



Trace Elements in Carbonates

A Short Course VU March, 2009 Peter Swart University of Miami

Trace Elements and Minor Elements

▪Minor Elements (Usually concentrations over 1000 ppm)

- Strontium**
 - Aragonite-7000 to 10000 ppm(usually)
 - Low Mg-calcite- 1000 ppm
 - High Mg calcite- 3000 ppm
- Sodium**
 - Aragonite-4000 ppm
 - LMC- 1000 ppm
 - HMC- 2000 ppm
- Magnesium**
 - Aragonite- 1000 ppm
 - LMC- 1000 ppm
 - HMC- 2 to 4 wt%



Trace Elements and Minor Elements

▪Trace Elements (Usually concentrations below 1000 ppm)

- Iron**
 - Aragonite- Less than 1 ppm
 - LMC- 1 to 2 ppm
 - HMC- 1 to 2 ppm
- Manganese**
 - Aragonite- Less than 1 ppm
 - LMC- 1 to 2 ppm
 - HMC- 1 to 2 ppm
- Uranium**
 - Aragonite- 2 to 3 ppm
 - LMC- 0.01 to 0.02 ppm
 - HMC- 0.1 to 0.5 ppm

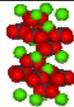


Location of Trace Elements

- Trace and minor elements have three possible locations
 - Substitution for the major cation, usually Ca or Mg in carbonates (Sr, Mn, Fe) 90-95%
 - Adsorption onto crystal faces to satisfy charge imbalances (Na, K) 5-10%
 - Inclusion of additional mineral phases, such as fluid inclusions or distinct minerals (Na, Cl) 5-10%



Principal Location

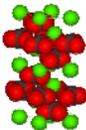


- The principal location involves substitution for Ca in calcite and aragonite and for either Mg or Ca in dolomite.
- The concentration of a minor or trace element can be described relative to the element for which it substitutes by a partition (**K**) or distribution coefficient (**D**).
- These two coefficients are essentially the same, but one describes the concentrations as activities and the other as concentrations.



Distribution Coefficient

$$D_M = \frac{M/Ca \text{ (mineral)}}{M/Ca \text{ (seawater)}}$$

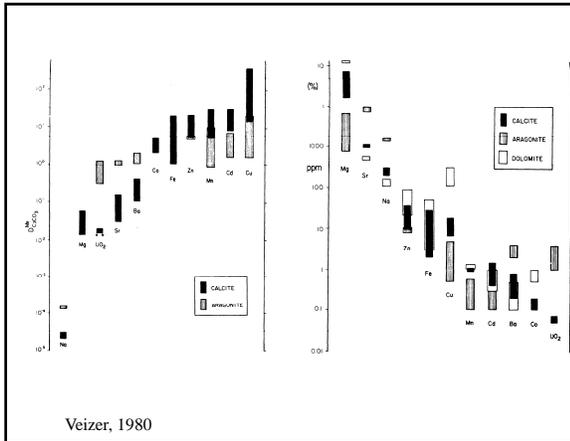


M= Sr, Mn, Fe, etc
D= Distribution coefficient

If **D** is greater than unity, then the trace or minor element is preferentially accumulated into the mineral phase.

If **D** is less than unity then the trace element is discriminated against and the concentration of M is less than expected.





Mineralogy

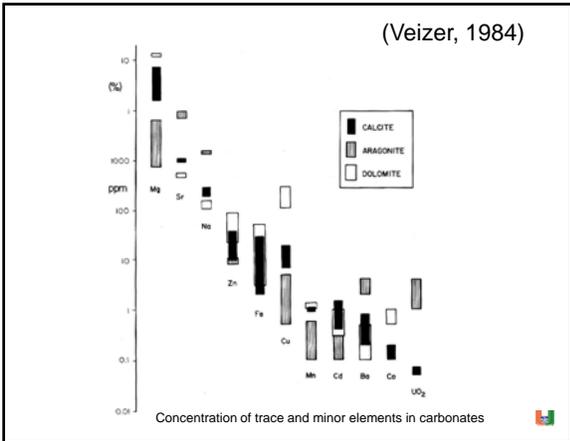
- Carbonates belong mainly to either the orthorhombic or hexagonal group of minerals.
- Aragonite is an orthorhombic mineral and favours the inclusion of elements with larger ionic radii.
 - Elements which have an ionic radius larger than Ca (0.99 Å), U, Ba, Pb, and Sr have higher distribution coefficients for incorporation into aragonite greater than unity.
 - Conversely smaller radii elements are discriminated against.
- Minerals in which the principal cation is one of the larger elements are all orthorhombic.



Mineralogy

- Calcite and dolomite are hexagonal minerals with smaller spaces between the cations.
 - Elements such as Mn, Fe, Zn, Cu etc have ionic radii smaller than Ca are preferentially incorporated into the hexagonal minerals and have distribution coefficients greater than unity
- Minerals in which the principal cation is one of the smaller elements are all hexagonal.



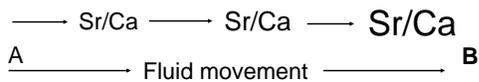


Recrystallization of aragonite

- Most aragonite contains around 7000 ppm Sr. As the distribution coefficient of Sr into aragonite is approximately unity (1) then dissolution by itself will tend to move the Sr/Ca ratio of the solution towards 9×10^{-3} (the same ratio as seawater).
- However, calcite precipitation combined with aragonite dissolution will result in an increase in the Sr/Ca ratio of seawater as precipitation proceeds.

Recrystallization of Aragonite

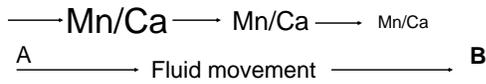
This increase arises because Sr is preferentially rejected by the LMC and therefore builds up in the fluids



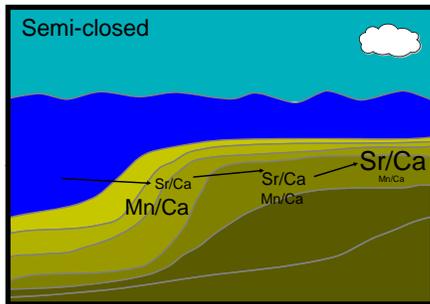
If fluid is moving along a pathway from A to B then the Sr/Ca ratio will increase along the path from A to B

Recrystallization of Aragonite

As a result of the higher distribution coefficients for elements such as Fe and Mn into LMC, these elements will decrease with continued recrystallization.



Kohout Convection



Geochemical patterns in Kohout convection

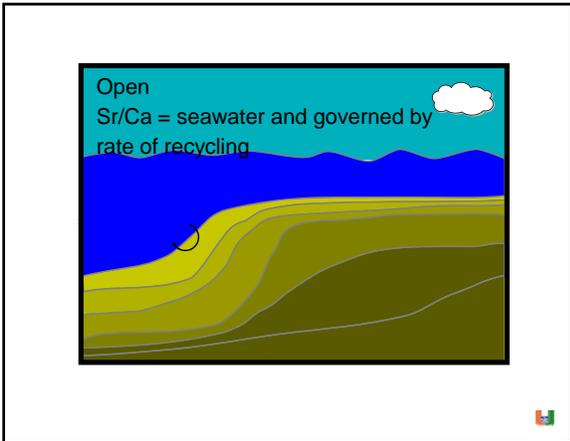


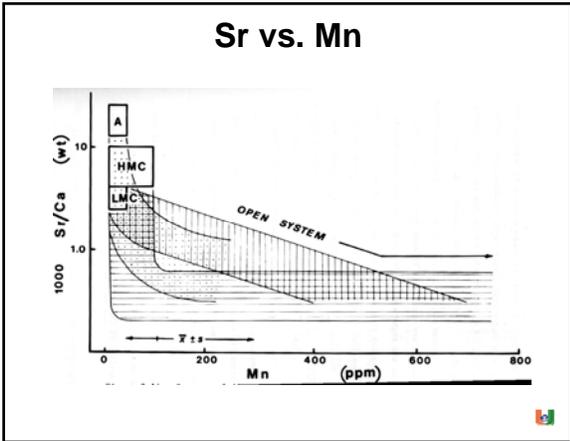
Open vs Closed System

A closed system is defined as one in which the chemical equilibrium is controlled by the influence of successive geochemical reactions. Hence the patterns of Mn and Sr just shown occur only in a closed system

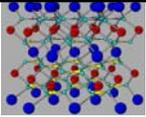
An open system is one in which the reactants are rapidly removed from the system







Dolomites

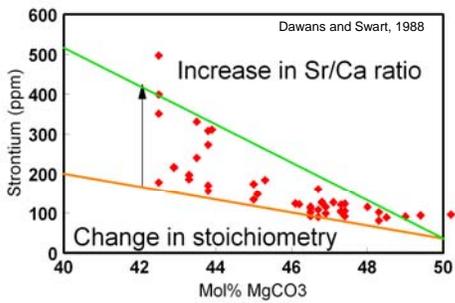


- Dolomite has two cation substitution sites (Mg and Ca).
- In a fully ordered dolomite layers of calcium atoms are separated by layers of carbonate groups. All Ca atoms are in the Ca layers and Mg in the Mg layers.
- The larger trace elements (Sr) are considered to be partitioned only in the Ca sites and the smaller trace elements only in the Mg sites

Dolomites

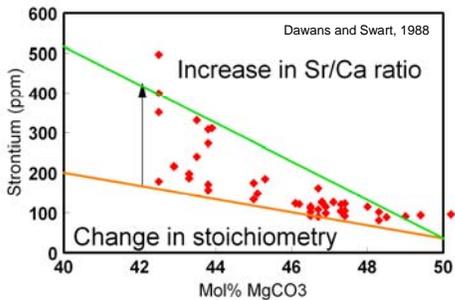
- ✓As Sr is considered to be partitioned only into the Ca sites, the distribution coefficient is similar to that of low-Mg calcite ($D=0.05$).
- ✓However because dolomite frequently contains excess Ca, the distribution coefficient varies as a function of Ca content or stoichiometry.
- ✓Essentially the amount of Sr that dolomite can hold at equilibrium increases with increasing amount of Ca.





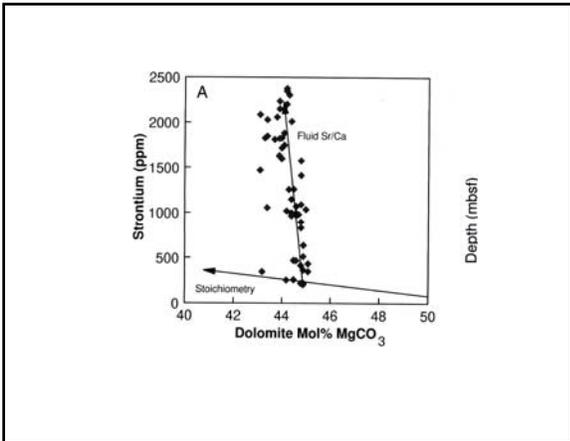
Equilibrium seawater values for Sr in dolomite are around 100 ppm for stoichiometric dolomite and 250 for non-stoichiometric dolomite

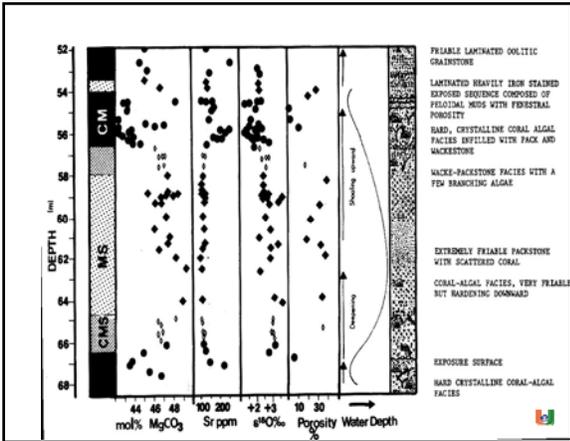


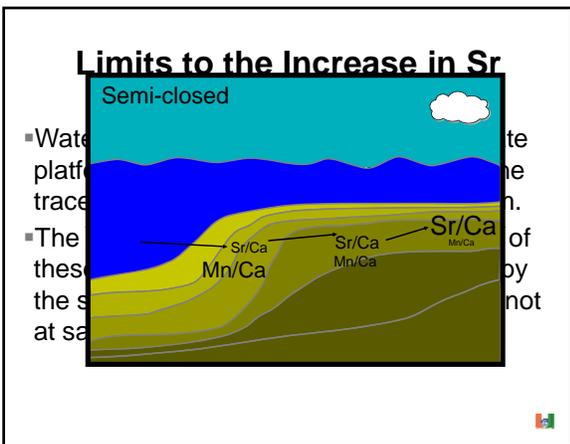


Excess in the concentration of Sr are probably a result of the build up of Sr arising from the recrystallization of calcite.









Limits to the Increase in Sr (continued)

- Sr, which has a maximum concentration of 93 μM in normal seawater, cannot exceed a concentration of approximately 600 μM in normal seawater.
- Above this level the solubility of the mineral celestite (SrSO_4) is exceeded and this mineral is easily precipitated as nodules and vein filling cement.



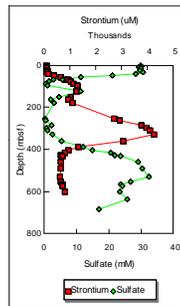
Limits to the Increase in Sr (continued)

- In instances where there is the oxidation of organic material utilizing sulphate, the concentration of sulphate can be reduced from normal seawater concentrations and consequently the maximum amount of Sr that seawater can hold can be much higher.
- Maximum Sr values in pore fluids have been measured as high as 4000 μM .
- In the absence of changes in Ca, this could produce a dolomite with a Sr concentration of 4000 ppm



Sr in Pore Waters

- Strontium concentration in pore fluids on a carbonate platform (Great Bahama Bank, Leg 166, Site 1005).
- Note the approximate inverse correlation between the concentration of sulphate and that of Sr.
- The removal of sulphate allows the concentration of Sr to build up to extremely high levels.
- Carbonates precipitated from these solutions will have very high Sr values.

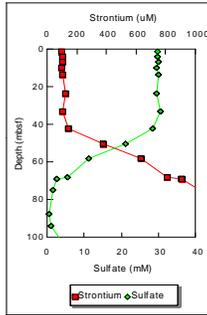


Eberli et al., 1996



Other Uses for Sr in Pore fluids

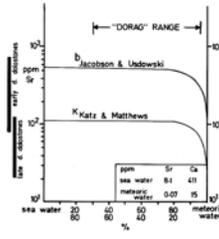
- Note the vertical profile and sulphate profile in the upper portion of this profile. There are three interpretations
 - No recrystallization
 - Rapid Sedimentation
 - Advection (fluid flow)



Eberli et al., 1996

- As freshwaters typically have small amounts of Sr and Ca in them, the mixing of freshwater and marine water will normally produce a fluid with a similar Sr/Ca ratio to that in seawater.
- Only with low amounts of seawater will the ratio change.
- Hence low Sr calcites and dolomites do not indicate formation or alteration in a mixed-water environment

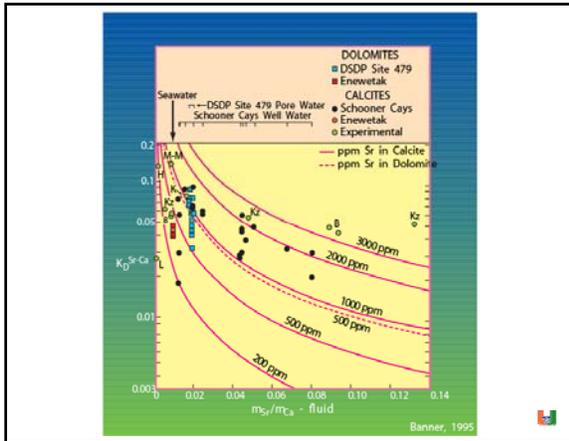
Mixing Fluids



Implications

- High Sr-values in carbonates are not
 - A result of precipitation in an evaporitic environment, but rather a result of the evolution of fluids and the involvement of sulfate reduction
- Low Sr-values can be produced in normal seawater and do not indicate alteration in a mixed water or even freshwater environment.

Eberli et al., 1996



Other Important Elements

▪ **Uranium:** Uranium is concentrated in aragonite and as the element exists as a carbonate complex, it tends to track the carbonate ions. Hence during marine diagenesis high uranium concentrations are transferred to the diagenetic carbonates. During dolomitization uranium concentrations are also retained and consequently dolomites frequently have high uranium.

**Other Important Elements
(continued)**

▪ **Manganese:** Mn is an element which tends to increase in diagenetic carbonates and also increase in open systems. Mn has very low concentrations in the marine environment and consequently has low concentrations in modern carbonates. Mn has been linked to the phenomenon of luminescence. High concentrations induce luminescence. Concentrations as low as 20 ppm can produce luminescence.

Other Elements(continued)

▪ **Iron:** Fe behaves similar to Mn in the marine environment and differences in abundance compared to Mn are caused by slightly different redox conditions. Fe can act a a quencher of luminescence. Concentrations of both Fe and Mn are kinetically controlled with higher concentrations being related to slower rates of precipitation.

▪ **Sodium:** Na is a strange element and suffers greatly from contamination.



Seawater Composition

- Sr 8 ppm 8/87.62= 89 μM
- Ca 420 ppm 420/40.08= 10.11 mM
- Cl 19,844 ppm 19844/35.5 = 559 mM
- Mg 1200 ppm 1200/24.3 = 55 mM
- SO₄ 680 ppm 680/96 = 28 mM
- HCO₃ 120 ppm 120/61 = 2 mM
- CO₃²⁻ 12 ppm 12/60 = 0.2 mM



Ratios

- Sr/Ca = 0.089/10 = 0.0089 mM/M = 8.9 μM/M
- Mg/Ca = 55/10 = 5.5 M/M
- Ca/Cl = 10/559 = 17.8 mM/M
- Mg/Cl = 55/559 = 98 mM/M
- SO₄/Cl = 28/559 = 50 mM/M



Important Reactions

- Oxidation of Organic Material
– $2\text{CH}_2\text{O} + \text{SO}_4^{2-} = 2\text{HCO}_3^- + \text{H}_2\text{S}$
- Dissolution
– $\text{Ca}_{(1-x-y)}\text{Sr}_x\text{Mg}_y\text{CO}_3 = \text{CO}_3^{2-} + \text{Ca}^{2+} + x\text{Sr}^{2+} + y\text{Mg}^{2+}$
- Precipitation
– $\text{CO}_3^{2-} + \text{Ca}^{2+} + x\text{Sr}^{2+} + y\text{Mg}^{2+} = \text{Ca}_{(1-x-y)}\text{Sr}_x\text{Mg}_y\text{CO}_3$
- Alkalinity
– $\text{Alkalinity} = \text{CO}_3^{2-} + \text{HCO}_3^-$



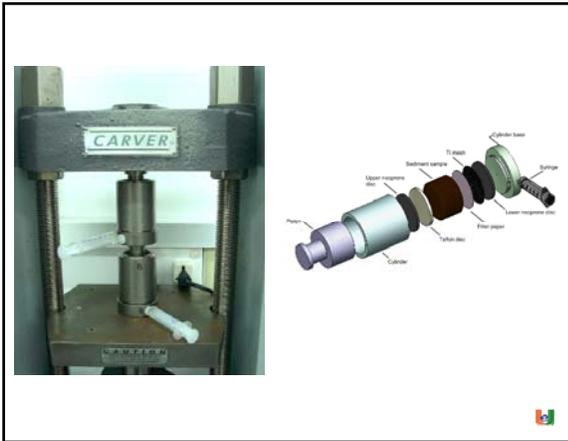
Other Reactions

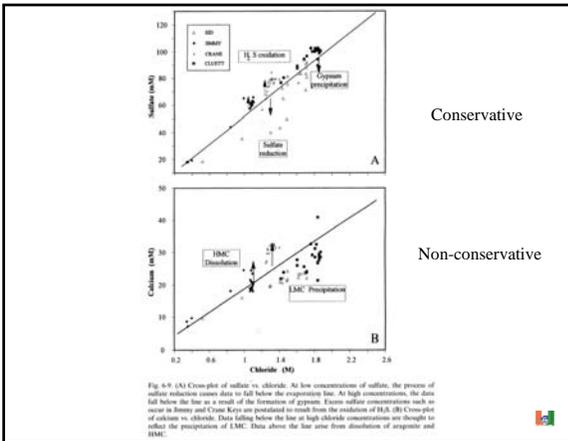
- $\text{H}_2\text{S} + \text{O}_2 = \text{SO}_4^{2-}$ Hydrogen Sulphide oxidation
- $\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$ Gypsum

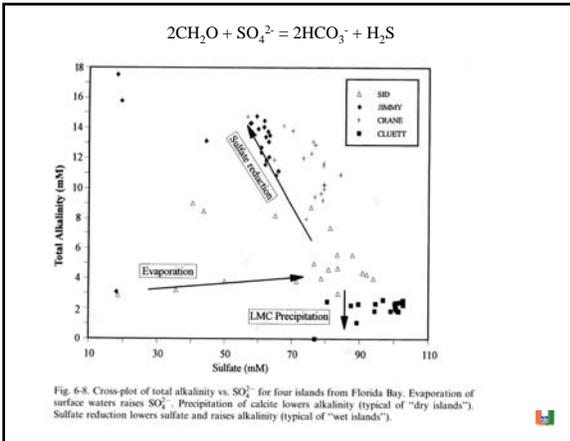


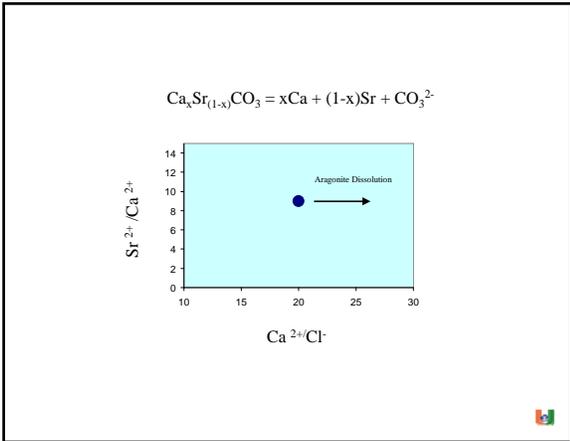


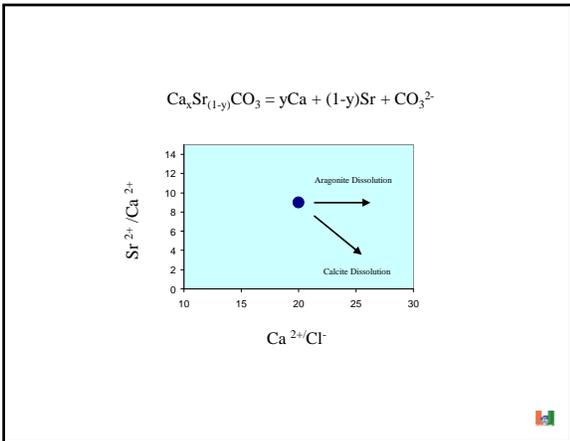


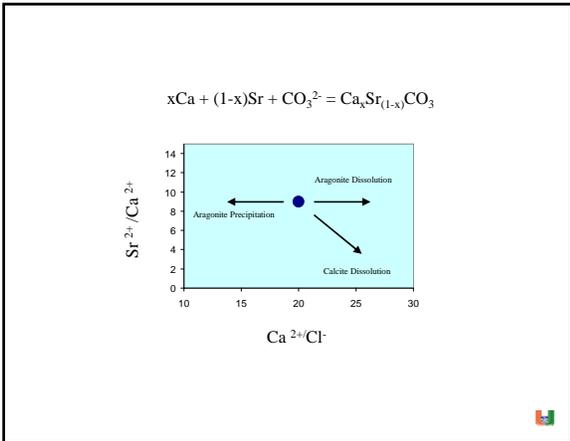


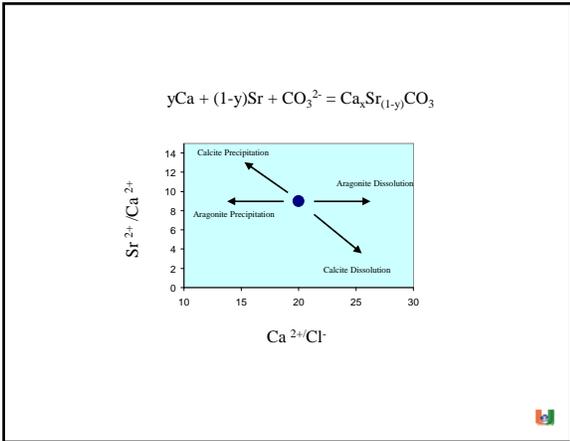


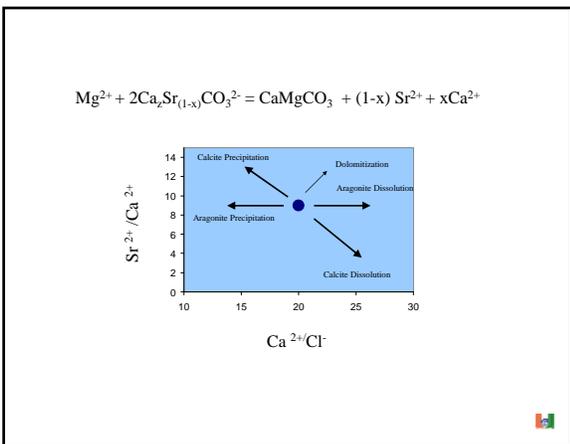


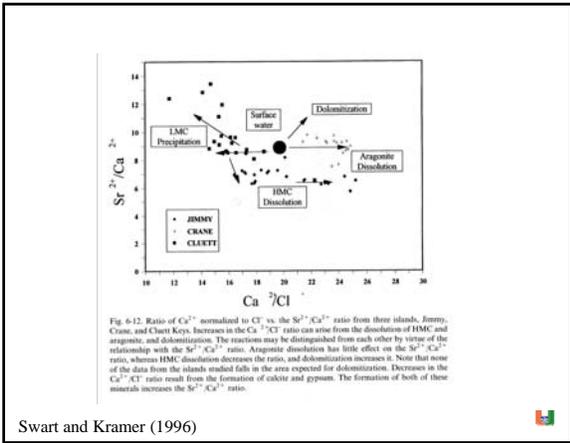


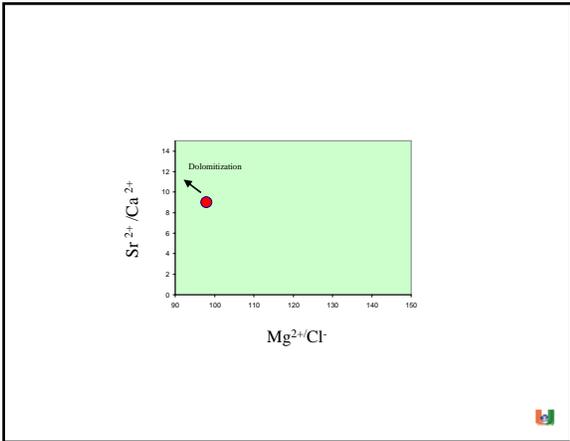


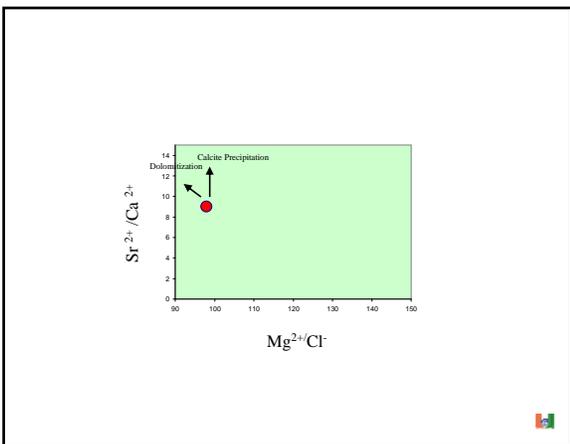


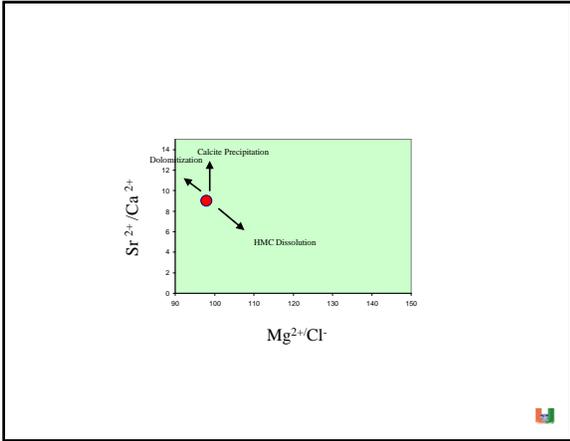












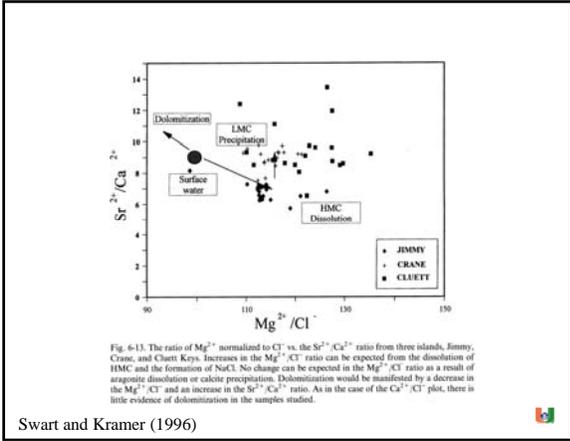
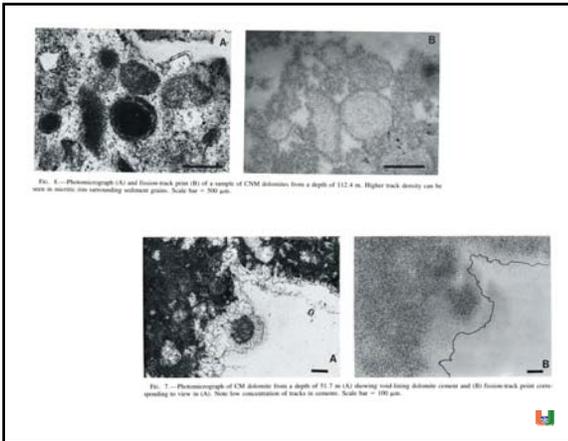


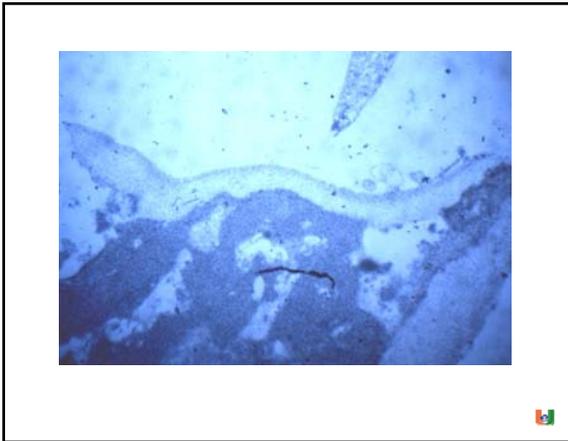
Fig. 6-13. The ratio of Mg^{2+} normalized to Cl^- vs. the Sr^{2+}/Ca^{2+} ratio from three islands, Jimmy, Crane, and Cluett Keys. Increases in the Mg^{2+}/Cl^- ratio can be expected from the dissolution of HMC and the formation of NaCl. No change can be expected in the Mg^{2+}/Cl^- ratio as a result of aragonite dissolution or calcite precipitation. Dolomitization would be manifested by a decrease in the Mg^{2+}/Cl^- and an increase in the Sr^{2+}/Ca^{2+} ratio. As in the case of the Ca^{2+}/Cl^- plot, there is little evidence of dolomitization in the samples studied.

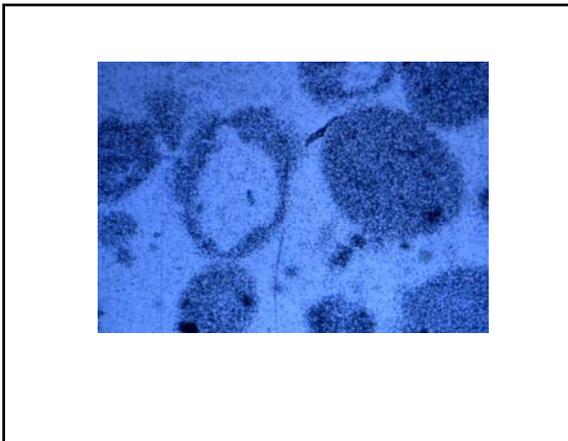
Swart and Kramer (1996)

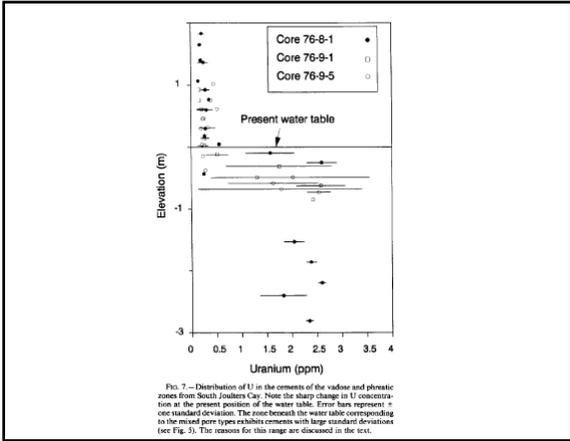
Why Trace Elements in Porewaters?

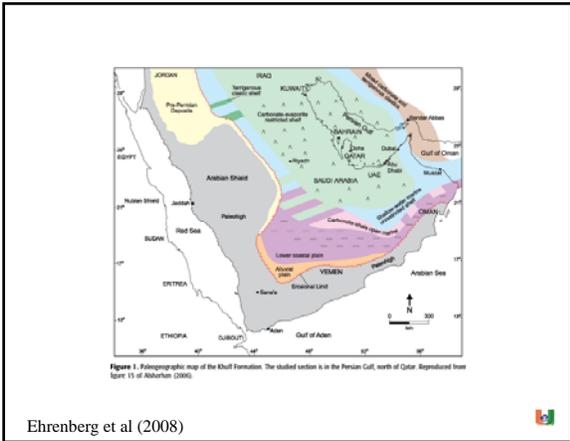
- Concentrations of trace elements can be measured to levels of less than 1%.
- Try finding 1 % of calcite or dolomite in a sediment!
- Porewater trace elements are very sensitive indicators of recrystallization



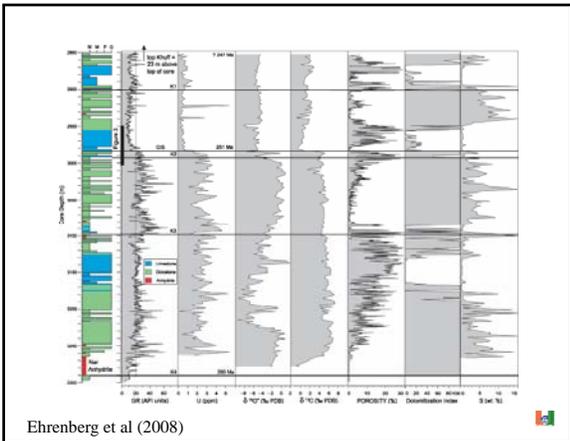




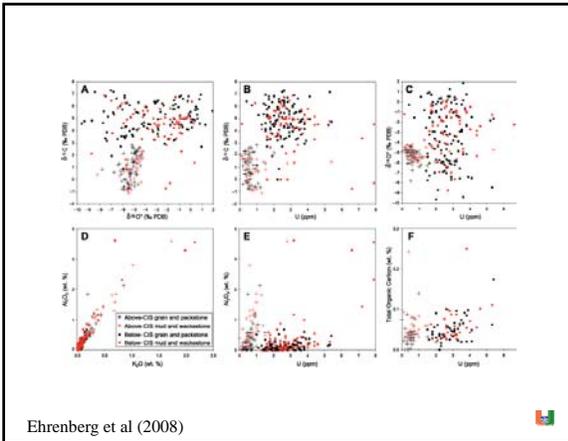




Ehrenberg et al (2008)



Ehrenberg et al (2008)



Ehrenberg et al (2008)

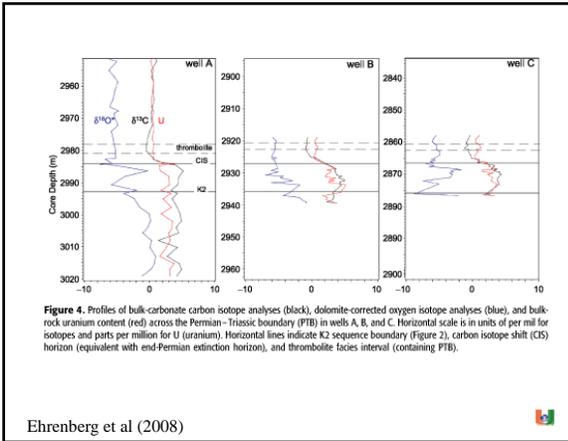


Figure 4. Profiles of bulk-carbonate carbon isotope analyses (black), dolomite-corrected oxygen isotope analyses (blue), and bulk-rock uranium content (red) across the Permian-Triassic boundary (PTB) in wells A, B, and C. Horizontal scale is in units of per mil for isotopes and parts per million for U (uranium). Horizontal lines indicate K2 sequence boundary (Figure 2), carbon isotope shift (CIS) horizon (equivalent with end-Permian extinction horizon), and thrombolite facies interval (containing PTB).

Ehrenberg et al (2008)

Summary

- Trace elements
 - Provides additional constraints on diagenesis
 - Information on the amount of diagenesis
 - Information on the environment of diagenesis

NEXT:

Strontium Isotopes
