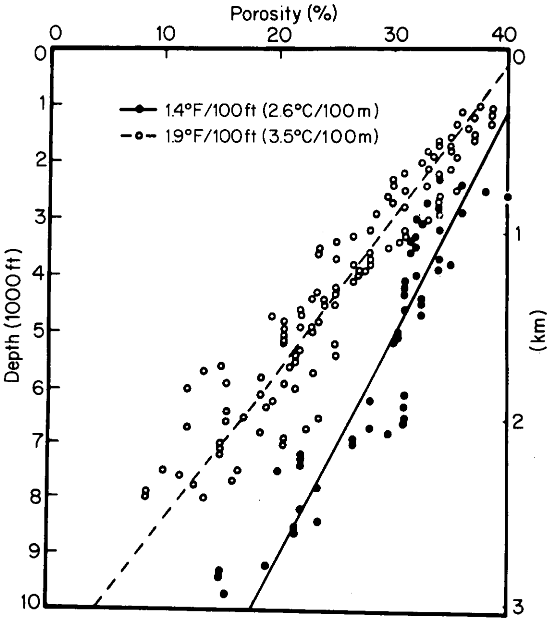


Fig 2.3 Porosity of sandstones with depth for two geothermal gradients [Jenyon 1990 (Magara 1980)]

## Cementation

Cementation is the partial or complete filling of the pore space with precipitated minerals. Cementation will change a **unconsolidated** sand to a **consolidated** sandstone. Common cementation minerals are silica, calcite, and clay minerals. In areas where rainfall is less than evaporation, the dissolved minerals will precipitate at the soil surface and cement the soil. If the precipitating mineral is calcite, the consolidated soil is called "**caliche**".

## Mineral Diagenesis

Minerals in rocks are distinguished between **detrital** minerals and **authigenic** minerals. A detrital mineral is any mineral that originated from the mechanical breaking of the parent rock and subsequent transport and deposition. An authigenic mineral is a mineral that formed or was generated in place. Precipitated silica or calcite are authigenic minerals but the most interesting are the authigenic clays generated by the weathering of feldspar.

The type of clay formed from the weathering of feldspar is dependent on the chemical environment of the feldspar. Feldspar is an alkaline mineral. In regions of high precipitation, the ground water will have an abundant supply of carbonic acid and a high flux of water to remove silica and feldspar will weather to kaolinite or even gibbsite ($Al_2O_3 \cdot 3H_2O$). In dry climates there is not enough water flux to remove the alkali ions ($K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$) and silica and as a result, smectite or illite are formed as authigenic clay minerals. The stability diagram in Figure 2.4 illustrates the authigenic minerals that can form from the weathering of the feldspar microcline with different concentrations of $SiO_2$ and the ratio of concentrations of $K^+/H^+$.

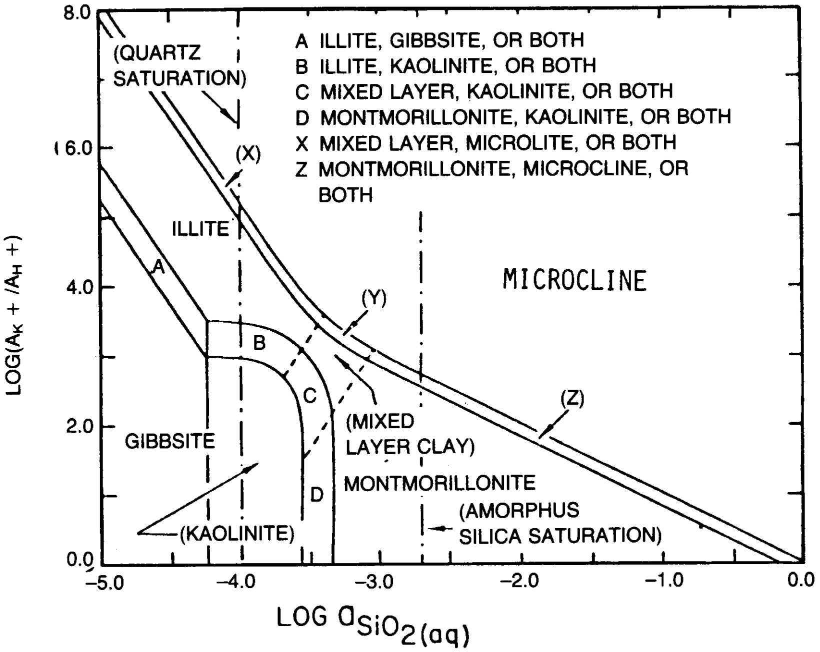


Fig. 2.4 Stability diagram of various minerals as a function of the concentration of $SiO_2$ and the ratio of concentration of $K^+/H^+$ [Aagaard andHelgeson 1982, (Bjorlykke 1989)]

An example of diagenesis without a chemical change is the transformation of the biogenic opal in diatomite to chert and finally to quartz with increased burial temperature and time. An example of chemical substitution is the replacement of a part of the calcium in calcite with magnesium to form dolomite. An example of diagenesis with a change of oxidation state is the reduction of ferric oxide in hematite to the ferrous ion in solution and precipitation as ferrous carbonate (siderite) or ferrous sulfide (pyrite).

**Lithification and Diagenesis of Carbonate Sediments**

Lithification is the process which turns loose sediment into rock. It occurs through new minerals (cements) being precipitated which bind together the primary particles or gragments. To cause precipitation of carbonate cement, we must have pore water which is oversaturated with respect to a carbonate phase. This may happen through sediment being flushed with oversaturated porewater. Cementing of beach sand takes place because it is flushed by surface water which washes in over the shore (Fig. 2.5). Beach sand which is cemented early in this manner is called *beach rock*. Beach rock may form in the span of only 10-20 years.

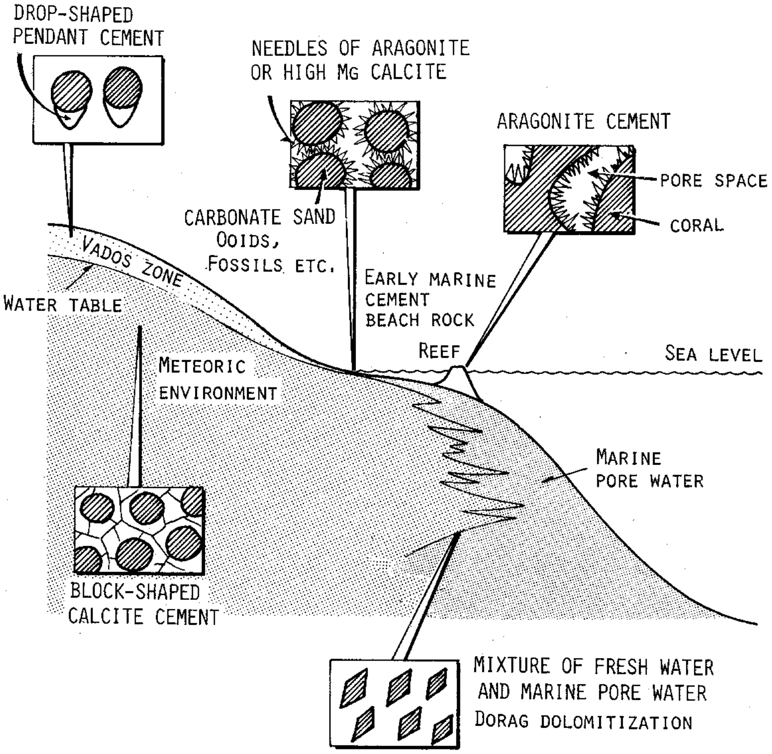


Fig. 2.5 Types of carbonate cement as a function of diagenetic environment. Reefs containing many fossils with high-Mg calcite and aragonite will turn into calcite, particularily if fresh water later percolates through the reef. (Bjorlykke, 1989)

In zones with meteoric water (groundwater), calcite cement is formed because the low $Mg^{2+}$ content makes it easier to precipitate calcite directly. Freshwater may dissolve the more soluble aragonite from fossils and ooids, and precipitate calcite which grows in large crystals (block-shaped cement). When calcite replaces earlier aragonite or high-Mg calcite by *neomorphism* [*def*. all transformations between one mineral and itself or a polymorph, whether the new crystals are larger or smaller is simply differ in shape from the previous ones, or represents a new mineral species.], we sometimes see “ghosts” of the earlier crystals, Fig. 2.6. If the more soluble mineral is dissolved but not replaced, then a cavity or “*vug*” may remain. Vugs formed in this manner may not be connected except through the microporosity in the surrounding matrix. This type of vug is

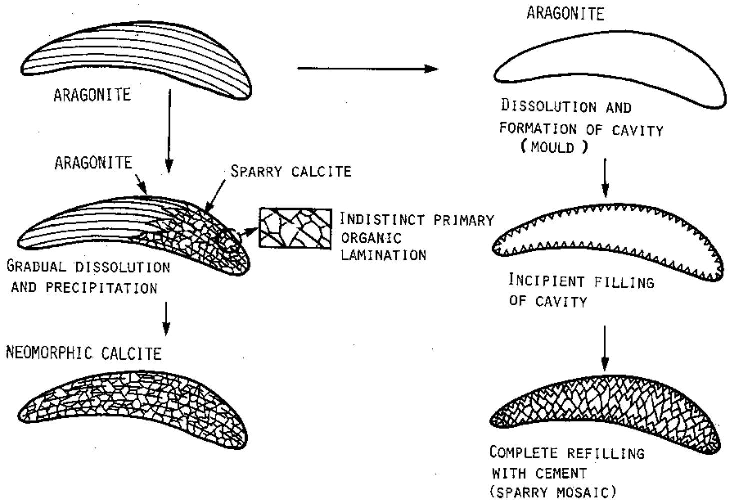


Fig. 2.6 Two types of conversion of aragonite to calcite. Left, neomorphic replacement. Right, solution and precipitation in the cavity. (Bjorlykke, 1989)

called a *separate-vug* pore space to distinguish from *touching-vug* pore space.

Compaction can occur in carbonate sediments, similar to sandstones. Besides mechanical crushing of grains due to the force of the overburden, chemical dissolution (pressure solution) at the points on contact is important because of the relatively greater solubility of the carbonate minerals.

Solution of grains due to pressure will often be concentrated in particular horizons. *Stylolites*, which are surfaces where a considerable amount of solution has taken place, will often form. The horizon will be enriched with finely divided silicate minerals and other insoluble materials in the sandstone (Fig. 2.7). Clay minerals seem to enhance pressure solution and stylolites may start forming along primary clay lamellae.

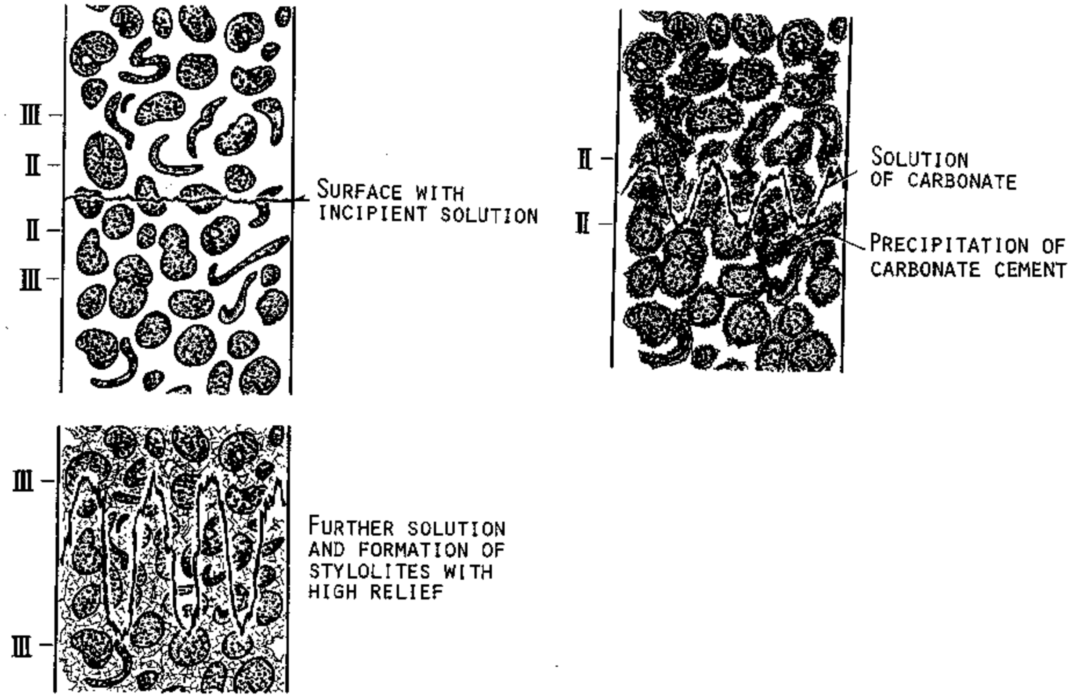


Fig. 2.7 Development of stylolites in carbonate grainstone. (Bjorlykke, 1989)

The term “dolomite” is used to designate both a mineral and rocks in which this mineral is the main constituent. The mineral dolomite [$CaMg(CO_3)_2$], consists of layers of $CO_3^{2+}$ groups alternating with layers of $Mg^{2+}$ and $Ca^{2+}$. This crystal structure is highly organized thus entropy does not favor it formation compared to calcite. Also $Mg^{2+}$ is strongly hydrated and in aqueous solution and thus its activity is less than the concentration. These two effects are less significant at elevated temperatures. Dolomite is not formed directly, but as a secondary mineral and as a result of reaction between different forms of $CaCO_3$ and $Mg^{2+}$.

$$2CaCO_3 + Mg^{2+} \rightleftharpoons CaMg\left(CO_3\right)_2 + Ca^{2+}$$

In sea water there is far more magnesium than calcium ($Mg^{2+}/Ca^{2+} \approx 5$), and except for the hydration effect, we would expect magnesium carbonates to be the predominant minerals formed. However, the sulfate ion $\left(\mathrm{SO}_4^{2+}\right)$ is very efficient at preventing dolomitisation. Consequently, it takes place more easily when there are few sulfate ions. Mixing with fresh water will lower the sulfate concentration without necessarily changing the $Mg^{2+}/Ca^{2+}$ ratio.

The significance of dolomitisation it that the process creates secondary porosity because calcite or aragonite dissolves and the precipitated dolomite does not fill the entire volume which has been dissolved away. Dolomite has approximately 12% smaller molar volume than calcite, and this fact may help to explain why dolomitisation leaves extra pore space. Since dolomitisation involves large-scale percolation of porewater, we may also have net leaching associated with the process. This means that the volume of dolomite precipitated is less than the volume of calcite dissolved. Fine-grained, early diagenetic dolomite has a low permeability, and if it is not fractured it has poor reservoir quality. Dolomite formed at greater depths tend to have larger crystals (0.1-1.0 cm), and its permeability may consequently be very high if there is intercrystalline porosity. Crystalline dolomite may be *sucrosic* (sugary appearing) with crystals interlocking at different angles, generally allowing space for considerable porosity between crystals.

The carbonate diagenesis process most familiar to the non-specialist is the formation of *caverns* by pore water dissolution. Precipitation by loss of carbon dioxide from the water leads to deposition of a banded (laminated) carbonate called *travertine*. *Stalactite* and *stalagmite* are travertine deposits hanging from the ceiling or growing on the floor of caverns. The collapse of the ceiling of caverns may result in accumulation of angular, broken rock fragments, called *breccia*.

## Morphology of the Pore Space

### Grain Size, Shape and Packing

The grain size can be quantified by measuring the grain diameter. The chart in Figure 2.8 relates the grain diameter to the common nomenclature of sand, silt, clay, ect.

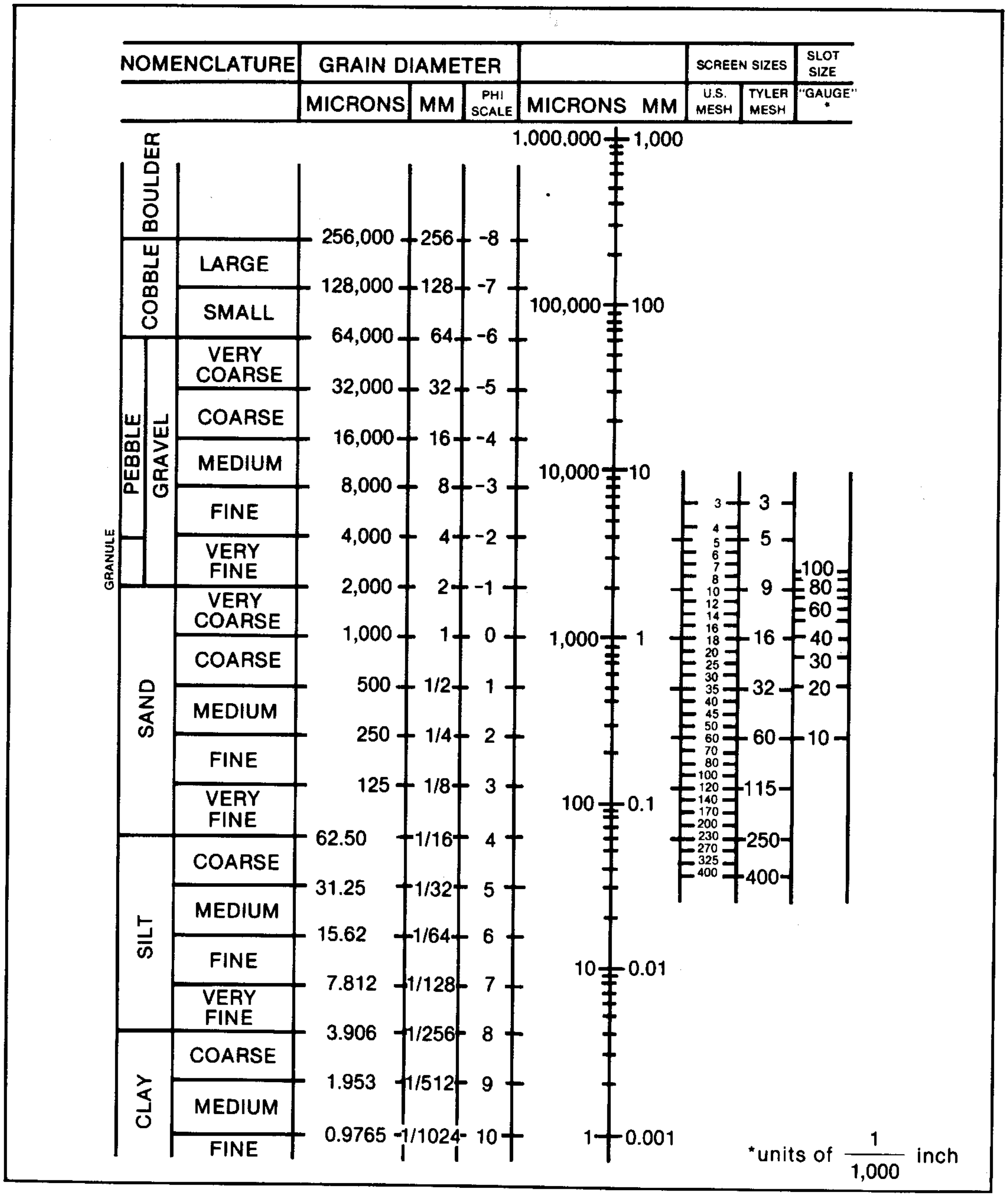


Fig. 2.8 Classification of clastic rocks according to texture (Jorden 1984)

The **shape** of sand grains can be described by its roundness and sphericity. **Roundness** describes the angularity of the particle. **Sphericity** describes the degree to which the particle approaches a spherical shape. Figure 2.9 shows the difference between roundness and sphericity.

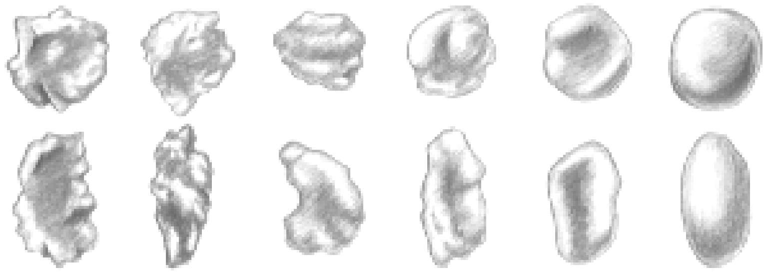
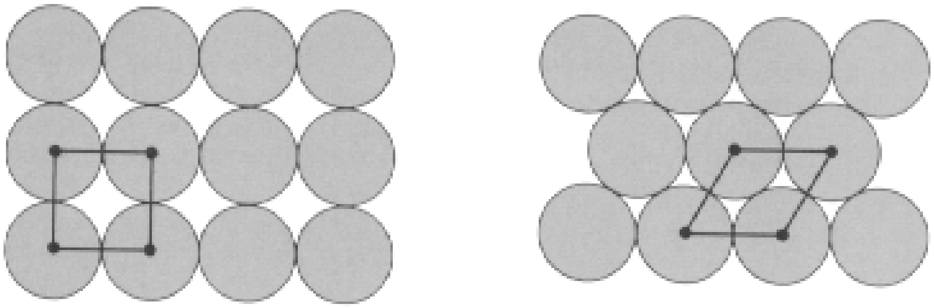


Fig. 2.9 Sand grains showing the difference between roundness and sphericity (Selley 1985)

The **packing** of sand is best illustrated by showing the packing of uniform spheres that give the maximum and minimum porosity, Figure 2.10. Random packing will result in a porosity of about 0.4.



Cubic packing
(48% porosity)

Rhombohedral packing
(26% porosity)

Fig. 2.10 Cubic packing of spheres has a porosity of 0.48; rhombohedral packing has 0.26 (Selley 1985)

### Clay Distribution and Morphology

The manner in which clays are distributed in the pore space has an important bearing on its effect on permeability. Pore lining and pore filling clays will greatly reduce the permeability while the replacement or fracture filling clays will have less effect. See Figure 2.11 below.

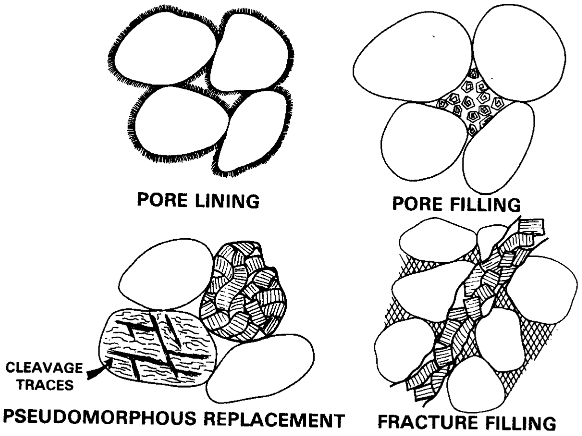


Fig. 2.11 Types of cement formed by authigenic clay minerals in sandstones [Bjorlykke 1989 (Wilson and Pittman 1977)]

The clay minerals have different morphology that makes them easy to identify. Figure 2.12 shows electron micrographs of kaolinite and illite in sandstone. Authigenic kaolinite precipitates in packets that has a "book-like" appearance. Illite is fibrous and occupies more of the pore space for a given mass of clay. Sometimes the illite is so delicate that the clay is "matted" down by ordinary drying and rock samples with illite should be cleaned with "critical-point" drying. Figure 2.113 shows pore lining chlorite, an example of a pore lining clay.

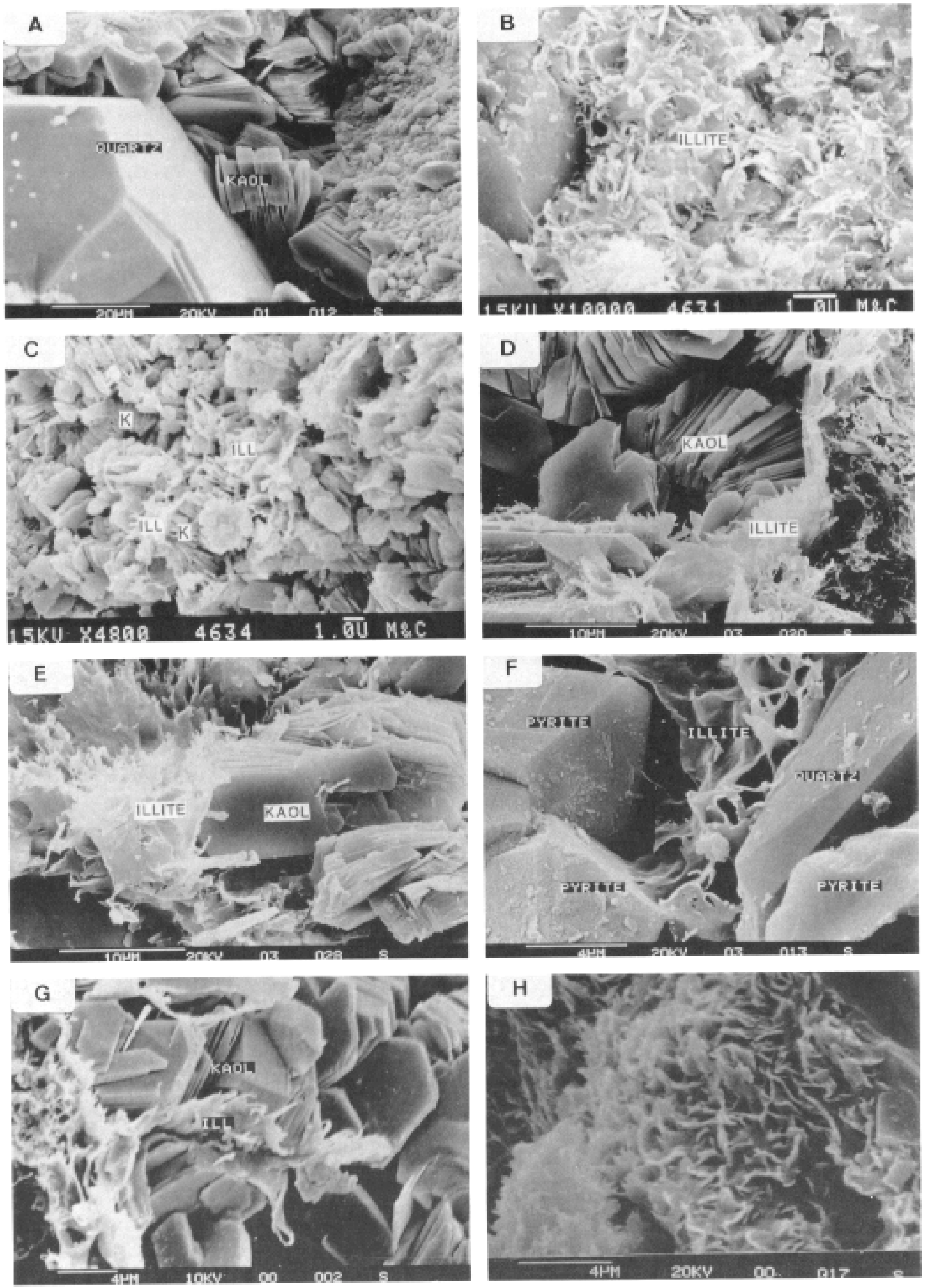


Fig. 2.12 SEM photomicrographs of kaolinite and illite in sandstone (Houseknecht and Pittman 1992)

Fig. 2.13 SEM picture of grain-coating authigenic chlorite (Bjorlykke 1989)

The clay that has the greatest effect on flow properties is smectite. It exists in thin sheets whose separation is governed by the balance between van der Waals attraction and electrostatic repulsion. If the electrolyte concentration becomes low enough the sheets will separate and be carried by the water until it lodges in a pore throat. Sandstones containing smectite is called "fresh water sensitive" rock. Figure 2.14 is a TEM (transmitting electron microscope) picture of sheets of smectite on a TEM grid.

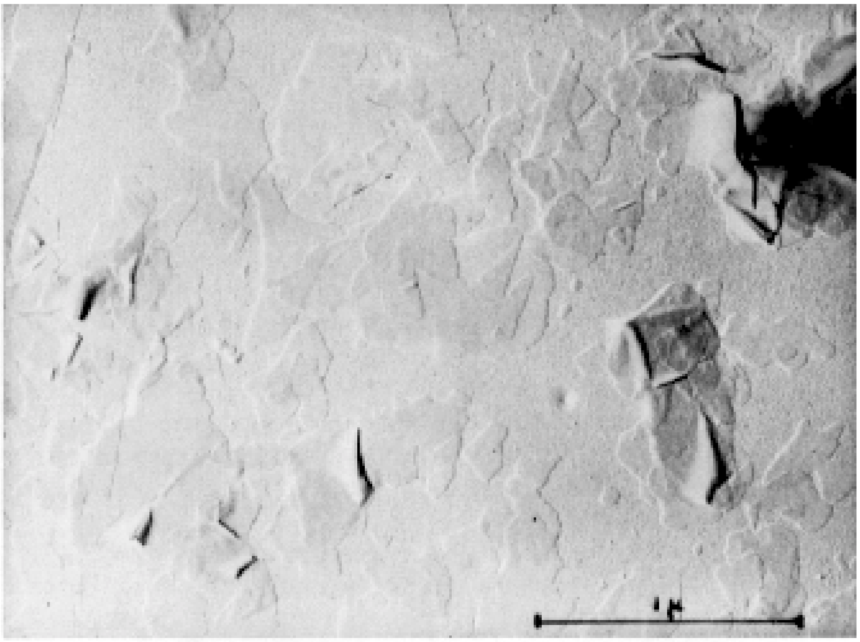


Fig. 2.14 TEM picture of the smectite, Wyoming bentonite on a TEM grid (van Olphen 1977)

## Morphology of Carbonate Rocks

There are several classifications for carbonate rocks. The classification we use here is the Dunham classification which is analogous to sandstones in that it is based on particle size. This classification is related to the energy of the deposition environment, see Fig. 2.15.

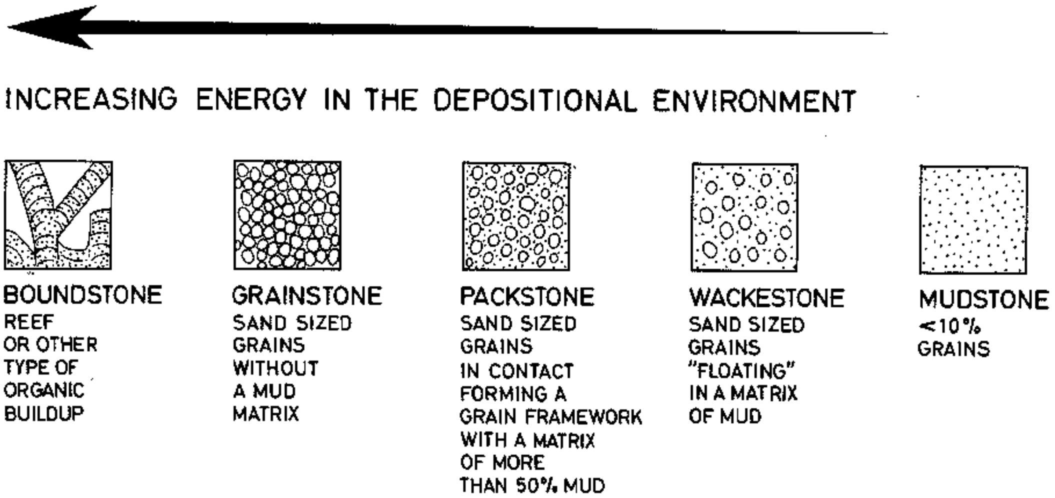


Fig. 2.15 Dunham's classification of carbonate rocks is based on particle size and thus on the energy of the depositional environment (Bjorlykke, 1989)

Lucia suggested that in addition to classification by particle size, additional description by sorting and interparticle porosity will better describe the petrophysical properties of carbonate rocks, Fig. 2.16.

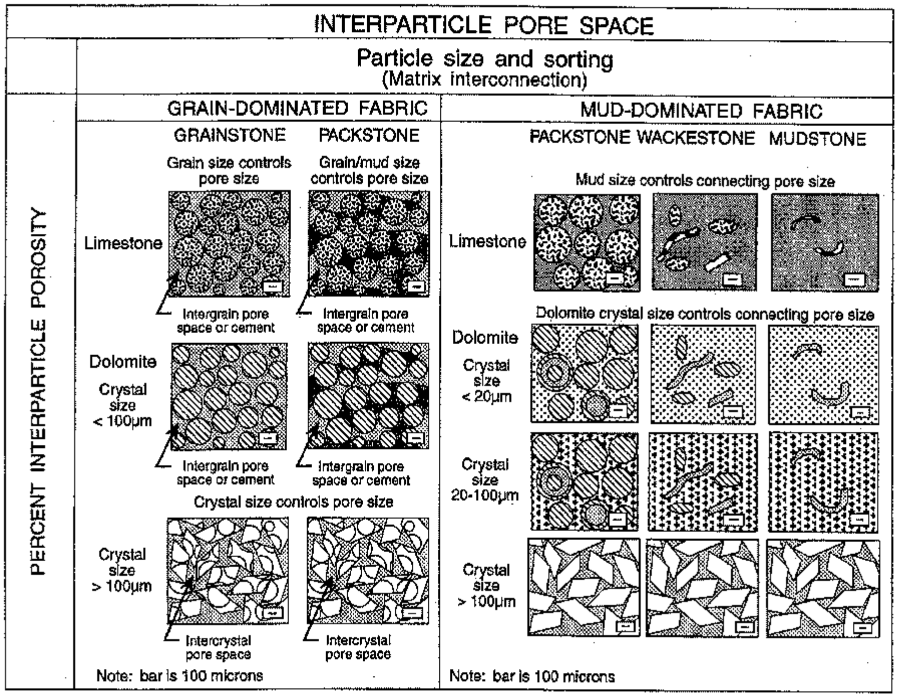


Fig. 2.16 Classification of carbonate rocks based on size and sorting of grains and crystals. (Lucia, 1999)

### Classification of Vuggy Pore Space (Lucia, 1999)

A *vug* is is often referred to a pore or cavity that is much larger than the surrounding pores. Lucia (1999) has classified vuggy spore space as *separate-vug* and *touching-vu*g pore spaces. He has defined separate-vug pore space as pore space that is 1) either within particles or is significantly larger than the particle size (generally >2× particle size), and 2) is interconnected only through the interparticle porosity, Fig. 2.17. The pore space within grain particles is often called *intra-particle* porosity or *micro-porosity* rather than separate-vug porosity, and that is the practice we will use here. Separate vugs are typically fabric-selsective in their origin. Intrafossil pore space such as the living chambers of a gastropod shell; moldic pore space, such as dissolved grains (oomolds) are examples of intraparticle, fabric-selective separate vugs.

Touch-vug pore systems are defined as pore space that is 1) significantly larger than the particle size and 2) forms an interconnected pore system of significant extent, Fig. 2.17. Touching vugs are typically nonfabric selective in origin. Caverous, breccia, fracture, and solution-enlarged fracture pore types commonly form an interconnected pore system on a reservoir scale and are typical touching-vug pore types. Fracture porosity is included as a touching-vug pore type because fracture porosity is an important contributor to permeability in many carbonate reservoirs.

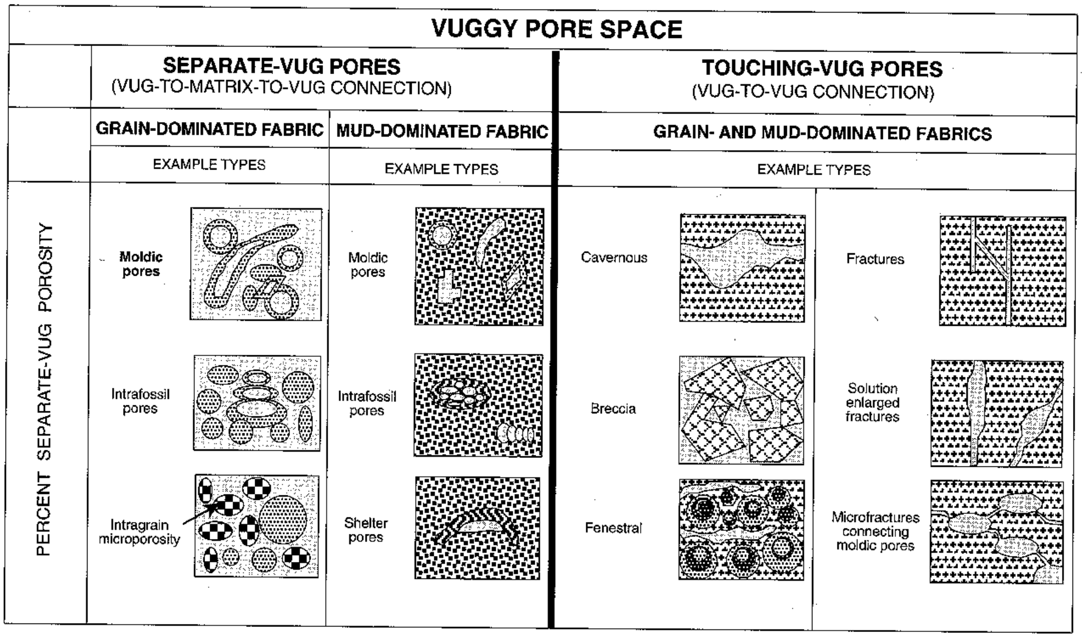


Fig. 2.17 Geological/petrophysical classification of vuggy pore space based on vug interconnection. (Lucia, 1999)

### Examples of Carbonate Pore Types

The following photographs are examples of the various carbonate pore types. Fig. 2.18 is a scanning electron microscope image of a chalk formation. Note that the scale is 5 microns. Fig. 2.19-21 are thin-section micrographs.

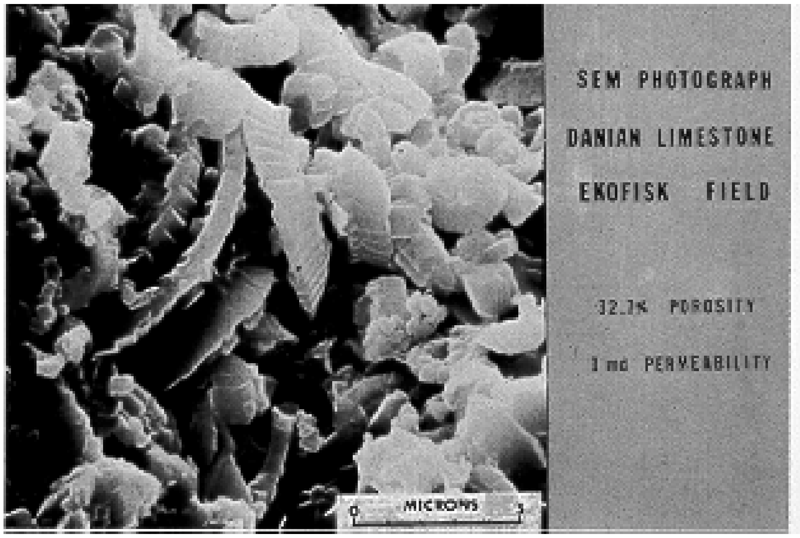


Fig. 2.18 Coccoliths from the upper part of the Upper Cretaceous in the Ekofisk field. Petroleum occurs between the small plate-like coccolithophore shells (about 5 microns). The chalk limestone has 32% porosity and 1 md permeability. (Bjorlykke, 1989)

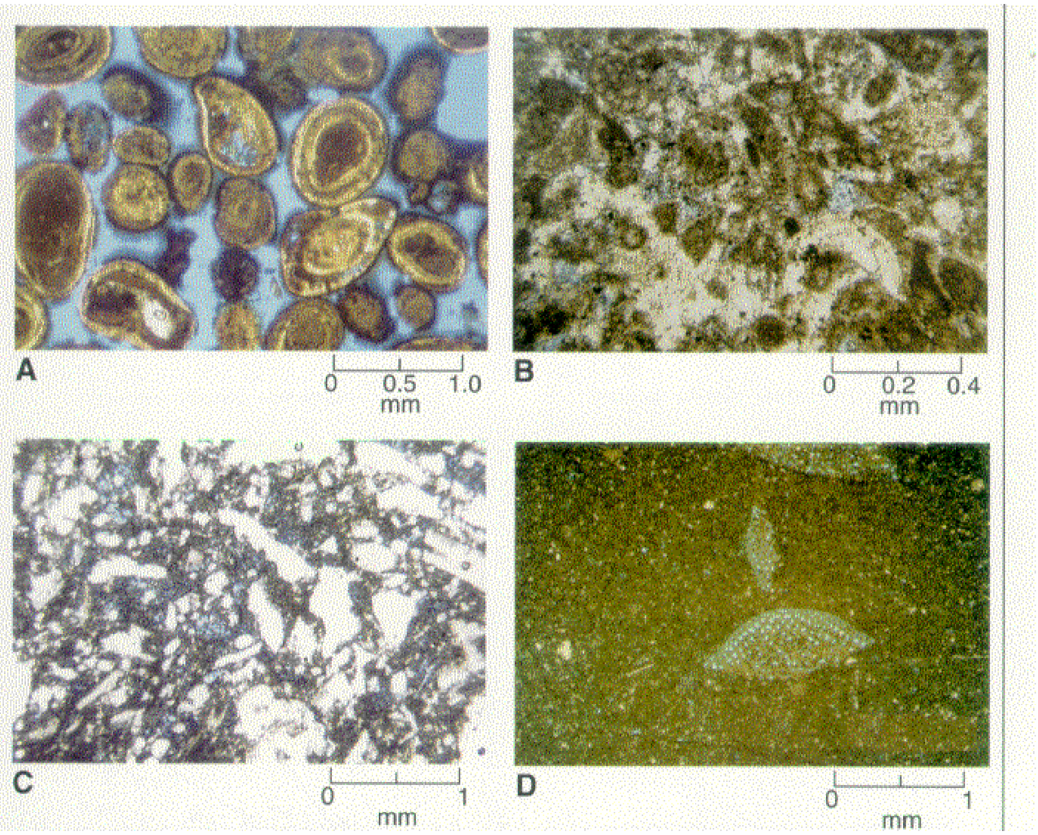


Fig. 2.19 Examples of nonvuggy limestone fabrics. **A** Grainstone, $\phi$=25%, $k$=15,000 md. **B** Grain-dominated packstone, $\phi$=16%, $k$=5.2 md. Note intergrain cement and pore space. **C** Mud-dominated packstone, $\phi$=18%, $k$= 4md. Note microporosity. **D**. Wackestone, $\phi$=33%, $k$=9 md. (Lucia, 1999)

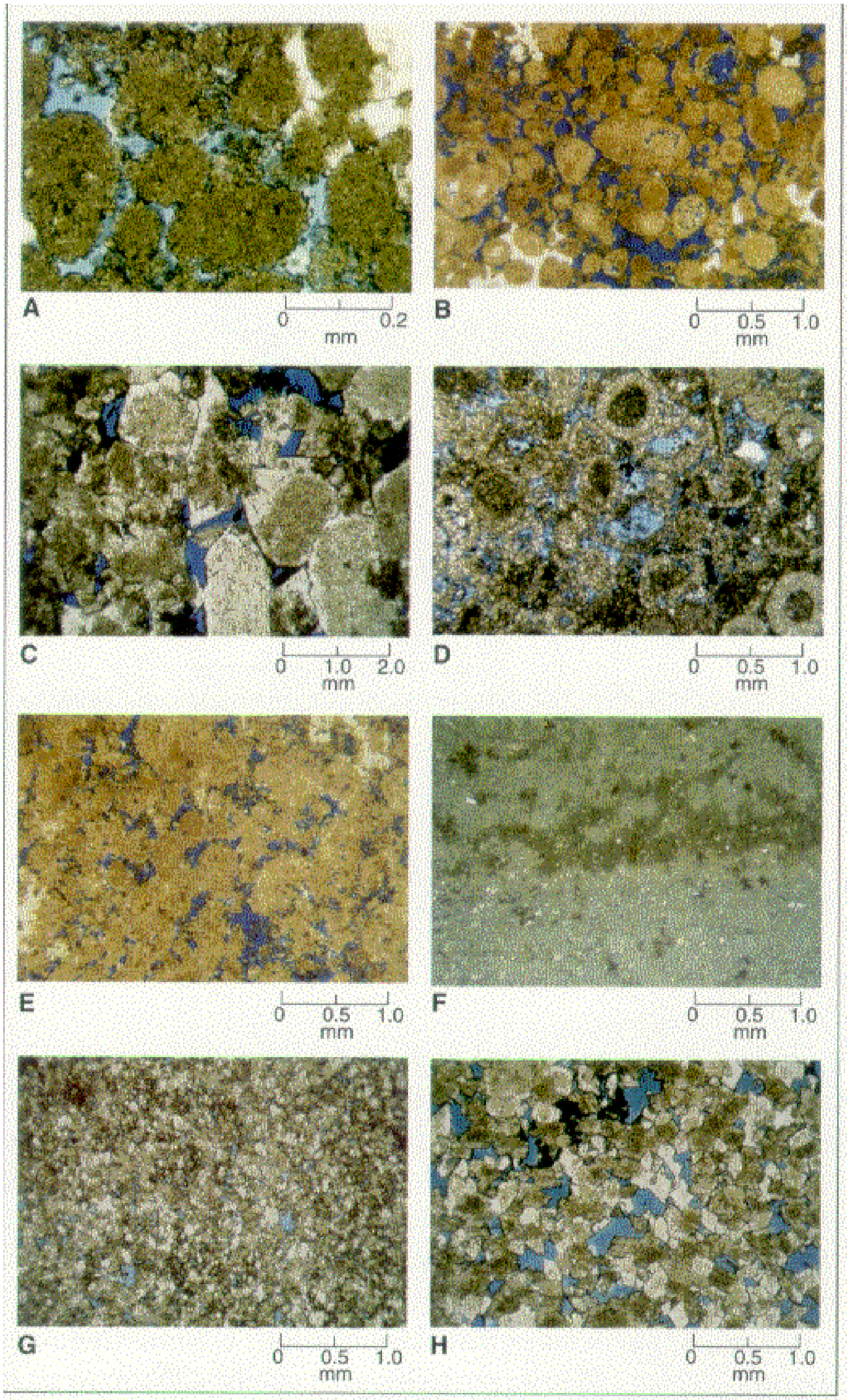
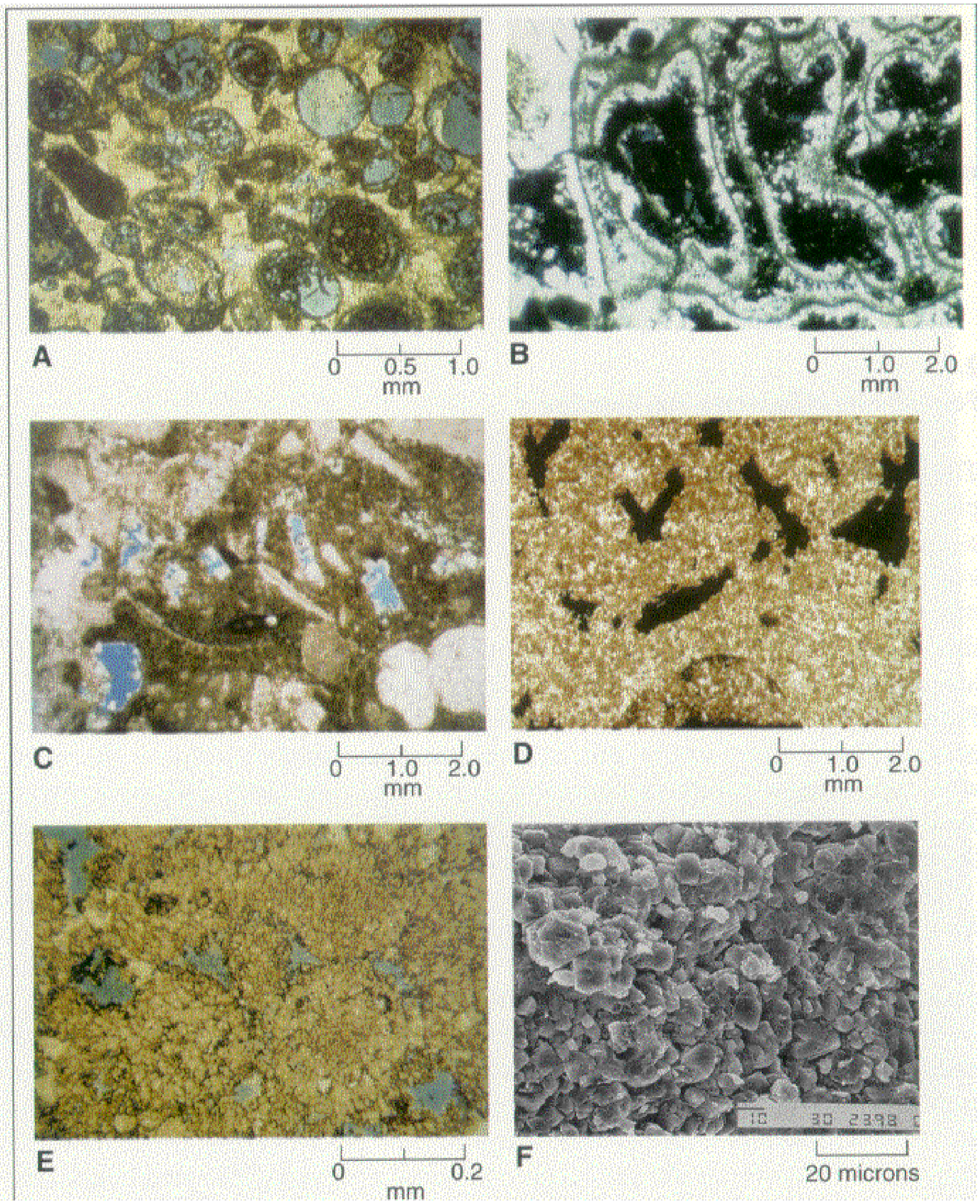
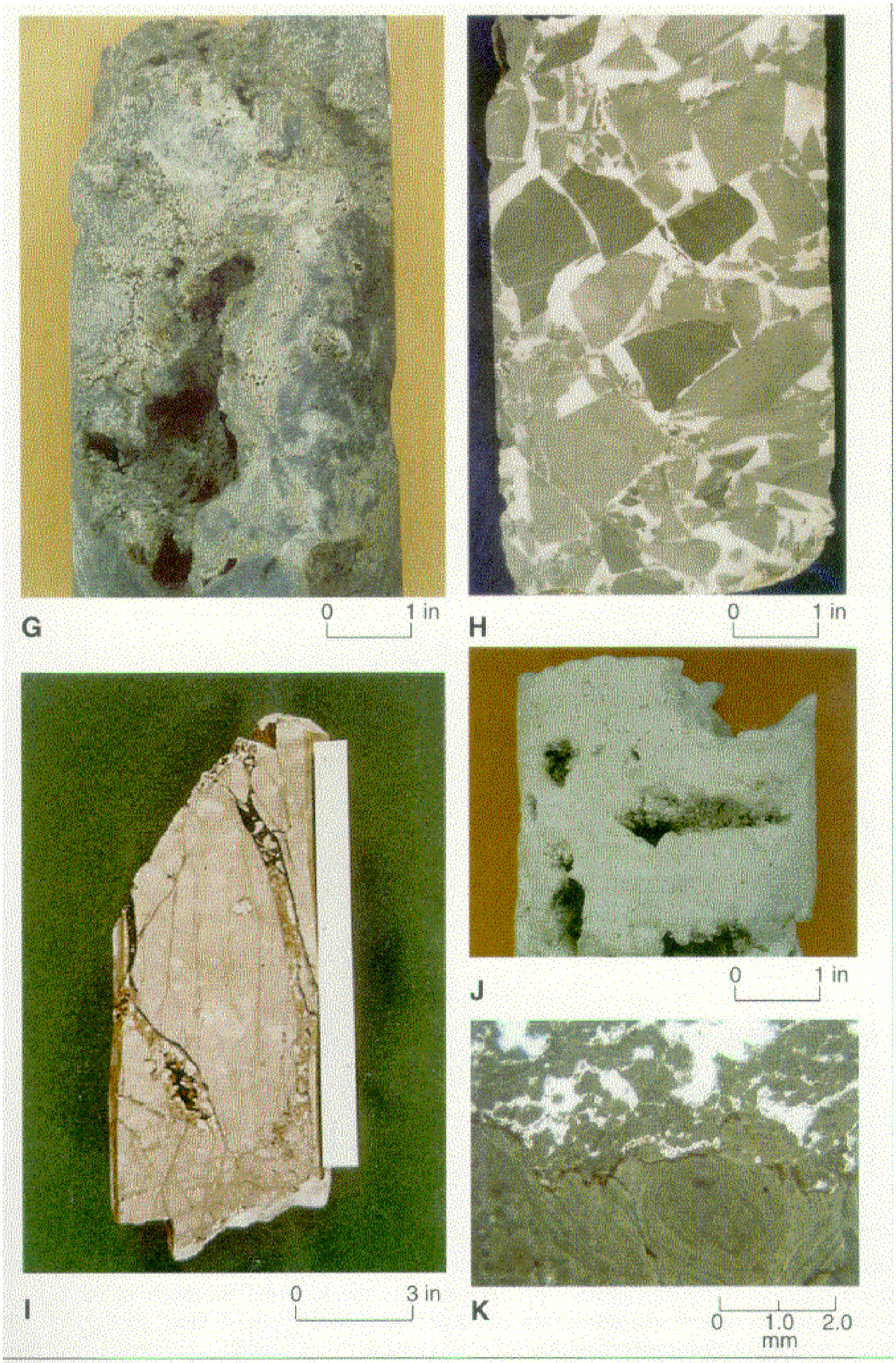


Fig. 2.20 Examples of nonvuggy dolomite fabrics. **A** Dolostone, 15-µm dolomite crystal size, $\phi=16.4\%$, $k=343$ md, Dune field (Bebout et al 1987). **B** Dolograinstone, 30-µm dolomite crystal size, $\phi=7.1\%$, $k=7.3$ md, Seminole San Andres Unit, West Texas. **C** Dolograinstone, crystal size 400 µm, $\phi=10.2\%$, $k=63$ md, Harmatton field, Alberta, Canada. **D** Grain-dominated dolopackstone, 10-µm dolomite crystal size, $\phi=9\%$, $k=1$ md, Farmer field, West Texas. **E** Grain-dominated dolopackstone, 30-µm dolomite crystal size, $\phi=9.5\%$, $k=1.9$ md, Seminole San Andres Unit, West Texas. **F** Fine crystalline dolowackestone, 10 µm dolomite crystal size, $\phi=11\%$, $k=0.12$ md, Devonian, North Dakota.

**G** Medium crystalline dolowackestone, 80 μm dolomite crystal size, ϕ=16%, *k*=30 md, Devonian, North Dakota. **H** Large crystalline dolowackestone, 150 μm dolomite crystal size, ϕ=20%, *k*=4000md, Andrews South Devonian field, West Texas. (Lucia, 1999)




G
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1 in
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mm

Fig. 2.21 Examples of vug pore types. *Separate-vug types*: **A** oomoldic porosity, $\phi$=26%, *k*=3md, Wolfcampian, West Texas. **B** Intrafossil porespace in a gastropod shell, Cretaceous, Gulf Coast. **C** Fossil molds in wackestone, $\phi$=5%, *k*=0.05 md. **D** Anhydrite molds in grainstone dominated packstone, $\phi$=10%, *k*<0.1 md, Mississipian, Montana. **E** Fine crystalline dolograinstone with intergranular and intragranular microporosity pore types, $\phi$=10%, *k*=3md, Farmer field, West Texas. **F** Scanning electron photomicrograph of dolograinin E showing intragrannular microporosity between 10-μm crystals. *Touching-vug types*: **G** Cavernous porosity in a Niagaran reef, northern Michigan. **H** Collapse breccia, Ellenberger, West Texas. **I** Solution-enlarged fractures, Ellenburger, West Texas. **J** Cavernous porosity in Miami oolite, Florida. **K** Fenestral porosity in pisolith dolostone. Note that the fenestral pores are more than twice the size of the enclosing grains. (Lucia, 1999)

## Mineral Surface Chemistry

### Hydrogen Bonding of Water

When more than one phase is flowing through porous media, the flow behavior is strongly dependent on which phase is wetting the mineral surfaces. The wettability of surfaces with respect to water is often described as **hydrophilic** (water loving) or **hydrophobic** (water hating). An example of a hydrophilic surface is a clean glass plate where water will drain as a film, even to thickness where interference colors can be seen. An example of a hydrophobic surface is a freshly waxed automobile surface where rain water will bead up. Whether a mineral surface is hydrophilic or hydrophobic depends on whether or not the surface has a greater affinity for water than water does for itself. The reason why water has such a large surface tension of 72 mN/m (or dyne/cm) is because 51 mN/m is due to hydrogen bonding. The van der Waals component of the surface tension is only 21 mN/m, about the same value as for n-pentane. Compared to hydrocarbons of similar molecular size, water has large surface tension, density, viscosity, normal boiling point, and heat of vaporization because water has intermolecular interactions due to hydrogen bonding in addition to the usual van der Waals interactions. The hydrogen bonding interactions in water come about because the electronic structure of the water molecule has two electropositive sites located near the hydrogen atoms and two electronegative sites near the oxygen atom on the side opposite to where the hydrogen atoms are located.

The surface of clean, hydroxylated silica has a strong affinity for water. Even though the molecular formula for silica is $SiO_2$, the molecules at the surface can be terminated with hydroxyl (-OH) groups. The Si-OH group is called the silanol group. Investigations on the adsorption of water on hydroxylated silica have shown the water firsts adsorbs in steps corresponding the filling the first two layers. Adsorbed water films greater than 10 nm thick have been measured on hydroxylated silica. The enhanced (compared to physical adsorption with only van der Waals interactions) is thought to be due to hydrogen bonding as illustrated in Figure 2.22.

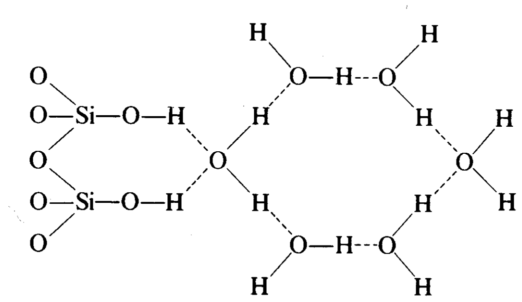

Fig. 2.22 Hydrogen bonding of water on silanol sites on silica surface (Iler 1979)

## Surface Charge

Surfaces in aqueous medium have a electrical charge that can be measured by a method such as electrophoresis. For example, Figure 2.23 shows the surface charge of mineral surfaces and electrophoretic mobility (proportional to charge) of some organic materials as a function of the pH.

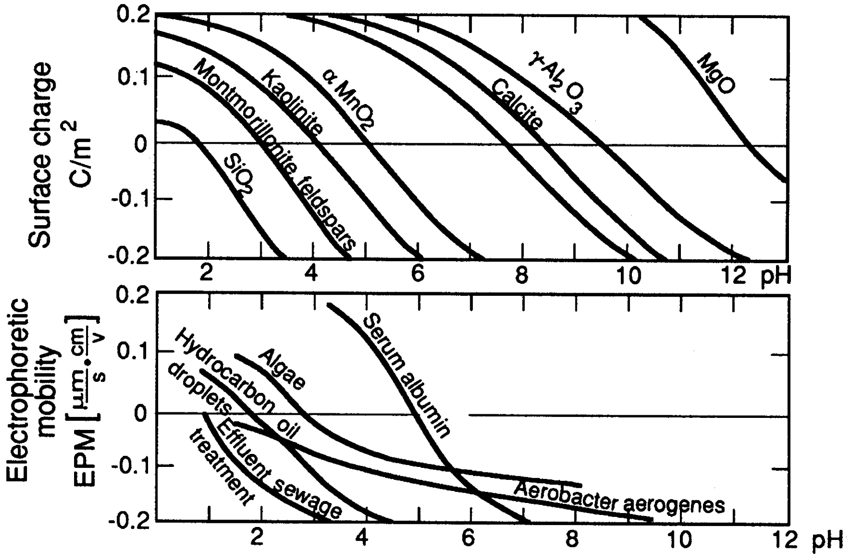

Fig. 2.23 Effect of charge and electrophoretic mobility.(Stumm 1992)

When the two surfaces have charge with the same sign, there will be an electrostatic repulsion between the surfaces. When the two surfaces have charges with opposite sign, there will be electrostatic attraction between the surfaces. The charge that is a function of pH is thought to be due to disassociation or protonation of surface functional groups such as -Si-OH, -Al-OH.

Clay and mica surfaces have a greater charge that that which can be attributed to protonation or dissociation. The primary mechanism for the surface charge on these surfaces is due to isomorphous substitution. The structure of a three layer clay or mica is illustrated in Figure 2.24. If each tetrahedral cell contained a silicon atom and each octahedral cell contained an aluminum atom, then the charges would be balanced and there would be no net charge. However, if Al is occasionally substituted for Si in the tetrahedral sheet or if Ca or Mg is occasionally substituted for Al in the octahedral sheet, then there would be a net negative charge that must be compensated by adsorption of a cation on the surface. It is this mechanism that results in the large cation exchange capacity of clays (especially smectite).

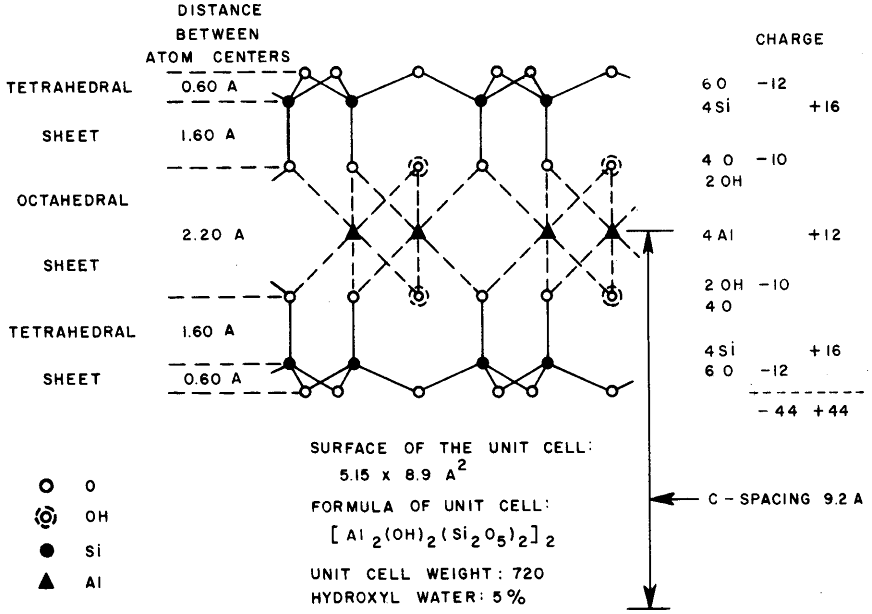

Fig. 2.24 Atomic arrangement in the unit cell of a 2:1 layered clay (van Olphen 1977)

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