EOSC221

DIAGENESIS
LECTURE OUTLINE

- Introduction and Diagenetic Zones
- Sandstone Diagenesis
- Mudstone Diagenesis
  - Marine
  - Non Marine
- Carbonate Diagenesis
  - Major Processes
  - Diagenetic Environments
  - Dolomitization
Diagenesis = any chemical, physical, biological change after deposition. It does not include weathering and metamorphism. Diagenetic processes occur at relatively low temperatures and pressures and cause changes to original mineralogy and texture. The boundary of pressure and temperatures where diagenesis passes into metamorphism is not clearly defined.

Compaction will occur as sediments are buried. Some minerals will be recrystallized or dissolve. New minerals may also grow (authigenesis). Grains become cemented by minerals that precipitate from solutions moving through pore spaces. Generally porosity decreases during diagenesis, apart from where dissolution of minerals occurs and during dolomitization.

An appreciation of the diagenetic development of a sediment can also help in our understanding of its tectonic history and the kinds of fluids that have moved through it. This is VERY important information for the mineral and hydrocarbon industries as it relates to the porosity (spaces within a rock expressed as Φ) and Permeability (the interconnectedness of those spaces expressed as K). Rocks with high Φ and K make excellent reservoirs for oil gas or water. Diagenesis is also important in understanding the various process that convert organic material in sediments into oil and gas.
The style of diagenesis will vary depending on the type of sediment and the environment in which the sediment is undergoing diagenesis either marine or terrestrial. If terrestrial, with depth you can divide diagenetic zones:

1. The Vadose zone is the position at which the groundwater (the water in the sediments pores) is at atmospheric pressure ("vadose" is Latin for "shallow").

2. The phreatic zone (zone of saturation) = portion of an aquifer, below the water table where pores and fractures are saturated with water. The phreatic zone may fluctuate during wet and dry periods.
A number of processes may occur in this shallow zone of burial.

1. Porewaters may “wash” clay grade material into a sandstone changing its original textural composition. A sandstone that was originally a high Φ and K quartz arenite may take on the texture of a wackestone.

2. Unstable components (pyroxenes, amphiboles, plagioclase) may continue to degrade becoming pitted and etched.
3. Growth of authigenic minerals such as illite and kaolinite. The lack of clays at the contacts between the sandstone grains indicates that the clay was not deposited with the sandstone but grew after deposition of the sandstone. Clays may grow as a result of the dissolution / alteration of more unstable mineralogical components in the sandstone.

4. Diagenetic reddening of sediments. Red rims of hematite can occur as a primary deposition feature (see desert sands earlier). Red staining can also occur during diagenesis either by hematite being washed in the sediment following deposition or from the alteration / dissolution of unstable minerals within the sediment leading to the release of iron and the formation of diagenetic hematite. Diagenetic hematite can be distinguished from primary hematite rims by the absence of hematite at grain contacts in the case of diagenetic hematite.
Pressure solution or pressure dissolution = dissolution of minerals at grain-to-grain contacts into an aqueous pore fluid. This releases silica into the pore fluid which can then be re-precipitated as a silica cement. NOTE: this is not the only source of silica for cements. Silica dust can also be present in desert sandstones and silica can also be released from silicate minerals undergoing dissolution.
iii. Growth of cements: silica and calcite

- Silica often as quartz overgrowths in optical continuity

- Calcite can be both an early or a late stage cement.

Silica cements are commonly precipitated in optical continuity with the quartz grain they are surrounding creating a quartz overgrowth. Calcite cements are common (although dolomite and siderite cements can also occur). Calcite cements can form either early or late, early cements forming sometimes very soon after the deposition of the sediment. Early precipitation of calcite may inhibit the formation of quartz overgrowths. Later calcite cements can develop from the release of ions during mineral dissolution in later diagenesis.
The diagenesis of organic rich mudstones is probably the most important “economic process” that we will cover. It is from the progressive chemical alternation of the organic material and release of various ions and water from mudstones that control the formation and initial migration of petroleum. Diagenesis occurs in a numbers of zones as sediment gets progressively buried over time:

**Zone 1: 0 - 0.5m**
This thin zone contains pore waters that are oxic. Porosity is high, around 80% as the sediment in this zone is relatively uncompacted. Organic matter is oxidized by bacteria which produces CO₂ (as this is biologically produced this will be isotopically light ¹²C). This CO₂ dissolves in the pore waters producing HCO₃⁻ most of which is lost to sea water and as such generally doesn’t react with Ca to form calcite. Bioturbation (mixing of sediments by organisms) is important in this zone and into the top of zone 2 which helps keep this zone in the oxic zone.

**Zone 2: 0.5 – 10m**
The zone of bacterial sulfate (SO₄²⁻) reduction generally by *Desulphovibrio vulgaris*. The sulfate (from sea water – and ultimately from the erosion of continental rocks) will eventually get exhausted with depth. The S²⁻ produced by sulfate reduction may form H₂S which may react with Fe³⁺ to produce pyrite (FeS₂) giving the rock a dark colour. The CO₂ produced by sulfate reduction may react with Ca to form calcite concretions.
Zone 3: 10 – 1000m
- Zone of Organic Fermentation: no more sulfate reduction
  \[ \text{CH}_2\text{O} \rightleftharpoons \text{CH}_4 + \text{CO}_2 \]
- Possible formation of Siderite
- Expulsion of pore water by compaction

Zone 4: 1 – 2.5km
- Breakdown of remaining organic matter by decarboxylation

\[ \text{R.CO}_2\text{H} \rightarrow \text{R-H} + \text{O=O} \]
- More pore water expelled

Zone 3: 10 – 1000m
In this zone all the sulfate has been reduced and as such pyrite and calcite concretion production stops. This is the zone of Organic Fermentation. As Fe is now not being taken in the formation of FeS$_2$ it is free to react with the available CO$_2$ to form minerals such as Siderite (FeCO$_3$). Further compaction in this zone sees the expulsion of much of the pore waters and an increase in the sediment density.

Zone 4: 1 – 2.5km
Remaining organic matter broken down further by decarboxylation (breaking down carboxyl COOH groups):
\[ \text{R.CO}_2\text{H} \rightarrow \text{R-H} + \text{CO}_2 \]
Pore water continues to be expelled in this zone.
Zone 5: 2.5 – 7km
- Zone of Hydrocarbon generation (about 70 – 90°C)
- Breakdown of unstable mineral components releases H₂O
- Release of H₂O expels SiO₂, Mg²⁺, Fe²⁺ and any generated petroleum
- At higher temps gas rather than liquid petroleum produced.

Zone 6: >7km
- Zone of metamorphism
- illite -> Sericite -> Muscovite (at 300°C)
- Kaolinite -> Dickite/Nacrite -> Chlorite (at 200°C)

Zone 5: 2.5 – 7km
The zone of hydrocarbon diagenesis. Here the remaining organic matter (called Kerogen) is broken down further (“cracked”) generating petroleum.

Conversion of clays and other unstable components releases H₂O (bound water – water contained in the clay mineral crystal structure), SiO₂, Mg²⁺ and Fe²⁺. This final release of water allows these components to migrate to other formations where they are used in the diagenesis of other rocks. This expulsion of bound water also helps move any petroleum formed out of the source rock and into reservoirs. As temperature increases, gas rather than liquid petroleum is produced.

Zone 6: >7km
By the time you get to these depths you leave the zone of diagenesis and pass into metamorphism. Illite clay alters into sericite and eventually muscovite at around 300°C.
As you can see, to generate petroleum or gas, the organic material contained in the mudstone has to survive a lot of processes.
Due to the lack of sulfate in freshwater systems, diagenesis of organics skips the sulfate reducing stage and goes rapidly into bacterial fermentation. The CO$_2$ produced reacts with Fe in the groundwater to produce Siderite (FeCO$_3$).

The Mazon Creek fossil beds are a conservation lagerstätte (an area of exceptional fossil preservation) in Illinois. The fossil beds represent a freshwater delta system. Siderite concretions grew around dead organisms in the sediment. This has allowed for the preservation soft tissues in addition to the hard parts of animals and plants. In some instances completely soft-bodied organisms (that usually rot before they have a chance to fossilize - for example the “Tullimonster” above) can be found in the siderite nodules of this formation.
There are 5 major processes in carbonate diagenesis.

1) Cementation: The mineralogy of the cement in carbonates depends on a number of factors but in particular the amount of dissolved CO$_2$ in the pore waters, the magnesium : Calcium ratio and the supply of carbonate.

2) Neomorphism: basically “new growth” or recrystallization processes. Two important processes in neomorphism are aggrading neomorphism, where there fine grained micrite is recrystallized into slightly coarser sparite and calcitization where aragonite is recrystallized into more stable calcite (often with a loss of internal detail in the case of shell material).
3) **Dissolution**: In the meteoric zone and is generally caused by slightly acidic groundwater preferentially dissolving cracks in the bedrock. Fractures widen and eventually form an underground drainage system, allowing more water to pass through the area, and accelerating the formation of underground karst features. Dissolution can ALSO occur in deep burial. Dissolution will aid in the development of secondary porosity and the improvement of the reservoir potential of a carbonate rock. NOTE THOUGH – in carbonates dissolution can be accompanied by cementation resulting in dissolution porosity that is very rapidly filled with cement.

4) **Compaction**: Mechanical compaction (due to overburden of sediment) is not that common. This is probably due to the early cementation that many carbonates experience. In deeper burial though chemical compaction may occur. In this case fracture / dissolution occurs at grain contacts due to pressure solution. This releases Ca$^{2+}$ and CO$_3^{2-}$ ions into the rock which likely account for a lot of the cement in deep burial settings. Insoluble clays, pyrite and mineral oxides and left behind in stylolites which can make these areas more visually prominent. A change in texture of the rock might also highlight the presence of stylolites.

5) **Dolomitization**: The conversion of calcite into dolomite – see later in this lecture.
Diagenetic environments of carbonates are COMPLEX. The major zones are Marine, Meteoric and Burial diagenesis. In this class we will concentrate mostly on the meteoric setting.

1) Meteoric Zone – Probably a more significant zone in term of diagenesis than the marine zone: Significant diagenesis will occur as the sediment is exposed at the surface and is exposed to meteoric (rain water) infiltration – this is very significant during periods of glaciation when falling sea levels would lower the water table. The diagenesis in the Vadose zone is relatively rapid, commonly taking less than a 1000 years. In general cements in the meteoric zone tend to be low Mg Calcite.

i. Upper Vadoze Zone – zone of infiltration: The upper vadose zone is also known as the zone of infiltration. Rain water will be slightly acidic due to CO$_2$ dissolved in the water AND due to the presence of organic acids picked up from soils. Aragonite and high Mg calcite will be particularly susceptible to dissolution in this zone. Many grains in this zone will become pitted and dissolved: ii Lower Vadoze Zone – zone of percolation

Here the percolating water becomes saturated with CaCO$_3$. In addition, loss of CO$_2$ (degassing) helps precipitate low Mg calcite cements and conversion of aragonite and low Mg calcite into low Mg calcite. Internal detail of aragonite and Hi Mg calcite shelly material will be lost as they are converted to coarse crystalline low Mg calcite. Typical cements are meniscus cements that form within the film of water that clings between grains in the sediment (we are still above the water table here).
iii. The phreatic zone is continually saturated in water. Processes here are probably even more rapid than in the vadose zone. This area sees the precipitation of additional low Mg calcite cements initially as fairly fine rims (isopachous) cements and then later as coarser blades. Some calcite cements may also grow in optical continuity with the grains (commonly echinoid fragments) producing syntaxial overgrowths.
MARINE: Mostly Aragonite / high Mg calcite cements
METEORIC: Low Mg calcite cements
2) Marine Diagenesis
Diagenesis can start fairly soon after a carbonate grain is deposited. Micritization, the transformation of carbonate grains into fine grained micrite, can be caused by abrasion of material on the sea floor but also by organisms such as algae boring into shell fragments and the like and converting the material into micrite. In addition, early cementation of carbonate sediment can occur resulting in the formation of a hardground. The cements usually form around the rims of the grains and can be composed of iron oxides and high Mg calcite.

Hardgrounds or beachrock form when there is a pause in sedimentation, sometimes lasting 1000’s of years and are commonly colonized by encrusting organisms such as oysters and are often bored by various creatures including bivalves (clams). The detailed chemistry of hardground formation is something we will not cover in this course but you may get pendent cements in these deposits. Other marine cements will have isopachous bladed and fibrous cements like you get in the meteoric zone HOWEVER marine cements in shallow burial settings tend to be aragonite and high Mg Calcite
3) **Deep Burial**

- Cements fill remaining porosity
- Calcite made available by formation of stylolites
- Porosity can drop from 20 – 5%
- Tend to ferroan (iron rich) calcite cements (anoxic pore water)
- Often mosaic in form
- Possible aggrading neomorphism - patches of spar in micrite.

Deep burial diagenesis is not too well understood. Ions released from other strata undergoing diagenesis (particularly muds – see earlier) can make this a chemically complicated diagenetic environment.

Deep burial diagenesis will occur as temperatures and pressure increase and will often (but not exclusively) be characterized by larger crystal size and an increase in the iron content of the calcite cements (ferroan calcites). Ferroan calcite cements are often regarded as being indicative of deep burial diagenesis in ANOXIC conditions. It is thought that the majority of the calcite made available for the cements in this zone come from the dissolution of other material, particularly from the formation of stylolites.

Micrites in this zone may demonstrate aggrading neomorphism with patches of micrite being converted into spar.
Dolomitization is very poorly understood. Most dolomites are regarded as having formed by the alteration of calcium carbonate soon after deposition (penecontemporaneous) or the alteration of limestones in deep burial conditions that may take millions of years. There has been a suggestion that some fine grained dolomites that may have been directly precipitated out of sea water. At present though, no scientist has been able to precipitate dolomite in the laboratory at Earth standard surface pressures and temperatures. Some of the general factors that are thought to favor dolomite formation are high Mg / Ca to ratios and high temperatures.
A. Penecontemporaneous

These are environments where carbonate sediments are thought to be altered to dolomite soon after deposition. There are a number of models:

1. Evaporite–Brine Residue Model
   i. Reflux Model: Evaporation of sea water in a near shore environment causes the precipitation of gypsum, CaSO₄. The removal of Ca from the water concentrates Mg. The Brine formed by evaporation is dense and sinks into the sediment displacing the marine pore water and causing dolomitization as it moves down into the limestone. Although a neat and simple model it has yet to be observed occurring in nature.
ii. Evaporative Pumping
Another way in which gypsum can be precipitated in a coastal environment is by evaporative pumping close to shore. Here intense evaporation draws saline ground waters through the limestone. Eventually the concentration of those waters in the near surface causes the precipitation of gypsum and increases the concentration of Mg relative to Ca and allows for the formation of dolomite. We will deal with this environment again when we study evaporites.
2. Groundwater Mixing
When freshwater mixed with up to 30% marine water brackish ground waters are produced. This may also be conducive to the production of dolomite.
3. Sea Water Model

In this model sea water is continually flushed through the sediment pores bringing the calcite into contact with higher levels of Mg that is being continually replenished by fresh sea water. This can be accomplished by rising tides (particularly spring tides) and during periods of sea level rise.
B. DEEP BURIAL

The majority of dolomites probably form by the alteration of limestones in deep burial settings. The original textures of the limestones can sometimes be faintly seen. The dolomitic Devonian limestones in the Western Canada Sedimentary Basin probably formed at depths between 500 – 3000m over millions of years. Dolomitization in these settings would require the circulation of Mg rich pore waters and a limestone with sufficient porosity to permit the passage of these fluids.
GLOSSARY
All lecture material is potentially examinable. It is up to you to know unfamiliar terms / names / people. Use this space to create your own lecture glossary.

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