Chapter 7
DIAGENESIS

1. INTRODUCTION

1.1 *Diagenesis* is the term used for *all of the changes that a sediment undergoes after deposition and before the transition to metamorphism*. The multifarious processes that come under the term diagenesis are chemical, physical, and biological. They include compaction, deformation, dissolution, cementation, authigenesis, replacement, recrystallization, hydration, bacterial action, and development of concretions. (Soft-sediment deformation can be included in diagenesis, but not hard-rock folding and faulting.) You can see from that complete, albeit not exhaustive, list that diagenesis involves a wide range of disparate, but in many cases related, processes. If you like, you could think of diagenesis as weird and terrible things that happen to sediments when they are buried.

1.2 The two most important diagenetic processes are *compaction* (the topic of a later section), and *lithification*, the term used for the complex of processes—including compaction—by which a loose sediment is converted into a solid sedimentary rock. A variety of processes mentioned or described in later sections of this chapter contribute to the general process of lithification.

1.3 The study of diagenesis continues to be an active field of research in sedimentary geology, in part because the variety and complexity of the processes involved has left many uncertainties, but also because of the importance of diagenesis to petroleum geology, inasmuch as diagenesis is a significant control on porosity and permeability of deeply buried sedimentary rocks, comprising the fine siliciclastic source beds, the coarser reservoir rocks, and the seals that cause those reservoir rocks to be petroleum reservoirs. Diagenesis is an essential aspect, although quite different in processes and effects, of mudrocks, sandstones, and carbonate rocks.

1.4 This chapter concentrates on the most important diagenetic features and processes in mudrocks, sandstones, and carbonate rocks. You have already learned some things about diagenesis of cherts and evaporites in the preceding chapter.

2. COMPACTION

2.1 Most sediments deposited under normal surface conditions have primary porosities of on the order of 30% to 70%. The lower values are more typical of coarser, sandy sediments, and the higher initial porosities are more typical of finer-grained, clay-rich sediments. Porosity in conglomerates and sandstones is largely

a matter of pore spaces among the framework grains, as modified by later cementation together with certain other diagenetic changes (more on those later). In muds the initial porosity is commonly higher, owing largely to the tendency for clay-mineral particles to be surrounded by envelopes or cushions of tightly bound water. Porosity in carbonate rocks varies widely, depending upon sediment type: the porosity of well-sorted carbonate sands is in the same general range as that of the corresponding siliciclastic sands, whereas reef carbonates commonly have much higher initial porosities.

BACKGROUND: FLUID PRESSURE AND ROCK PRESSURE IN THE SUBSURFACE

1. Provided that connected porosity exists between the material at some depth and the surface, the fluid pressure in the pore spaces of a sediment or sedimentary rock at some depth below the surface is just the hydrostatic pressure. It's the same as filling a tall drinking glass with loose sand and then filling it to the top with water. The pressure at the base of the glass is the ***hydrostatic pressure***— and is the same as if the sand were not there.

2. In the sand-filled drinking glass, at any given horizontal level in the glass the entire submerged weight of the sand above that level is borne by the grain-to-grain contacts at that level. That's called the ***lithostatic pressure***.

3. Complications come where the pore spaces at a given depth are not freely connected upward to the surface. In that case, the fluid pressure can exceed the hydrostatic pressure, by a variety of effects. Then the lithostatic pressure is less, because some of the weight of the overlying sediment is borne by the excess fluid pressure.

4. Fluid pressures greater than hydrostatic are *characteristic of sedimentary basins*. In depositional settings where sedimentation is faster than compaction, fluid overpressure can develop. This is of great importance in both sediment diagenesis and petroleum generation and migration.

5. In SI units, the lithostatic pressure might be measured in kilograms per square meter. You could figure that out for any given depth by knowing the bulk density of the sediment or sedimentary rock. Lithostatic pressure within the Earth is usually quoted as kilobars. To convert from kilograms per square meter to bars, multiply by 10^{-4}.

2.2 Most fine-grained sediments lose pore water soon after deposition by ***consolidation***, the process by which clay-rich mud is changed to mudstone. This

is largely a consequence of compaction due to overburden pressure (that is, the weight, per unit area, of the overlying layer of later-deposited sediment). The compaction of clay at shallow depths has been studied intensively by civil engineers because of building requirements. The effects of compaction at greater depths is of interest to exploration geologists because to the need to understand ***porosity occlusion*** (by that term is meant the *partial elimination of pore spaces*) and its impact on the evolution of possible reservoir rocks.

2.3 At all depths below the usually shallow position of the groundwater table, the pore spaces of all sediments and sedimentary rocks are *filled with water* (or, more accurately, *aqueous pore solutions*, owing to the presence of solutes). Upon compaction, the expelled water has to go somewhere. The typical direction of flow is upward (not necessarily vertically upward; often updip).

2.4 Generally, depth profiles of compacting sediments show an exponential decay in porosity with depth. Fine-grained sediments often show a reduction of porosity from 70% to 20% within the first 2 km of burial (Figure 7-1). Thereafter, porosity is lost at a much slower rate and can be approximated as a linear function of depth. In contrast, curves of sandstone porosity during burial show an approximately linear porosity loss throughout their entire history of burial (Figure 7-2). The extreme compaction of fine-grained siliciclastic rocks is of great importance to petroleum geologists, because if those rocks contain mobile petroleum hydrocarbons, those fluids are expelled upward into overlying porous rocks, which can then become petroleum reservoirs if they are capped by an appropriate seal.
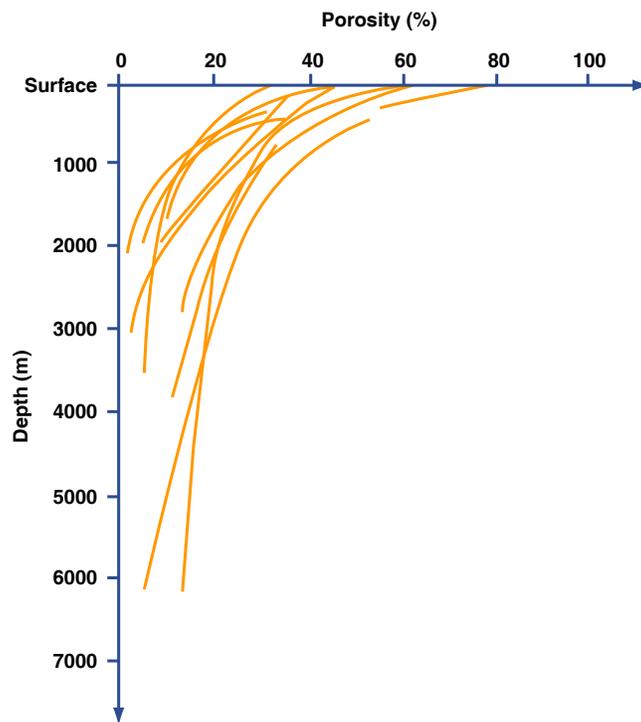

Figure 7-1: Reduction of porosity of fine-grained sediments with burial
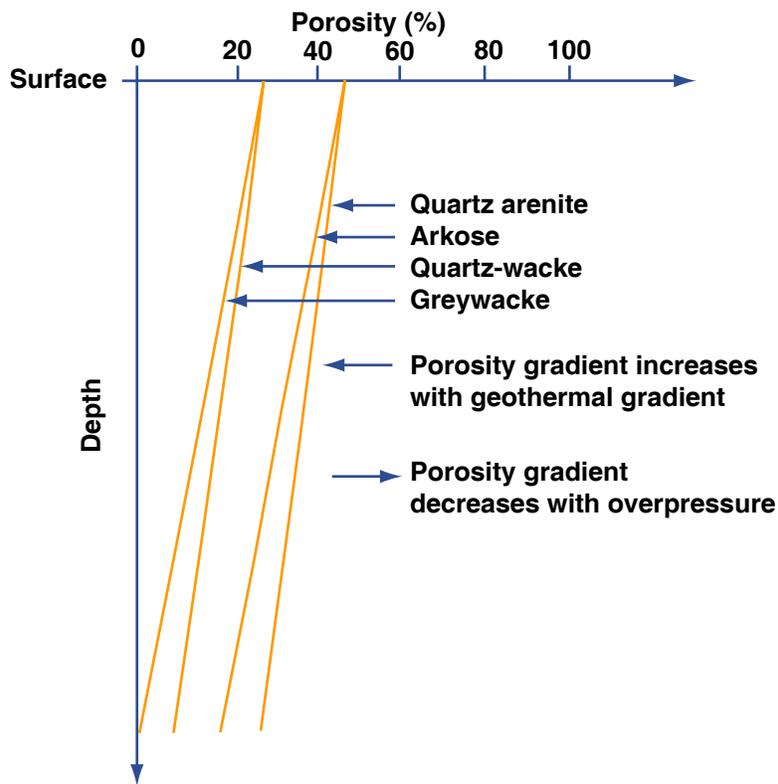
Figure by MIT OCW.

Porosity (%)

0   20   40   60   80   100

Surface

← Quartz arenite
← Arkose
← Quartz-wacke
← Greywacke

← Porosity gradient increases
with geothermal gradient

→ Porosity gradient
decreases with overpressure

Depth

Figure 7-2: Approximately linear porosity loss during burial of sandstones

Figure by MIT OCW.

2.5 Compaction commonly involves *deformation*, on scales ranging upward from individual grains.

• In thin sections (Figure 7-3) one often sees bent mica flakes or squeezed and deformed rock fragments (which, in more advanced stages, leads to pseudomatrix; see Chapter 4).
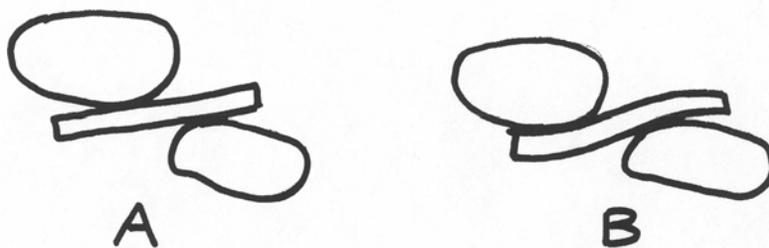
A   B

Figure 7-3. Deformation of a muscovite flake between two rigid detrital grains. A) Before deformation; B) after deformation.

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• Because of the difference in compaction between mudrock and sandstone, a sandstone dike emplaced vertically upward or downward before much compaction can become contorted because the mudrock undergoes so much more compaction than the sandstone (Figure 7-4).

Figure 7-4. Deformation of a vertical sandstone dike by compaction of mudrock. A) Before compaction; B) after compaction.
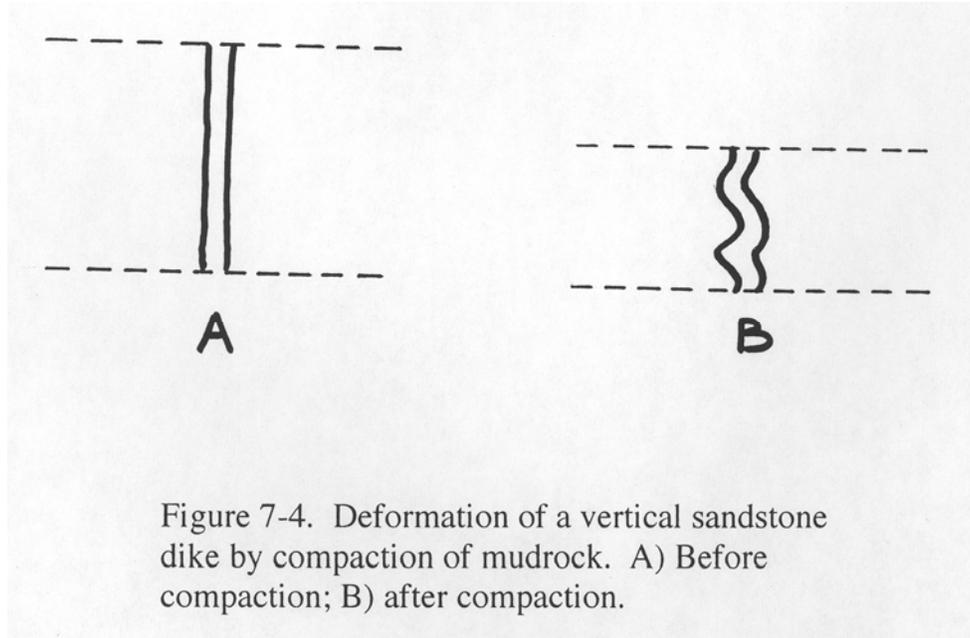
3. PRESSURE SOLUTION

3.1 Sandstones commonly show solution of grains at grain-to-grain contacts. This is especially important for quartz framework grains. This process is termed *pressure solution*. In its early stages, pressure solution involves only local areas at points of contact between adjacent grains. In later stages, a large percentage of the surface areas of adjacent grains are welded together. Such boundaries are said to be *sutured*. Thereby, almost all of the porosity of the rock has been eliminated.

3.2 How does pressure solution work? As with most minerals, the solubility of quartz increases slightly with pressure. Upon substantial burial, local grain-to-grain pressures at grain contacts are enormous, not only because the weight of overlying rock is great but also because the surface areas of grain contacts is, initially at least, small. That leads to slight dissolution of quartz at the grain contacts. Consequently, the local concentration of silica in solution is slightly greater in the immediate vicinity of the contacts, creating a gradient in silica concentration away from the contacts. The surfaces of the quartz grains adjacent to the contacts, where pressures are much less, thus feel a slightly supersaturated pose solution, leading to precipitation of quartz on those surfaces. The action of this simultaneous dissolution and reprecipitation causes grain boundaries to become broader (Figure 7-5).
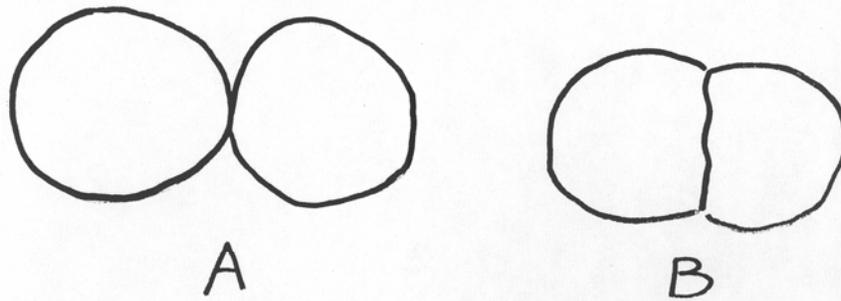
Figure 7-5. Suturing of quartz grains. A) Before suturing; B) after suturing.

3.3 Pressure solution also occurs in carbonate sediments. In addition to grain-to-grain suturing, pressure-solution seams commonly develop approximately parallel to bedding. The rock "closes up" along such surfaces, as the carbonate minerals (usually calcite) are dissolved and then removed from the vicinity by solution flow. Presumably, the reason stylolites are usually parallel overall to bedding is that bedding surfaces are usually the paths of easiest flow of pore solutions. Such surfaces of solution are called *stylolites*.

3.4 One usually sees stylolites on rock faces at a large angle to stratification. They look like a squiggly dark line, a bit like an electrocardiogram. (My all-time favorite graffito, on the limestone wall of a toilet stall in a men's room at MIT, labeled a stylolite "my electrocardiogram". The point, rightward, where the stylolite died out into non-dissolved rock, was labelled "entered MIT".)

3.5 Of course, the section one is seeing on the rock face is just a section through a three-dimensional stylolite surface that extends through the volume of the rock. It is uncommon to see an entire segment of the stylolite surface, but one can do serial sectioning to figure out the geometry. In that way, it's seen that the stylolite surface comprises *irregular pillar-like geometries pointing in both directions away from the average position of the surface*. The amplitudes of the pillars are usually a few centimeters, but in extreme case they can be much larger. (Incidental note: the origin of the term comes *stulos*, the Greek word for "pillar". A *stylite* was one of a number of early Christian ascetics who lived unsheltered on the tops of high pillars.)

3.6 Stylolite surface are the sites of accumulation of *insoluble residues* (clays, iron oxides, and others) as the rock closes up. That's what makes the stylolites dark. In a very general way, one can estimate the volume of carbonate rock that has been removed by solution, by comparing the average concentration

on insoluble residues in the rock to the amount that has accumulated in the stylolite.

3. PORE FLUIDS

3.1 *Pore-Fluid Composition*

3.1.1 Three varieties of pore solutions infill sediment pores: *meteoric*, *connate*, and *juvenile* (Figure 7-6). Meteoric water originates from the precipitation or rain and snow from the atmosphere. Connate water has evolved from the original water associated with deposition, and juvenile waters are of magmatic origin.
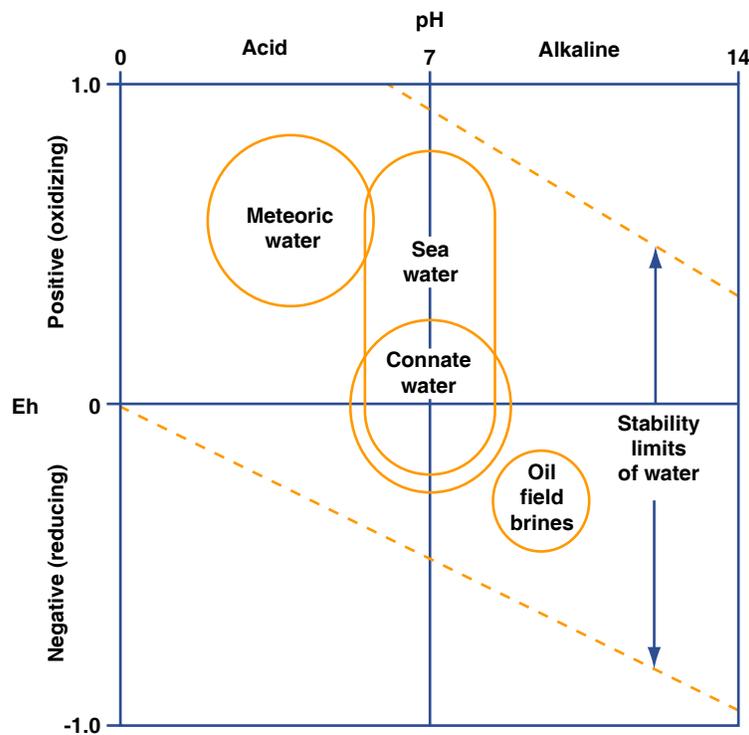
Figure 7-6: Types of water that fill sediment pores

Figure by MIT OCW.

3.1.2 *Rain water is oxidizing and acidic*. Acidity is acquired through nitrous acid formed during thunderstorms, carbonic acid from solution of carbon dioxide in the atmosphere, and sulfuric acid from volcanic gases. As rainwater seeps through soil horizons it also acquires humic acids from decaying organic matter. Thus, *when rain water enters a sedimentary unit it has considerable potential for causing chemical reactions*.

3.1.3 Within the shallow sedimentary profile there is an uppermost zone, the *vadose zone*, in which the pores are open to the atmosphere (Figure 7-7).
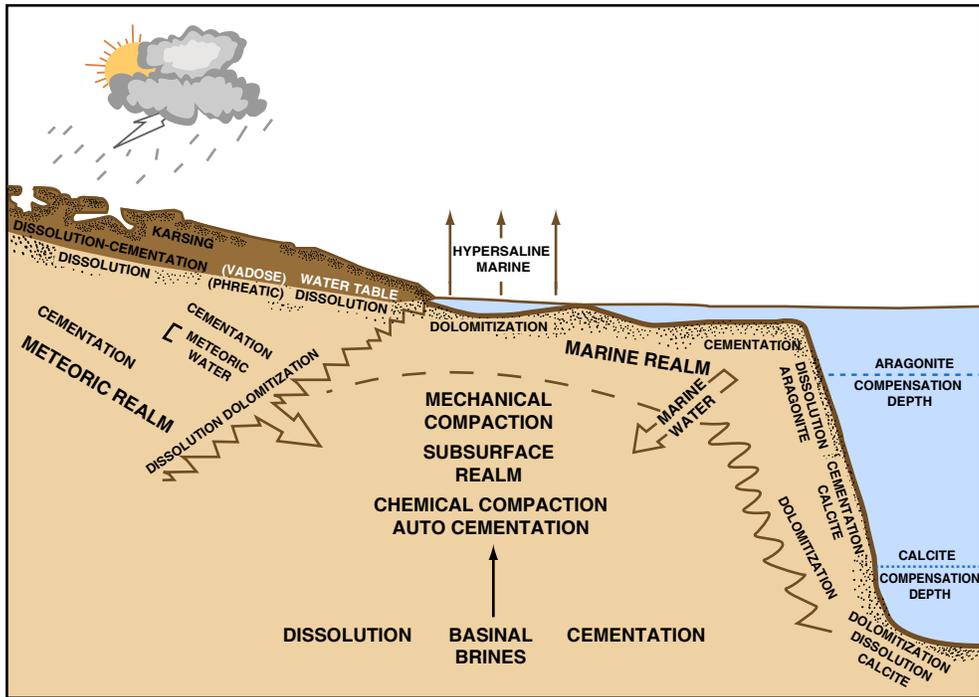
Figure 7-7: Zones of subsurface water in a coastal environment
Figure by MIT OCW.

Below the vadose zone is the ***phreatic zone***, where pores are saturated with water. The ***groundwater table*** separates the vadose zone from the phreatic zone. Bodies of sediment or sedimentary rock that are sufficiently porous and permeable to hold large quantities of pore water are called ***aquifers***. Sands, sandstones, gravels, conglomerates, and many carbonate rocks make good aquifers. Bodies of rock with low permeability, which inhibit flow of water, are called ***aquicludes***. Muds and shales make good aquicludes.

3.1.4 ***Connate water*** is defined most simply as the original (normally marine) water with which a sediment was deposited. It is important to realize, however, that the chemical composition of these fluids may have changed drastically because of various reactions between the sediment and original fluid that take place immediately after deposition. A distinction can be made between ***compactional water***, which is evolved connate water moving through the sediments as a result of compaction, and ***thermobaric water***, which is hot, highly pressured water of deep basinal origin, normally formed by dehydration of clays.

3.1.5 *Connate waters are commonly much different from meteoric waters in terms of their temperature, salinity, and chemistry.* The boundary between meteoric and connate water is sometimes quite sharp, because fresh (meteoric) water floats on more dense, chemical-laden connate water with its greater density due to solutes.

3.2 Pore-Fluid Flow

3.2.1 As with other liquids and gases, as you learned in Chapter 2, pore fluids move in response to pressure gradients. Meteoric waters flow because *at any point in the porous and permeable medium the fluid pressure varies from place to place along an imaginary horizontal plane through the medium*. This is called **meteoric flow** (Figure 7-8). The essential cause of such horizontal pressure gradients is the non-horizontal slope of the groundwater table above. The slope of the groundwater table tends to mimic the slope of the land surface, although the topography on the groundwater table is subdued relative to the topography of the land surface. (The pattern of deep groundwater flow is not intuitive, and it would take a lot more development of fluid dynamics here to account for it.)
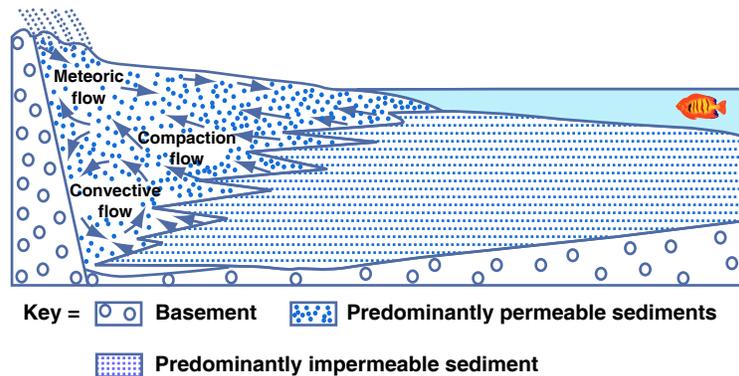
Figure 7-8: Subsurface flow of pore fluids in a coastal environment

Figure by MIT OCW.

3.1.2 Meteoric flow is *most important at shallow depths and in basins that have been uplifted above sea level*. Where there are topographic highs along marine basins, however, meteoric waters can displace connate fluids down to considerable depths. For example, fresh-water springs discharge at depths of several hundred meters beneath sea level in many coastal regions. *Meteoric flow is important as a mechanism for generation of secondary porosity* in both sandstones and carbonates in weathering zones that may be produced beneath unconformities.

3.1.3. *Compactional flow* (Figure 7-8) results when *excess pore water is squeezed out of the compacting sediment* as the overburden pressure increases during burial. However, as pore fluids move from compacting fine-grained sediments into more permeable coarser-grained sediments, hydrostatic pressures may be maintained and no further fluid movement need occur. Consequently, compactional flow is generally only a localized process and is not important in regional fluid movement.

3.1.4 At greater burial depths, *thermal gradients are sufficiently high as to induce convection of fluids* through permeable strata. Because such **convective flow** (Figure 7-8) can develop on the scale of entire basins, it is an extremely important process in diagenesis and emplacement of petroleum. Commonly, fluids leach minerals in one part of the basin and deposit them in others as thermal gradients or chemical regimes change.

4. DIAGENESIS OF FINE-GRAINED SEDIMENTS

4.1 *The shallowest diagenetic zone is one of oxygenation*. It is very thin or absent in deposited fine-grained sediments deposited in water. In continental environments, like ephemeral lakes on playas, however, subaqueous mud deposition may be followed by long periods of dehydration while muds remain above the water table. In such situations organic matter may be oxidized and removed. Iron may be precipitated as limonite and then become dehydrated to hematite, a red ferric oxide. (The term **limonite** is a general term for mixtures of hydrous ferric oxides, most commonly the mineral goethite but also others.) Often hematite develops during initial burial, forming deposits commonly referred to as **red beds** (also spelled redbeds, and pronounced "RED beds").

4.2 In subaqueous environments, where the oxygenating zone may be absent, sulfate-reducing bacteria are commonly active. In this situation sulfur may react with ferrous iron to form the ferrous iron sulfide mineral **pyrite**:

$$Fe(OH)_2 + 2S = FeS_2 + H_2O$$
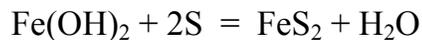
Sulfate ions may react with organic matter to form hydrogen sulfide:

$$SO_4^{2-} + 2CH_2O = 2HCO_3^- + H_2S$$
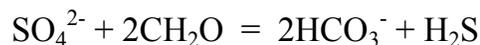
(where CH_2O represents, in a simplified way, organic matter)

4.3 Bacterial fermentation of organic matter also takes place during shallow burial. These reactions generate water, carbon dioxide, and biogenic methane. This increases the pH of the pore fluids, which can lead to precipitation of

carbonates. Carbonate precipitation of this kind often occurs patchily as *concretions* developed intermittently along bedding surfaces.

4.4 Freshly deposited muds contain a variety of clay minerals—the most important of which are smectite, illite, kaolinite, and chlorite, in various proportions. These clay minerals undergo significant diagenetic changes as the sediment is buried. The caused of these changes is not pressure but temperature. (Keep in mind the usual geothermal gradient of 25–30° C per kilometer of burial.) Smectite is changed to illite, with an intermediate range of mixed-layer illite–smectite. K^+ ions are incorporated into the smectite structure, and interlayer waster is lost. Smectite begins to disappear at temperatures as low as 70° C. At about the same temperature, kaolinite is replaced by illite and chlorite. Such changes develop upon burial to two to three kilometers. With incipient metamorphism, the illite undergoes further increase in lattice ordering and crystal size, to become what is called *sericite*, which is essentially fine-grained muscovite.

5. DIAGENESIS OF VOLCANICLASTIC SEDIMENTS

5.1 Fine-grained volcanic ash tends to undergo intense postdepositional alteration, producing bentonites. *Bentonites* are mixtures of smectite and devitrified glass. Palagonite is produced during the alteration and rehydration of volcanic glass.

5.2 Volcaniclastic sands may have good porosity if they are deposited on beaches or dunes. They lose porosity extremely quickly, though, because of their unstable mineralogy. During shallow burial they undergo hydration, leading to the formation of authigenic carbonate, clays, and zeolite minerals (*zeolites* are a class of hydrous aluminosilicate minerals). Thus, volcaniclastic rocks are generally very poor-quality aquifers or petroleum reservoirs.

6. SANDSTONE DIAGENESIS

6.1 Unlike in fine-grained sediments, in sandstones the effect of physical compaction is subordinate to chemical cementation. Thus the loss of porosity with depth is often not as predictable as it is in the case of finer-grained sediments. *The diagenetic history of a sandstone is controlled principally by the chemistry of the pore fluids that have moved through its pore system*. The main factors that determine mineral precipitation or solution are

- the chemistry of the sediment, and

- the composition, concentration, Eh, and pH of the pore fluids.

6.2 Although many reactions occur during sandstone diagenesis, only a few are of major importance in sandstone cementation and porosity evolution: *those that control the precipitation of silica, carbonate, and clay minerals* (Figure 7-9).

The solubility of calcite and silica are unaffected by Eh but are strongly affected—and in opposing ways—by pH. Silica solubility increases with pH, whereas calcite solubility decreases with pH. Thus in acidic pore fluids, like meteoric waters, calcite tends to dissolve and quartz overgrowths are precipitated, whereas in alkaline waters calcite cements precipitate and may even replace quartz. For mildly alkaline fluids (pH 7–10) both quartz and calcite cements may form.
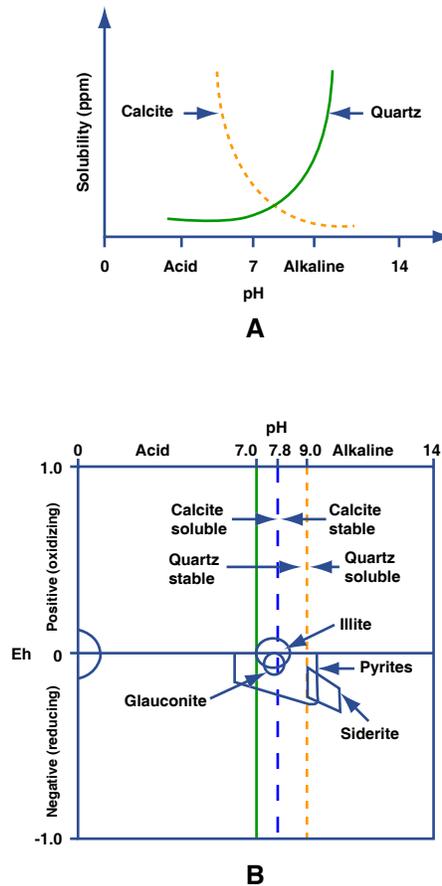
Figure 7-9: (A) Solubility of calcite and quartz vs. pH. (B) Stability of various diagenetic minerals in terms of pH and Eh

Figure by MIT OCW.

6.3 Clay minerals are similarly sensitive to pH. Kaolinite tends to form in acid pore waters, whereas illite develops in more alkaline conditions. Siderite, glauconite, and pyrite are all stable under reducing conditions.

6.4 Quartz-rich sandstones (quartz arenites) are *commonly cemented to various degrees by silica*. Usually this is quartz; only rarely is it in the form of opaline silica (amorphous colloidal hydrated silica)—which occurs in younger rocks, often in high-temperature settings, as in some hot springs. Opal dehydrates with age to microcrystalline quartz, termed **chalcedony.** Chalcedony is a common silica cement in sandstones of various ages.

6.5 One important mode of quartz cementation is pressure solution; see the earlier section in this chapter. The other important mode of quartz cementation is by the development of **secondary overgrowths** of quartz upon quartz framework grains. The new, authigenic quartz is precipitated in crystallographic continuity with the framework grains: the crystals are enlarged with no difference in crystallographic orientation. The boundaries between the framework grains and the overgrowths are commonly marked by thin, "dusty-looking" rims of very fine-grained mineral material (mostly iron oxides and clay minerals) that was present in small nooks and crannies on the original grain surface. Of course, for overgrowths to form, such rims must be patchy and discontinuous. It's often, but not always, easy to see the dusty rims in thin section.

6.6 In sandstones with lower percentages of quartz framework grains (lithic arenites and feldspathic arenites), however, there is much less cementation by quartz. In such sandstones—and in many quartz arenites as well—the more common cementing material is *calcite*. In contrast to quartz cements, calcite cement tends to be patchy and irregular, suggesting replacement of earlier constituents of the sediment. Much of this replaced material is probably quartz itself. The reason for this seems clear: the solubility of quartz increases with temperature, whereas the solubility of calcite decreases with temperature. That means that, given the substantial geothermal gradient, at sufficient depths of burial *quartz is dissolved and calcite is precipitated*—provided, of course, that there is a sufficiently high concentration of calcium carbonate in the pore solutions passing through the rock.

6.7 Both of the modes of cementation of a sandstone by quartz—pressure suturing and secondary overgrowths—result in loss of porosity, but pressure solution results in decrease of rock volume, whereas secondary overgrowths do not. In the case of secondary overgrowths, silica must be supplied in solution from elsewhere; in the case of pressure solution, there is likely to be net loss of silica, although suturing does not necessarily result in loss of silica.

6.8 Here's a final but important point about cementation of sandstones by either quartz or calcite: *the volumes of pore fluids that have to pass through the rock to do the cementing is extremely large*—hundreds or even thousands relative to rock porosity—owing to the low concentrations of the respective solutes. This

means strong flow (resulting from a combination of high permeability and strong pressure gradients) or long times, or some combination of both.

6.9 Sandstones may in some cases also be cemented by ***hematite***. In this case, iron is released during weathering of detrital iron-bearing minerals (e.g., pyroxene, amphibole, biotite) to form a coating of tan- to brown-colored hydrated iron oxide (usually mainly ***goethite***, although other hydrous ferric iron oxide minerals are involved as well). Following burial and temperature-induced aging, the *water is expelled* and the transformation to hematite occurs.

7. A NOTE ON LITHIFICATION OF SILICICLASTIC ROCKS

7.1 You may be wondering at this point how sands and muds become lithified to sandstones and mudrocks. The crucial element in lithification is *close and intimate contact between adjacent grains*. This close contact can come about by compaction alone, provided that at least some of the constituents of the sediment are deformable. If you go into the laboratory and try to lithify a pure quartz sand by squeezing it with a piston (and arranging the squeezing so that excess pore fluid can escape), you would fail: no matter how hard you squeeze, the sand stays loose. If, however, you include some soft rock fragments, or interstitial mud, you would end up with an at least partly lithified material: it would not fall apart readily in your hands.

7.2 To arrive at a more thoroughly lithified rock, you would need more than just compaction. You need *cementation*, whereby grain contacts are made more extensive by precipitation of authigenic mineral material around the original grains of the sediment. You have seen that this can come about in a variety of ways: pressure solution, deposition of cement, or recrystallization of the existing mineral constituents. Commonly, more than one of these processes is at work to lithify a sediment during burial.

8. LIMESTONE DIAGENESIS

8.1 *Introduction*

8.1.1 Limestones formed on carbonate platforms are *particularly susceptible to drastic, early diagenetic modification*. Marine carbonate sediments consist of metastable carbonate phases, like aragonite and magnesian calcite, which are *easily dissolved and recrystallized by fresh meteoric waters or mixtures of meteoric and marine waters*, such as are encountered in surface and shallow subsurface conditions. Because carbonate platforms can be maintained near sea level for extended periods, the possibility of fresh-water flushing of the platforms, with attendant massive diagenesis, is significant.

8.1.2 One of the major impacts of meteoric-water diagenesis is the basic rearrangement of calcium carbonate by dissolution of grains and the replacement

of calcium carbonate as cement in pore spaces. There is a *tendency for primary porosity in carbonate sequences to be destroyed early* by cementation with subsequent generation of secondary porosity during the dissolution phase. This in strong contrast to quartz sandstones, which are almost unaffected during early burial because of the low solubility and stability of most of the grains under surface and near-surface environments. Porosity in siliciclastic successions in the subsurface, therefore, is generally primary, can be tied directly to variations in depositional environments, and hence is highly predictable.

8.1.3 Carbonates not extensively altered during early diagenesis are particularly susceptible to chemical processes like grain-to-grain pressure solution and stylolitization during burial because of the relatively high solubility of calcium carbonate.

8.2 *Dissolution*

8.2.1 Aragonite and magnesian calcite are stable phases in the marine environment, but they are very unstable in other environments (Figure 7-10). *In freshwater lakes, or in vadose or phreatic zones, pure calcite is the stable phase.* Dissolution of metastable phases may often be selective, and originally aragonitic parts of shells may be dissolved while magnesian calcites remain intact.
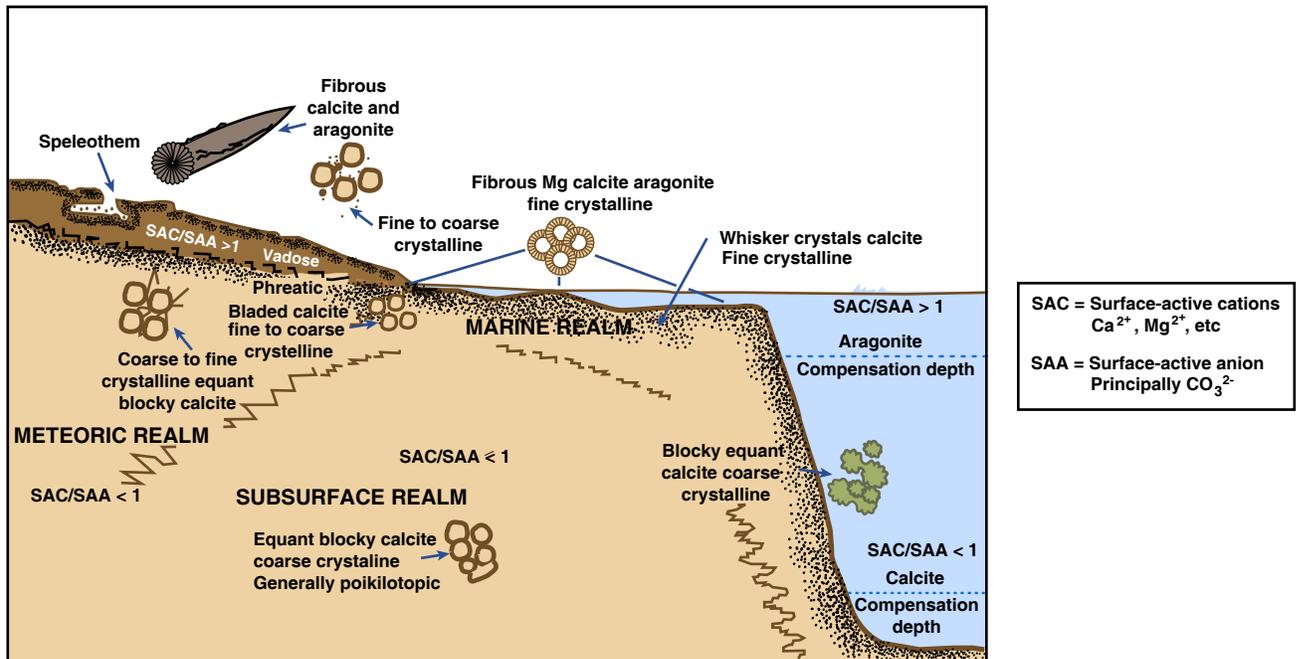

Figure 7-10: Diagenetic carbonates in coastal environments

Figure by MIT OCW.

8.3 *Cementation*

8.3.1 Cementation by calcite cements commonly occurs in the deeper parts of freshwater aquifers in the phreatic zone. *Saturation is achieved with respect to calcite as a result of dissolution of more soluble aragonite and magnesian calcite* in more updip locations, closer to the recharge area of the aquifer. As fluids move progressively downdip, they dissolve more and more aragonite and magnesian calcite until the fluid approaches saturation with respect to those phases. Because the solubility of pure calcite is lower than that of Mg-calcite or aragonite, however, the fluid at that point is supersaturated with respect to calcite and precipitates calcite *rim cements.* Rim cements (that is, those that encrust all exposed grain surfaces) are characteristic of cementation in the phreatic zone. Rim cements generally have a blocky habit.

8.3.2 Cementation by carbonate cements is not restricted to the fresh-water phreatic zone. In fact, it commonly occurs in pores spaces almost immediately after sedimentation of particles while fluids are still marine in composition. This mode of cementation, termed *early marine cementation,* is the process whereby reefs are made hard as rocks.

8.3.3 Marine cements may occur as magnesian calcite or aragonite drusy cements. Generally, the morphology of the crystals favors aragonite forming fine, fibrous fringes, whereas Mg calcite forms somewhat coarser, bladed fringes. These are precipitated as drusy cements, although during precipitation in the upper (supratidal) parts of tidal flats, where exposure in the shallow vadose zone may occur, cements may have more of a *microstalactitic fabric*. (You know already what stalactites are; the adjective *drusy* applies, in a pore space, to *a mineral surface that is covered with small projecting crystals*.) In this case, fine fringes may hang downwards from the undersides of grains and form by precipitation from marine fluids, introduced during storms, that percolate down through the shallow vadose zone.

8.4 *Replacement*

8.4.1 Carbonate petrologists have long recognized that some carbonate particles. like ooids or shells, or unstable marine cements that were originally sediments, are now different in both crystal size and mineralogy. This realization follows from recognition of *ghosts* of the primary mineral, represented by inclusions, pseudomorphs, or reproduction of an original outline. (A *pseudomorph* is a mineral whose outward crystal form is that of another mineral, owing to some process that changed the mineral composition without changing the crystal geometry.) It is obvious in many cases that the original material could not simply have been dissolved away and the new phase precipitated as cement. In order to preserve the evidence of the original material, *the growth of the new mineral must have taken place simultaneously with the step-by-step dissolution of the earlier material*. This situation implies that the fluid exists as a thin film, so as

to not generate void space, and to be delicately balanced in terms of composition so as not to dissolve faster than precipitation can proceed.

8.4.2 This process of replacement is commonly called ***neomorphism***. Neomorphism includes the diagenetic processes in which *older crystals, whether abiotic or biogenic in origin, are consumed and in their place simultaneously occupied by new crystals of the same mineral or a polymorph*. Thus, sparry cements can thus have two entirely different origins. (The adjective ***sparry*** is derived from the noun ***spar***, a term that's applied, loosely, to any transparent light-colored crystal.) In the first case dissolution and precipitation are sufficiently staggered in time so as to have the cement precipitate in a relatively large void. The sparry cement reflects this in the size and shape of crystals, with small crystals nucleating along the margins of the void space, and becoming increasingly large and blocky up to a maximum in the center of the void. In the case of neomorphic sparry cements, precipitation is intimately associated with dissolution, and subsequent morphology reflects the sediment particle that was replaced and not the void space. There is little variation in grain size except where it reflects primary variations in grain size.

9. DOLOSTONES

9.1 *Introduction*

9.1.1 By definition, ***dolostone*** *is a carbonate rock in which more than 50% of the carbonate minerals is dolomite*. Rocks with mixtures of calcite and dolomite are common (you can use the terms calcitic dolostone or dolomitic limestone), but my own experience is that there's a bimodal distribution, with fairly pure dolostones and fairly pure limestones more common than mixtures.

9.1.2 Warning on usage: the term dolomite is commonly used not only for the mineral but also for the rock, even though technically the rock should be called a dolostone.

9.1.3 *Dolostones are widespread and abundant in the sedimentary record, although not as abundant as limestones*. It's interesting that *the relative abundance of dolostone increases with age*: there is almost none in the Cenozoic, and only a few percent in the Mesozoic, but the proportions are about 3:1 limestone to dolostone in the Paleozoic, and just the reverse, 1:3, in the Precambrian. Why? It's not known for sure. Possibilities: deposition; replacement; preservation. Probably a combination of the first two.

9.2 *Kinds of Dolostone*

9.2.1 There are two broad groups of dolostone:

- **very fine-grained dolostones**, characteristically thinly laminated, often with various primary depositional structures like desiccation cracks, but few fossils;
- **coarse crystalline dolostones** with abundant evidence of replacement, and commonly showing relicts or ghosts of primary features like stratification, ooids, or fossils.

The usual assumption is that the first kind is nearly primary, forming soon after deposition of the calcium carbonate sediment. The second kind is secondary, formed by replacement of calcite by dolomite in limestones well after sedimentation occurs, after the carbonate sediment has been lithified.

9.2.2 In many carbonate rocks you can see good evidence of *incomplete dolomitization*: scattered rhombs of dolomite growing in a mass of calcite that commonly shows primary sedimentary textures and structures. The dolomite is neomorphic after the calcite.

9.2.3 Thorough dolomitization leads to a *totally crystalline dolostone* in which the dolomite forms an interlocking crystal mosaic. Such dolostones are often described as ***saccharoidal dolostone*** ox ***sucrosic dolostone***.

10.3 *Relationships Between Limestone and Dolostone*

9.3.1 Here are some generalizations about the spatial relationships between limestone and dolostone in stratigraphic sections, ranging from the small scale to the large scale.

- On the scale of individual beds, incomplete dolomitization is common. You see "mottled" rock with a patchy distribution of dolomite. The dolomite areas are irregular in shape, and they may or may not be interconnected.

- On the scale of successions of beds, you often see interbedding of limestone and dolostone on a scale of millimeters to decimeters to meters (or at least some beds show more thorough dolomitization than others).

- On the scale of meters to whole formations, irregular dolomitization can cut primary features indiscriminately. This is often clearly related to joints and faults, but sometimes its origin is obscure.

- On the scale of entire stratigraphic sections (to produce what could be called stratigraphic associations of dolostone), it's found that *dolostone tends to be nearshore and shallow-water, whereas limestone tends to be offshore and deeper-water*. There are many exceptions to this generalization, however.

9.4 *The Origin of Dolostone*

9.4.1 The origin of dolostones was deeply mysterious until quite recently; it's been only in the last twenty years that sedimentologists have developed even a partial understanding of the nature of dolostones. This is largely because there are *few places in the world today where dolomite is being precipitated* in anything like a primary depositional environment. In fact, up until the 1960s **NO** places were known!

9.4.2 It's clear that *dolomite crystals don't nucleate spontaneously from sea water*. Such nucleation is observed for aragonite in certain marine situations, but it's never been observed for dolomite. But sea water is oversaturated with respect to dolomite as well to calcite and aragonite (see the earlier chapter on limestones), and dolomite crystals are happy in sea water once they have formed. As noted in the chapter on limestones, the lack of nucleation and growth of dolomite in sea water is probably a matter of *kinetics*: it takes so long to build highly ordered structure of dolomite that dolomite loses out to calcite or aragonite in the competition for Ca^{2+} ions.

9.4.3 The general thinking is that the primary-looking dolostone we see is the result of dolomitization of fine calcium carbonate mud (presumably aragonite) very soon after precipitation, while the sediment is still at or close to the depositional surface. Conversion to dolomite before the sediment is finally deposited is suggested by the sometimes beautiful preservation of primary depositional features in fine-grained dolostones. This has been observed in the few modern settings where deposition of dolomitic sediment can be studied.

9.4.4 The other matter that needs to be addressed is the process(es) for partial or total replacement of calcite or aragonite by dolomite in the deposit long after deposition. In the case of late replacement along fractures, one has to appeal to dolomitizing solutions unrelated to the original deposition. But *most secondary dolomite seems to have been formed while the deposit was still within the depositional setting*, although probably deeply buried. Two major theories have been proposed: seepage-reflux dolomitization and brackish-water dolomitization (also called Dorag dolomitization).

Seepage Reflux (Figure 7-11): In a setting with restricted high-salinity water associated with the depositional area, one can picture dense water with lowered Ca^{2+} content and heightened Mg^{2+} content (owing to extraction of the Ca^{2+} by precipitation of calcite and/or aragonite) percolating downward and outward through the calcium carbonate sediment back to the open ocean. Water seeping through the body of a reef from the lagoon is the best example.
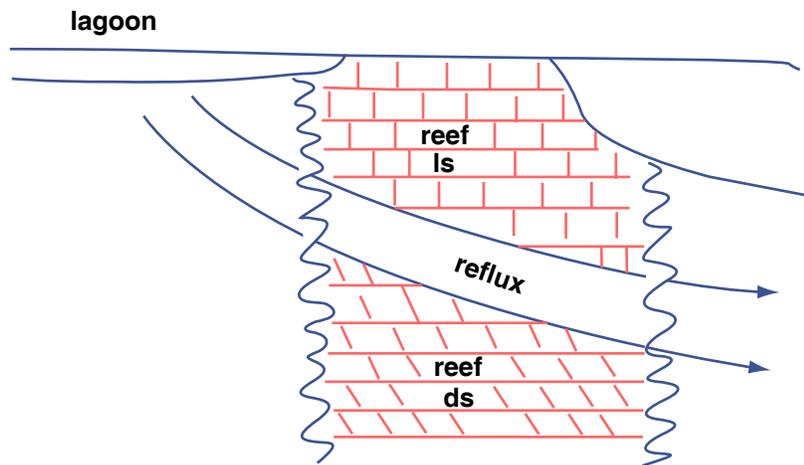
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Figure 7-11: Sketch of dolomitization by seepage reflux

Figure by MIT OCW.

Brackish-Water Dolomitization (Figure 7-12): It's known that mixtures of sea water and fresh water containing about 5% to 30% sea water are supersaturated with respect to dolomite but unsaturated with respect to calcium carbonate minerals. Brackish water percolating through an already-deposited sediment should therefore tend to dolomitize the sediment. This process has been invoked to account for dolomitization of various dolomitic units, both recent and ancient.
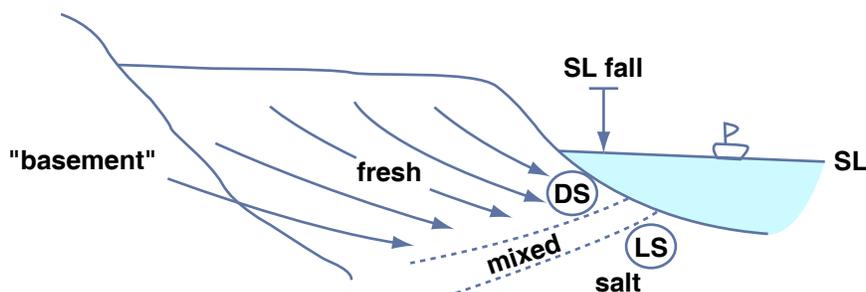

Figure 7-12: Sketch of do1omitzation by percolation of brackish water

Figure by MIT OCW.

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9.5 *Practical Things About Dolostone*

9.5.1 Dolostone doesn't fizz in the dilute HCl used for limestone identification, but if it's powdered with a knife, then it will fizz. This is a fairly reliable field test, although you have to be careful, because small amounts of calcium carbonate cement in a rock could produce about the same effect.

9.5.2 Dolostones tend to weather in tan to buff colors, presumably because there usually are small percentages of ferrous iron in the dolomite. Fairly pure limestones, on the other hand, tend to weather gray.

9.5.3 In arid to semiarid regions, the weathered-surface texture of limestones and dolostones are different. Limestone weathers by solution even in arid regions, and sloping bedrock surfaces show development of a network of fine solution rills. Dolostone, on the other hand, weathers by granular disintegration, and presents a granular-rough surface without solution rills.

9.5.4 Dolostones are seldom very fossiliferous: nearly primary dolostones were deposited in environments often hostile to macroorganisms, and replacement dolostone usually has its fossils partly or entirely obliterated. It's important to recognize, however, that there are well documented examples of dolomitized but nonetheless richly fossiliferous carbonates.