Diagenesis of Limestones

Diagenesis begins very early in limestones, right on the seafloor
Limestone Diagenesis

- Compaction and Cementation (mostly calcite) similar to that in sandstones
- Pressure solution - dissolution caused by pressure of one grain on another
- Replacement of Aragonite by Calcite
- Local replacement of limestone by chert
- Replacement of limestone by dolomite, called “dolomitization”
Pressure Solution

- Load pressure causes some calcite to dissolve
- In some limestones, as much as 40% of original carbonate may have dissolved
- Insoluble things (clay, organic matter) get concentrated or left behind and may form black marks called stylolites
Stylolites

- Irregular surface of interpenetrating “fingers” marked by concentrations of insoluble clay or organic matter
- In cross section, they look like the writing of a stylus
- See walls of bathroom stalls in White Hall (no more!!)
Stylolites
Stylolites

Bruce Railsback
U. of Georgia
Calcite and Aragonite are polymorphs of CaCO$_3$

Calcite is more stable at Earth-surface conditions than Aragonite, but some organisms make their hard-parts out of aragonite anyway.
Aragonite changes to Calcite during diagenesis

- Exposure to fresh water speeds up aragonite to calcite conversion
- Paleozoic limestones don’t have any aragonite left
Dolomitization

- Dolomite is rare in modern carbonates
- Makes up about 1/4 of Paleozoic limestones
- Makes up about 3/4 of Precambrian limestones

- Why?
- When and where does dolomite form?
Observations about Dolomite

• Almost all dolomite forms by replacement of pre-existing calcite and aragonite
• Dolomite rhombs cross-cut allochems
• Dolomite obscures fine structures in limestones
• Dolomite crosscuts bedding planes
• Dolomite is commonly associated with evaporites
Dolomite Rhombs in Thin Section
To form dolomite by replacement of calcite or aragonite you need

- Water of the right composition and
- A mechanism to move that water through the limestone

- There are two proposed mechanisms
Evaporative Reflux

- Requires periodic flooding of an exposed tidal flat or “sabkha” over a limestone
- Evaporation that causes evaporites (especially gypsum, CaSO$_4\cdot2$H$_2$O) to precipitate
- Two effects:
  - increased density of brine, so it sinks through the limestone
  - increase in the Mg/Ca ratio of brine
Evaporative Reflux:
Ca-depleted (Mg-rich) brine moves through the limestone, and Calcite (CaCO₃) is replaced by Dolomite (CaMg(CO₃)₂)

Works for dolomites associated with evaporites
Dolomites without Evaporites require a different model

- Mixing of fresh water and seawater, called “Dorag” which means “mixed blood” in Persian
- A mixture with ~5% to ~70% seawater is under-saturated with Calcite (wants to dissolve Cc), and super-saturated with Dolomite (wants to precipitate Do)
Calcite and Dolomite Saturation

Dolomite
Calcite

5-70% seawater, Dorag works, Dolomite replaces Calcite
Dorag Dolomite

• Landward of the shoreline, there is a zone of mixing of fresh groundwater and seawater

• It should be a dolomitizing zone

• Zone migrates landward as sea-level rises (during transgression)

• Zone migrates seaward as sea-level falls (during regression)

• This model is attractive for dolomites with no evidence of evaporites
Dolomite formation on the north side of Jamaica - Dorag model
Evaporative Reflux explains
Dolomites associated with Evaporites

Supratidal area — High tide line

Mg-rich brine
Mg-depleted brine
Limestone

Dolomitized zone

Ocean

Hope Gate Formation
Falmouth Formation
Vadose zone
Meteoric phreatic zone

Zone of dolomitization
Marine phreatic zone

Sea level

Dorag Model, north Jamaica