Evaluating Dolomite Stoichiometry as a Proxy for the Chemistry of Dolomitizing Fluids*

Cameron J. Manche[1] and Stephen E. Kaczmarek[1]

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[1] Geosciences, Western Michigan University, Kalamazoo, Michigan (Cameron.J.Manche@wmich.edu)

Abstract

Various proxies, such as stable isotopes and trace elements, are routinely used to constrain the conditions of dolomitization. Here, dolomite stoichiometry is evaluated as a proxy for the chemistry of the dolomitizing fluid. High-temperature experiments have shown that dolomite stoichiometry is controlled by Mg/Ca, temperature, and molarity (Na, K, Mg, Ca) of the dolomitizing fluid. Here, we evaluated systematic changes in dolomite stoichiometry as a means to provide geologically relevant information about the dolomitizing conditions. To do this, high-resolution stratigraphic measurements were acquired from an outcrop of the Cretaceous Upper Glen Rose Formation. In total, 292 vertical and 102 lateral samples were collected and examined at the centimeter scale using a suite of analytical tools, including powder X-ray diffraction (XRD), stable isotope geochemistry, thin section petrography, and scanning electron microscopy.

The Upper Glen Rose is characterized by high-frequency depositional cycles that fluctuate between subtidal mud-dominated miliolid packstones to supratidal mud-cracked dolomitic mudstone caps. High-resolution data exhibit two geochemical and mineralogical patterns within individual depositional cycles. Regressive facies successions are associated with vertical increases in dolomite stoichiometry, percent dolomite, and $\delta^{18}O$ values. In contrast, transgressive facies successions are associated with vertical decreases in dolomite stoichiometry, percent dolomite, and $\delta^{18}O$ values. These patterns are consistent with a model of dolomitization whereby temporal changes in fluid chemistry (e.g., Mg/Ca, temperature, and molarity) reflect relative sea-level fluctuations during deposition and penecontemporaneous dolomitization. The high-resolution XRD dataset presented here is the first of its kind and suggests that dolomite stoichiometry may provide a valuable proxy for interpreting the chemistry of dolomitizing fluids.

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Cameron J. Manche & Stephen E. Kaczmarek
Geological & Environmental Sciences – Western Michigan University

2018 Annual Convention & Exhibition – AAPG | Salt Lake City, Utah
New Insights on the Complexity of Carbonate Diagenesis | Tuesday, May 22nd, 2018

Geological & Environmental Sciences
Carbonate Petrology & Characterization Lab

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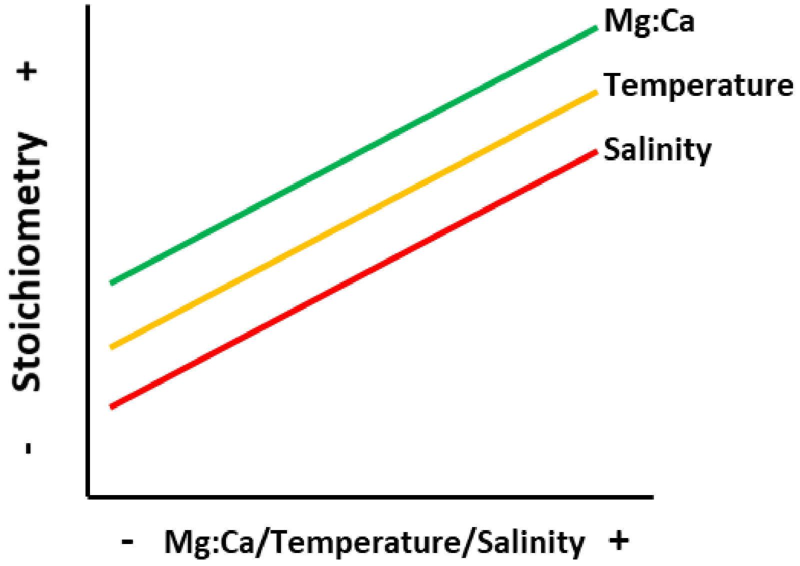
Problem

Dolomite:

- *Uncertainty in the hydrologic mechanisms responsible for dolomitization*



Existing Proxies:

- Stable isotopes and trace elements
    - Allow for multiple interpretations

Dolomite Stoichiometry:

- Commonly reported metric, but its utility as proxy is not understood
- Various factors control stoichiometry. Few studies have evaluated how these factors evolve in related dolomites.
    - Mg/Ca (Sibley et al., 1987; Kaczmarek and Sibley, 2011)
    - Temperature (Kaczmarek and Thornton, 2017)
    - Salinity (Na, K, Ca, Mg) (Cohen and Kaczmarek, 2017)

Hypothesis

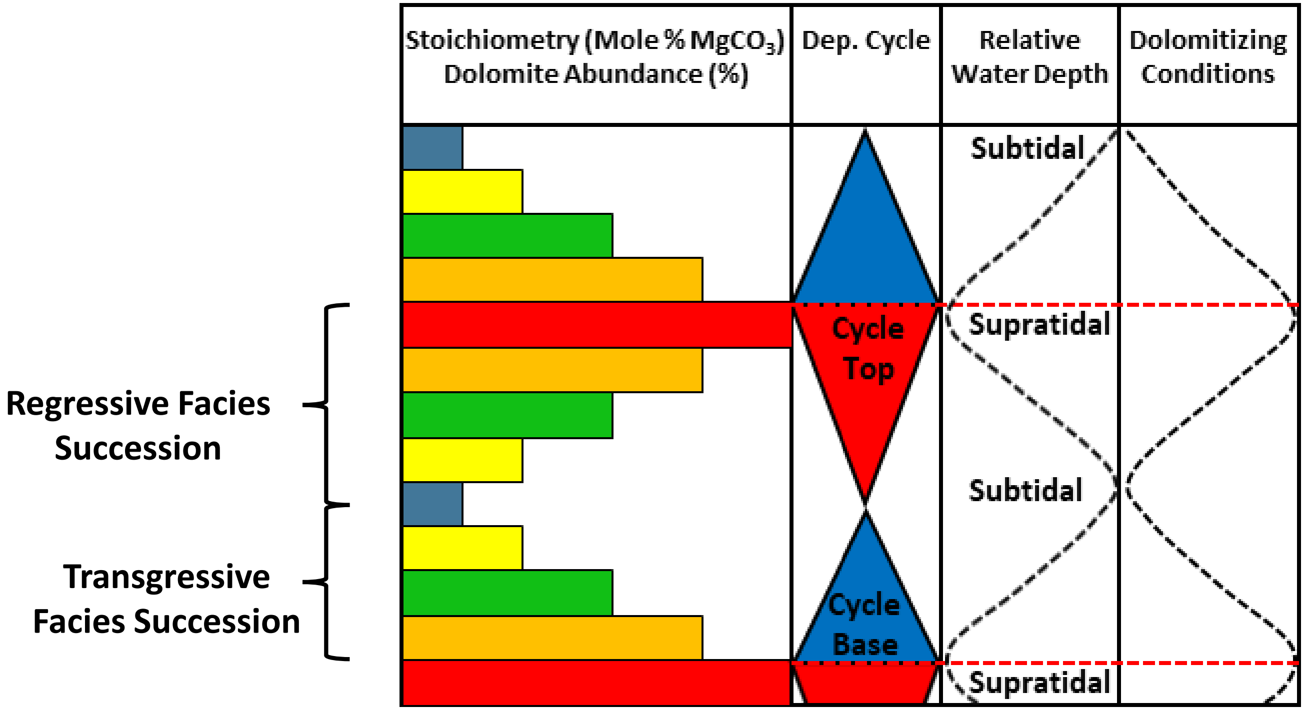
Objective:

- Evaluate the utility of dolomite stoichiometry as a proxy for temporal changes in the dolomitizing conditions.

Hypothesis:

- Dolomite stoichiometry is providing a record of changing dolomitizing conditions in response to changes in relative water depth
    - Mg/Ca
    - Temperature
    - Salinity

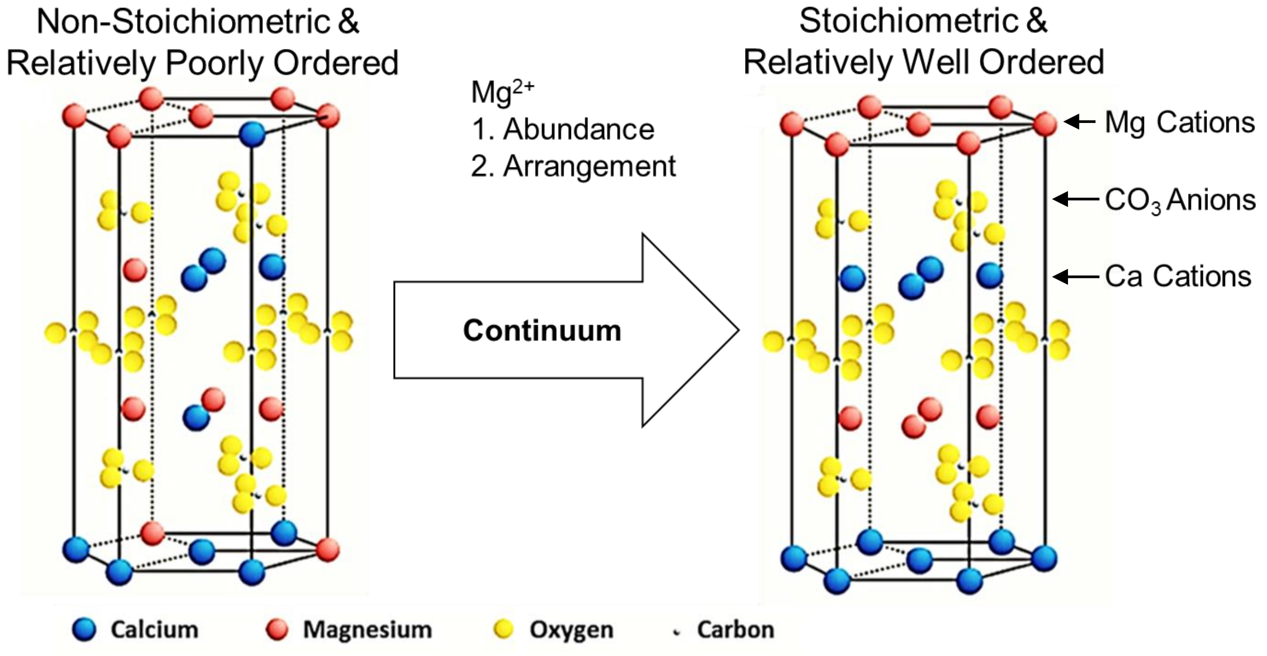
Conceptual Interpretation of Penecontemporaneous Dolomitization



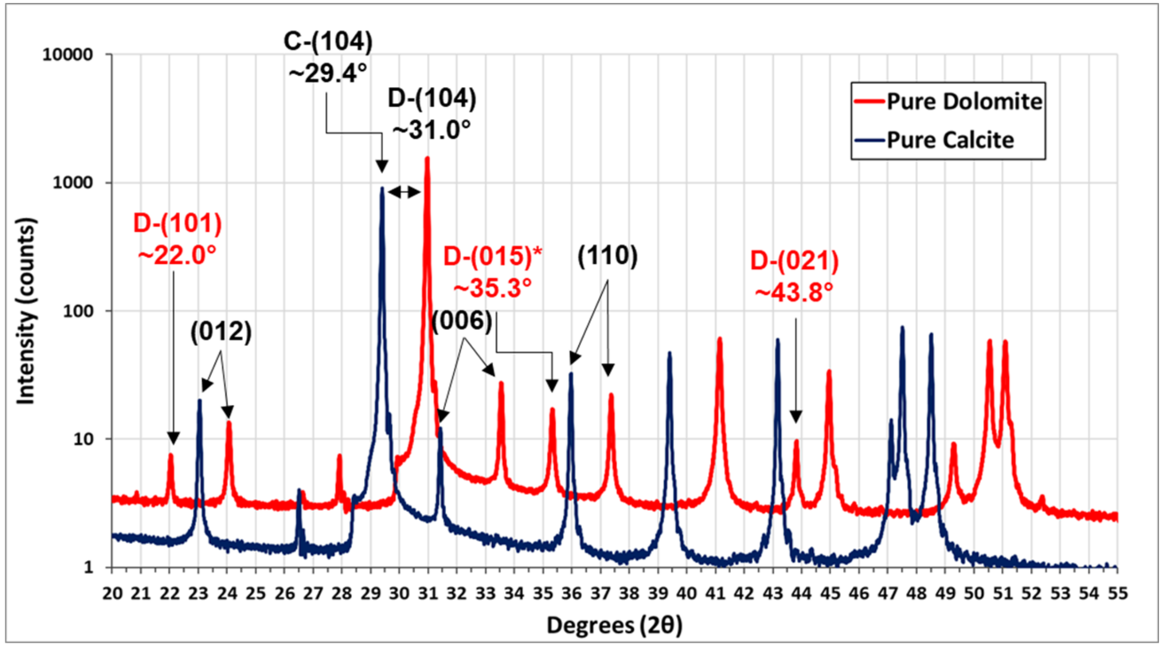
How do we characterize dolomites?

Dolomite [CaMg $(CO_3)_2$]

- Stoichiometry (**Composition**): abundance of Mg relative to Ca
    - Position of the (104) peak
- Cation Ordering (**Structure**): arrangement of cations in the appropriate plane
    - D-(101)
    - D-(015)
    - D-(021)



Modified after Scholle and Ulmer-Scholle, 2003

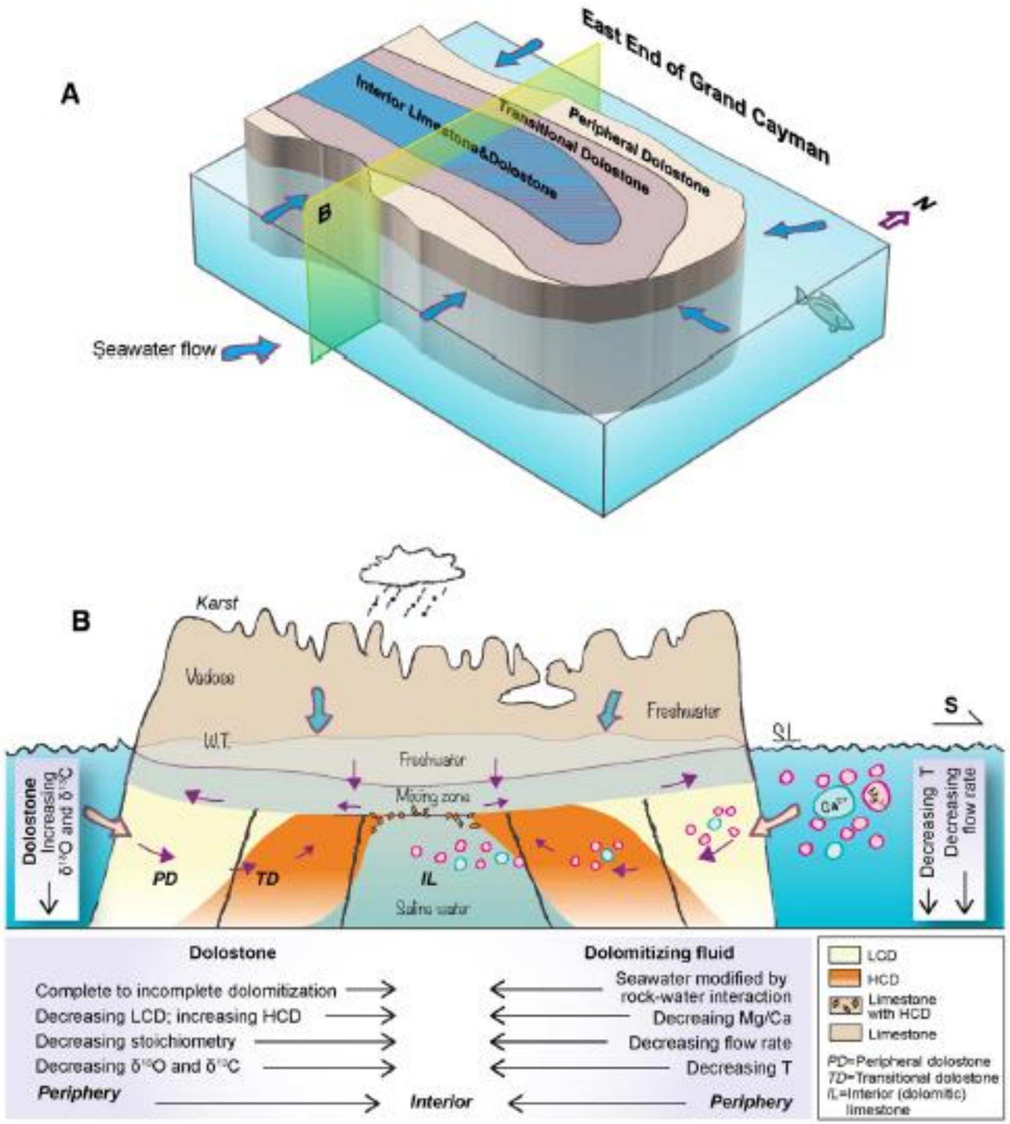


CuKα anode

What is known from nature?

Stoichiometry of Natural Dolomite

- Füchtbauer and Goldschmidt (1965)
    - Stoichiometric dolomites – evaporites
- Sperber et al. (1984)
    - Partially dolomitized sediments are less stoichiometric
- Lumsden and Chimahusky (1980)
    - Older dolomites – more stoichiometric
- Budd (1997)
    - Cenozoic island dolomites – typically more non-stoichiometric
- **Ren and Jones (2017)**
    - Spatial trends in dolomite stoichiometry across Grand Cayman Island



Ren and Jones, 2017

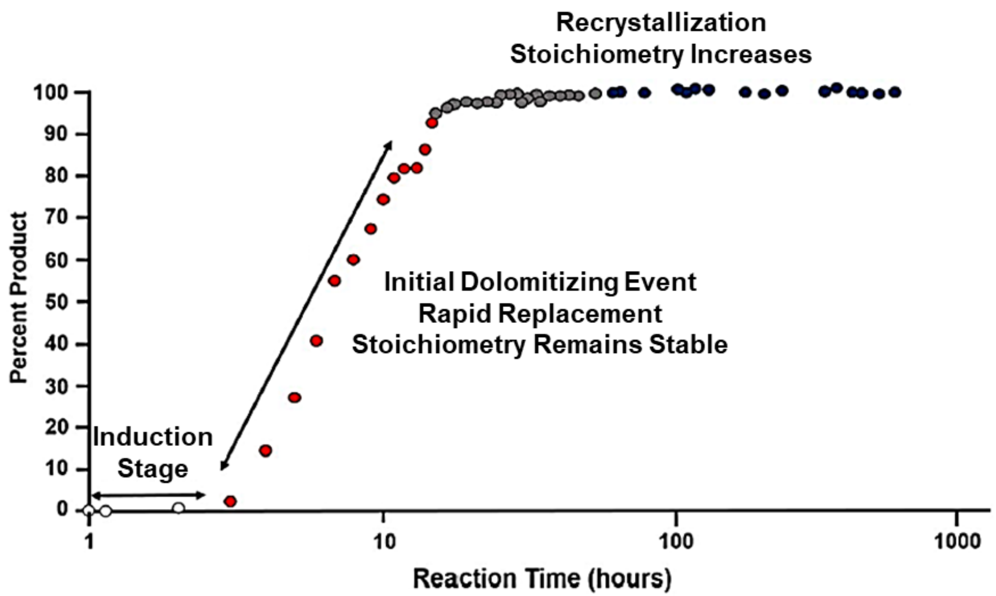
What is known from experiments?

High-Temperature Synthesis Experiments & Dolomite Stoichiometry

- During the replacement reaction (i.e., dolomitization) stoichiometry is controlled by:
  - Mg/Ca (Kaczmarek and Sibley, 2011)
  - Temperature (Kaczmarek and Thornton, 2017)
  - Salinity (Na, K, Ca, Mg) (Cohen and Kaczmarek, 2017)

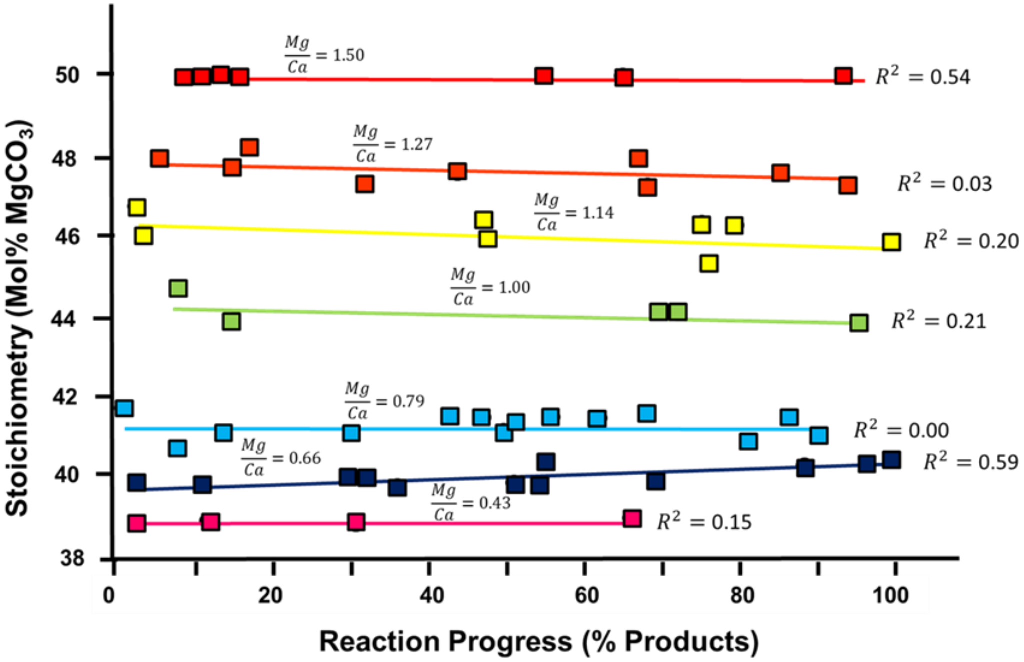
Generalized Dolomite Reaction Curve

- Modified after Kaczmarek and Thornton, 2017



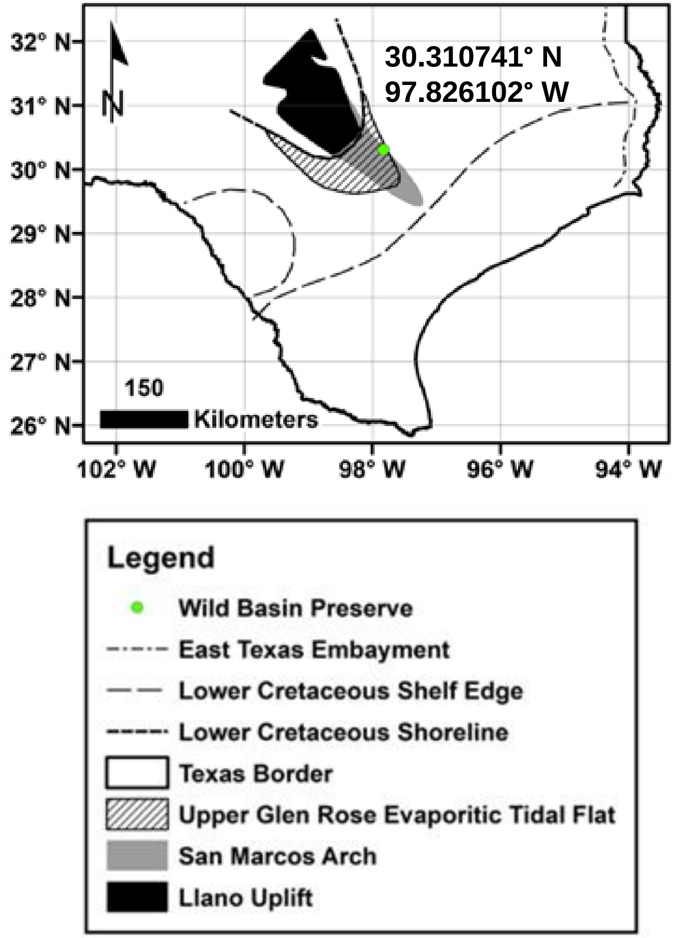
Relative Stability Prior to Recrystallization

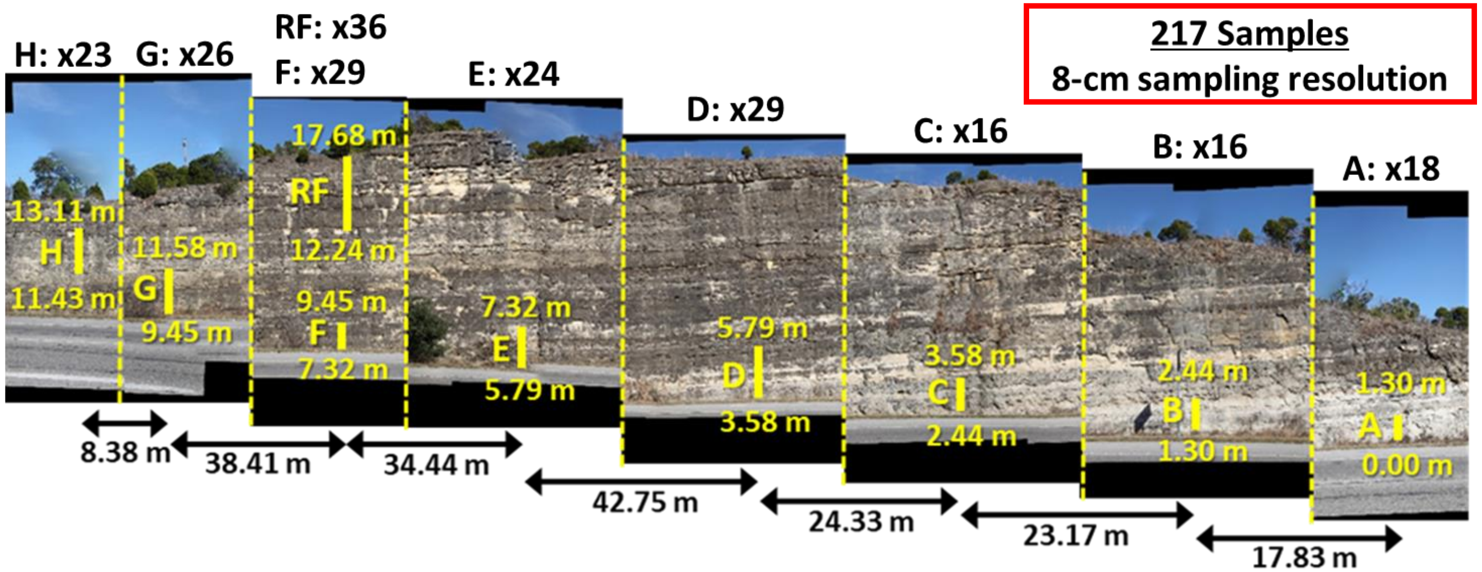
- Kaczmarek and Sibley, 2011



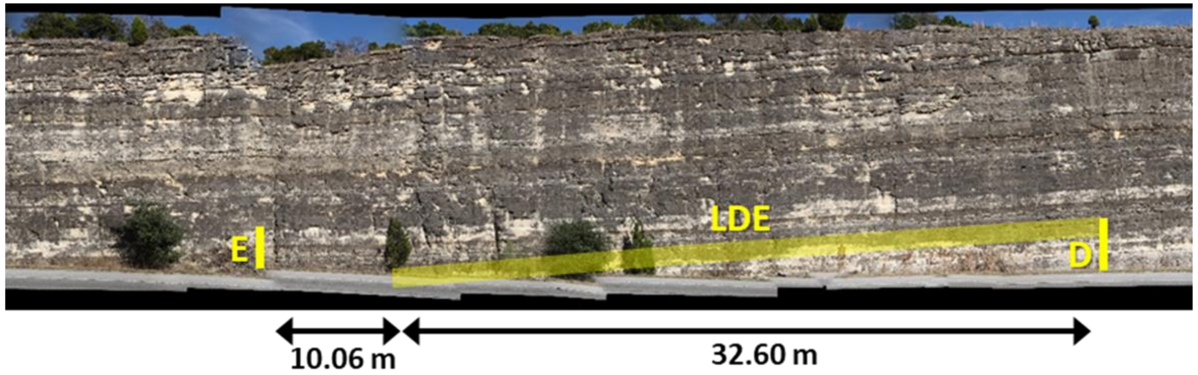
Key Point: Prior to recrystallization stoichiometry is recording these factors (i.e., Mg/Ca, Temp., Salinity)

Sample Acquisition





217 Samples
8-cm sampling resolution



102 Samples
30-cm sampling resolution

Analytical Methods

Powder X-Ray Diffraction:

- **Dolomite Stoichiometry (Lumsden, 1979)**

$$\text{mole \% CaCO}_3 = [(333.33 \times d - spacing\ (angstoms) - 911.99]$$

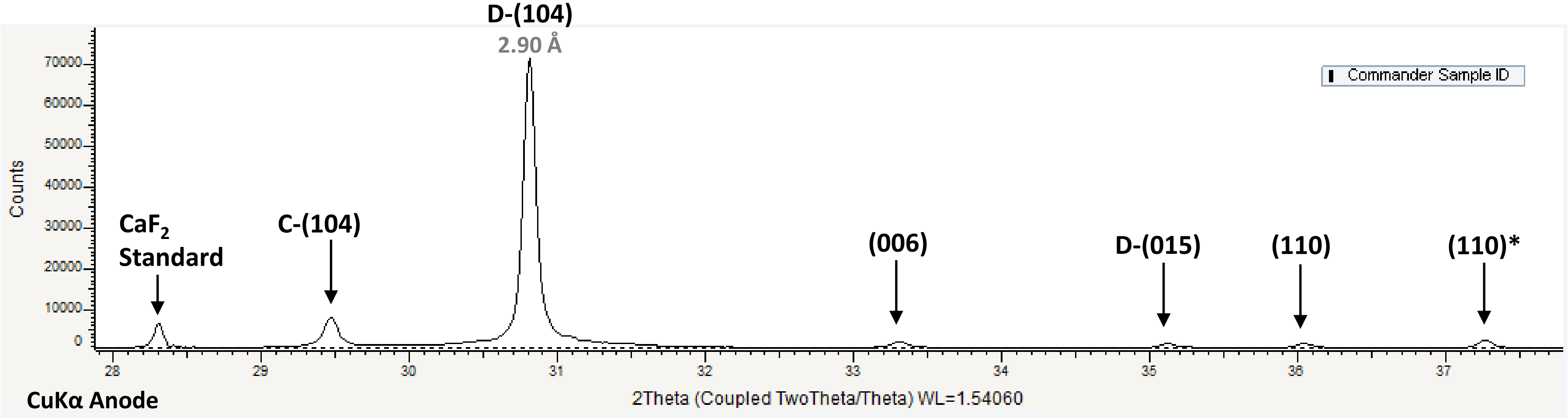
$$\text{mole \% MgCO}_3 = 1 - \text{mole \% CaCO}_3$$

- **Dolomite Abundance Relative to Calcite (Royse et al., 1971)**

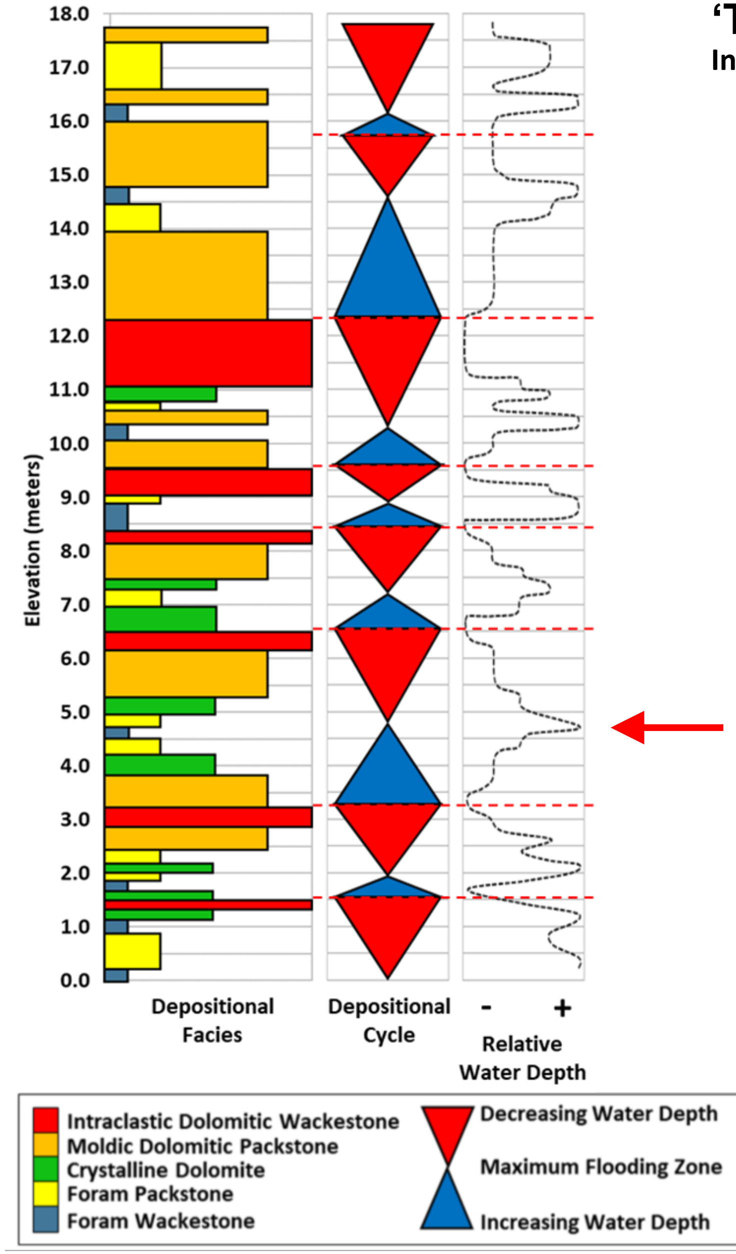
$$\text{\% Dolomite} = \frac{Intensity_{\mathrm{D-(104)}}}{Intensity_{\mathrm{C-(104)}} + Intensity_{\mathrm{D-(104)}}} * 100$$

- **Relative Cation Ordering (Goldsmith and Graf, 1958)**

$$Cation\ Ordering = \frac{Intensity_{\mathrm{D-(015)}}}{Intensity_{\mathrm{D-(110)}}}$$



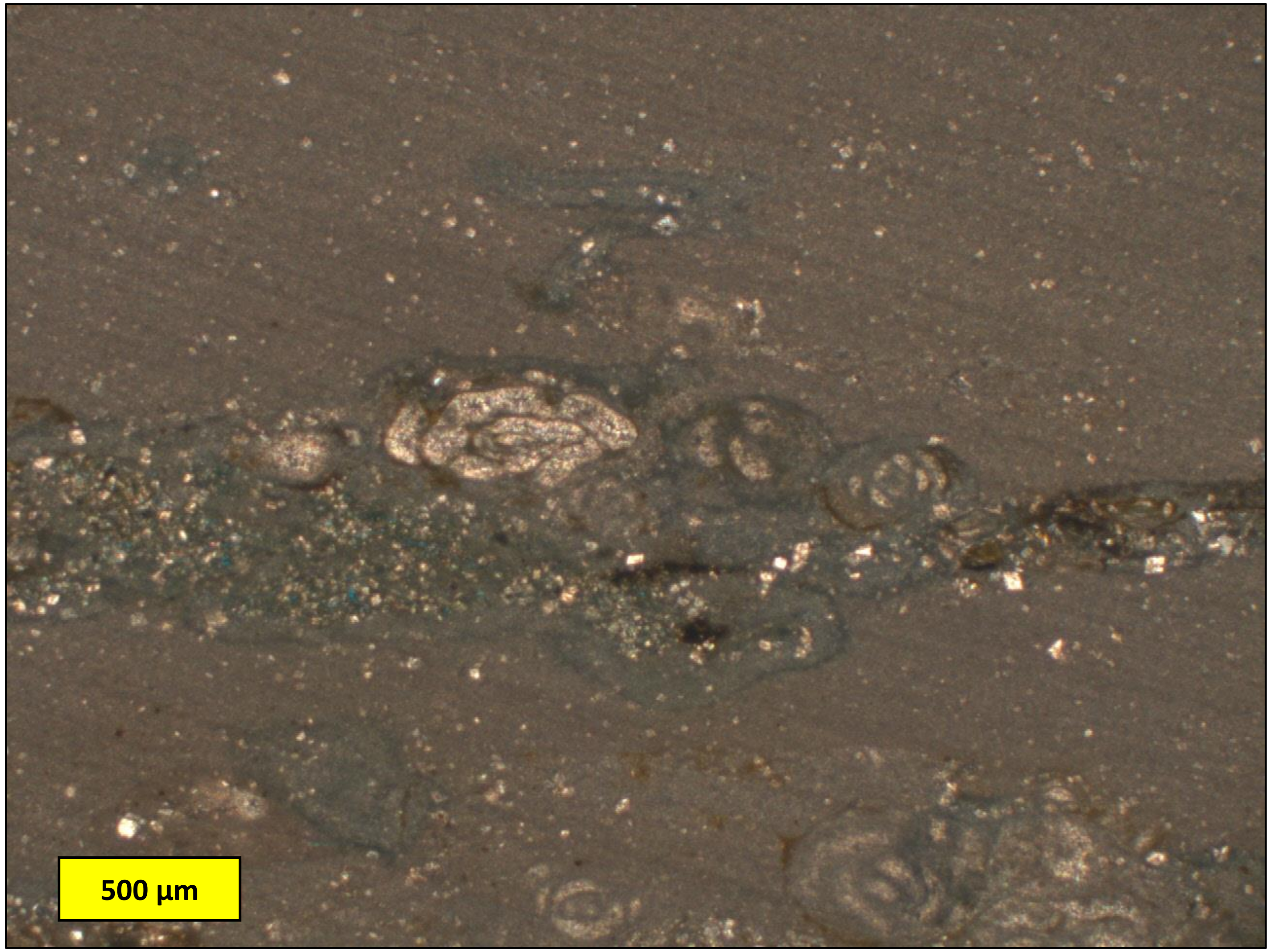
Depositional Facies & Dolomite Mineralogy



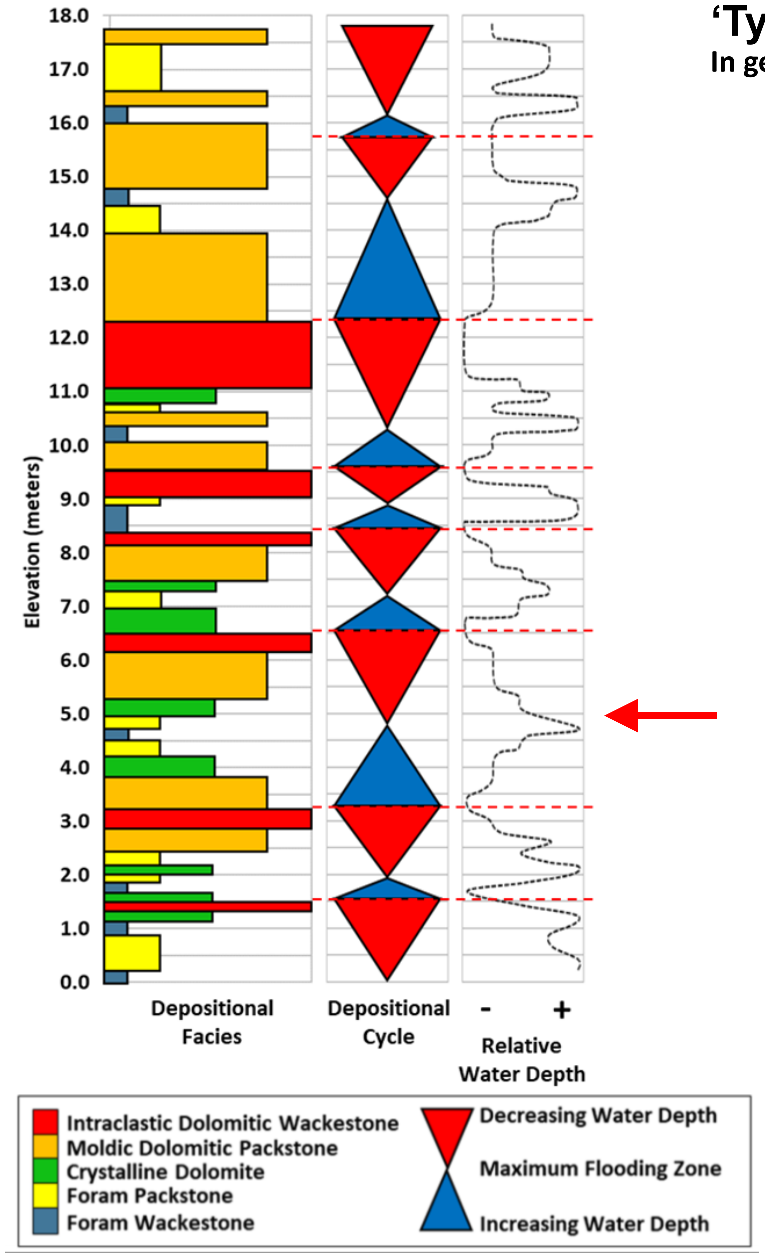
‘Typical’ Cycle

In general agreement with Fullmer (2005); Fullmer and Lucia (2010)

Foram Wackestone – Subtidal



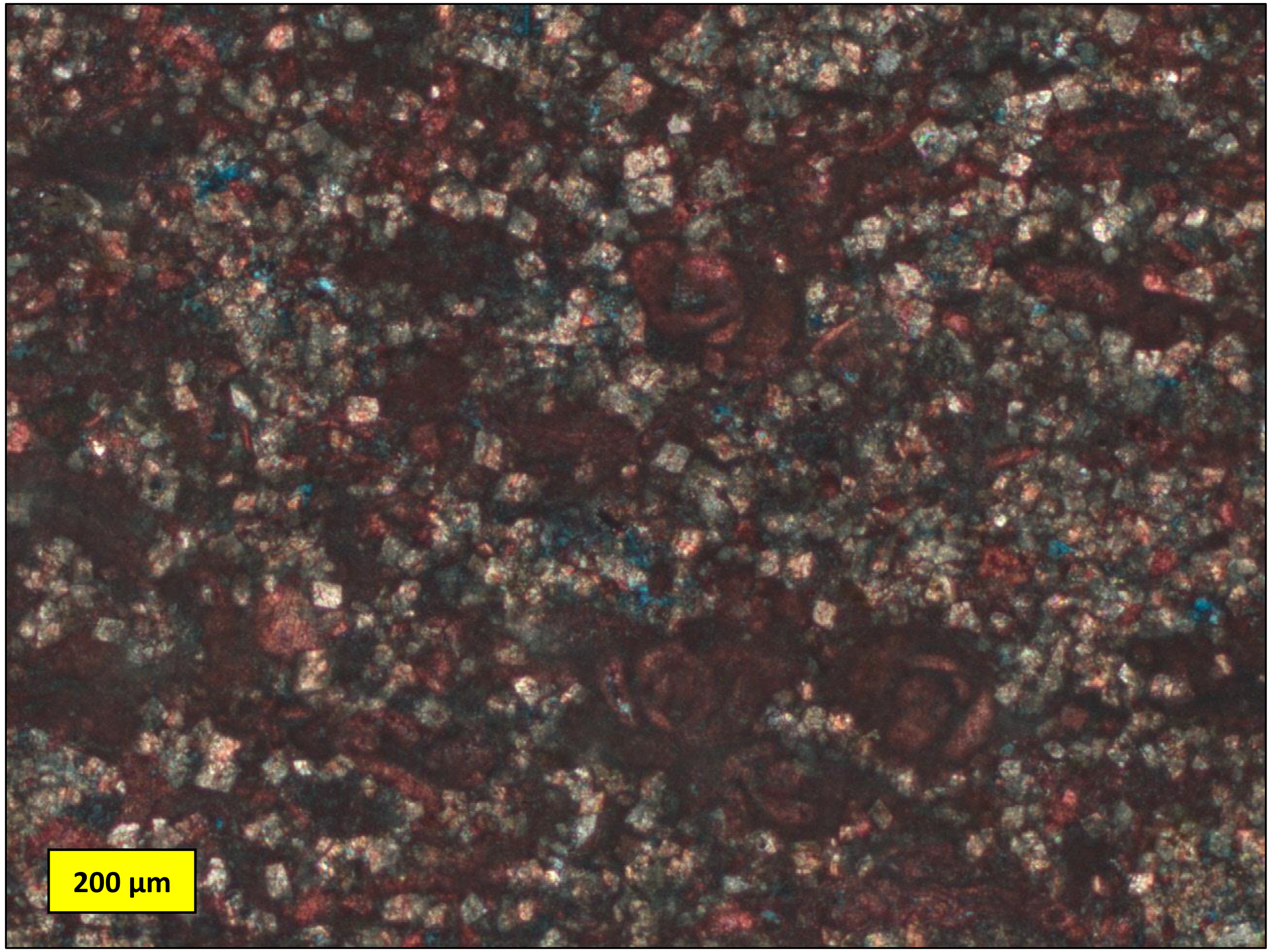
Depositional Facies & Dolomite Mineralogy



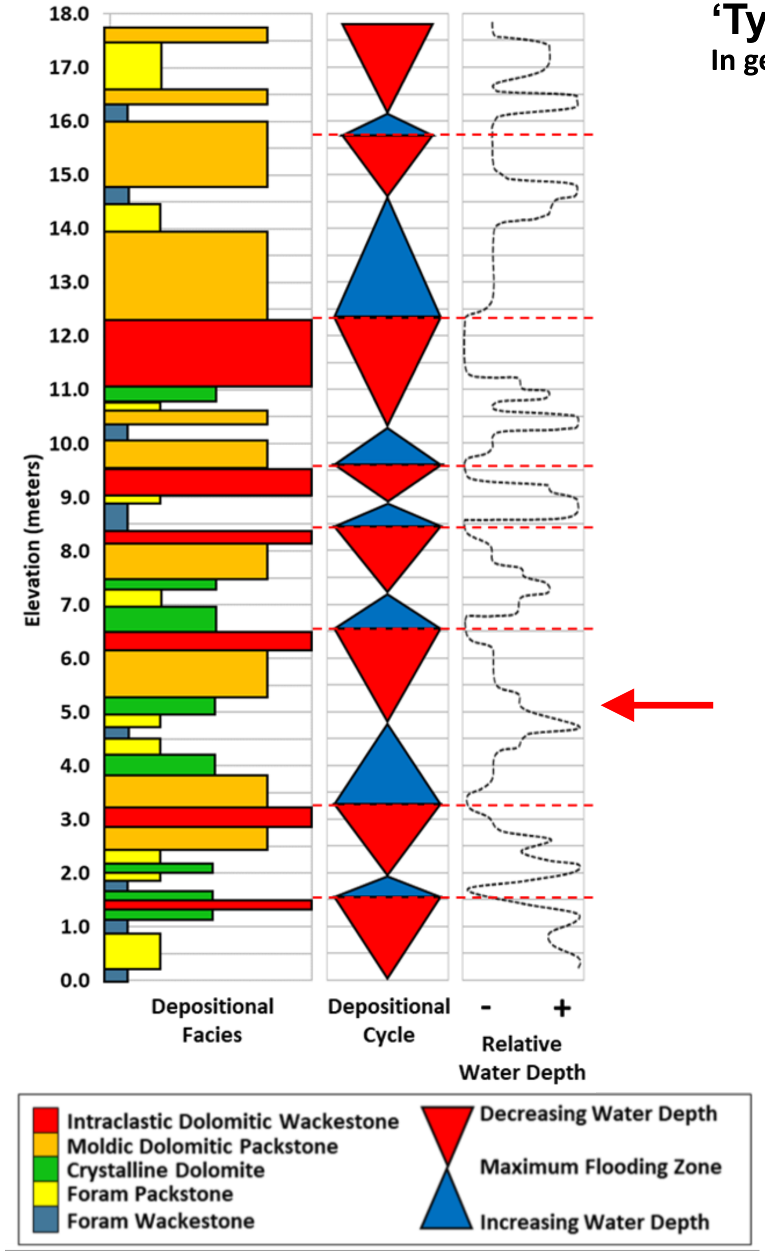
‘Typical’ Cycle

In general agreement with Fullmer (2005); Fullmer and Lucia (2010)

Foram Packstone – Subtidal



Depositional Facies & Dolomite Mineralogy



‘Typical’ Cycle

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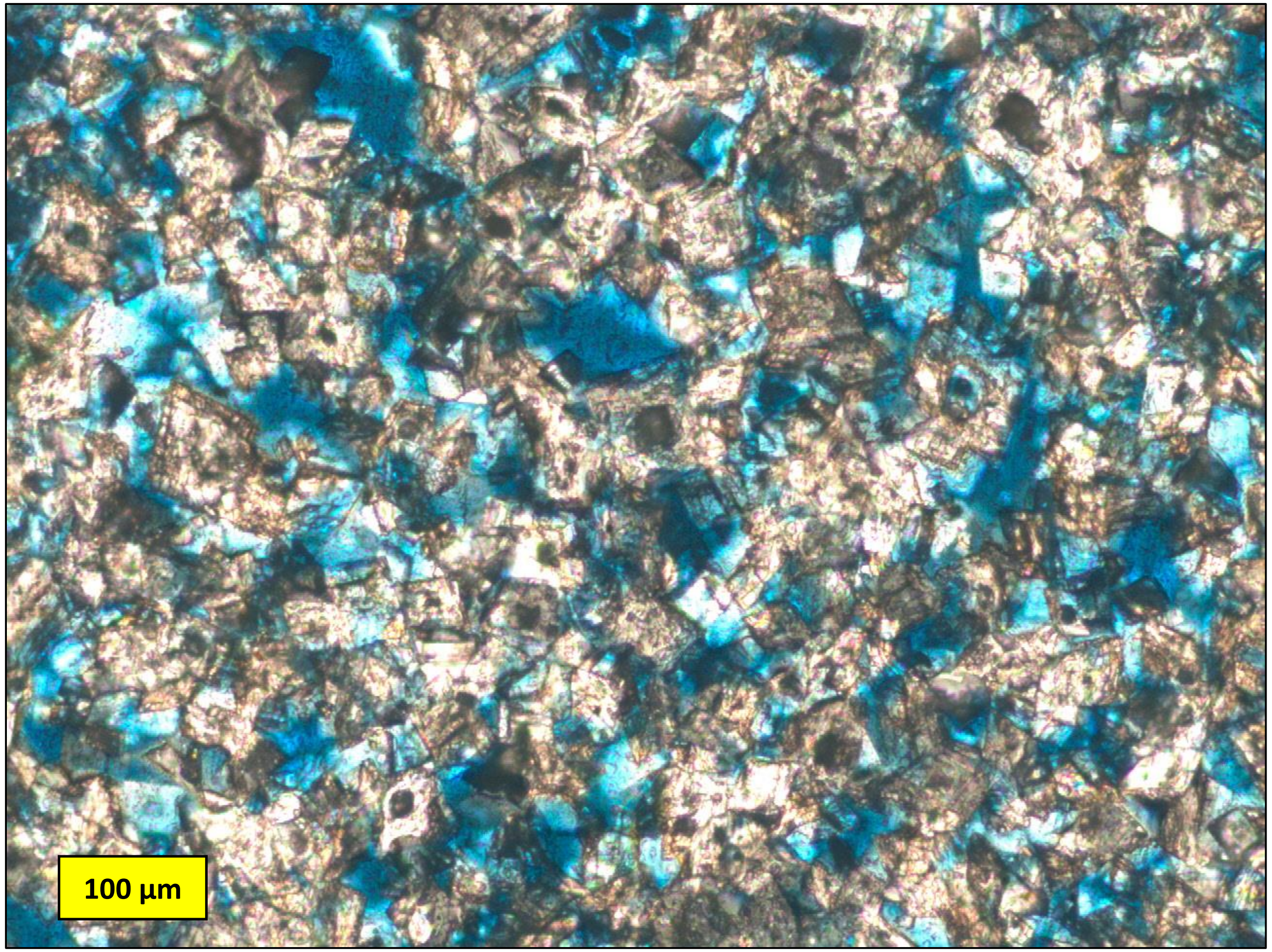
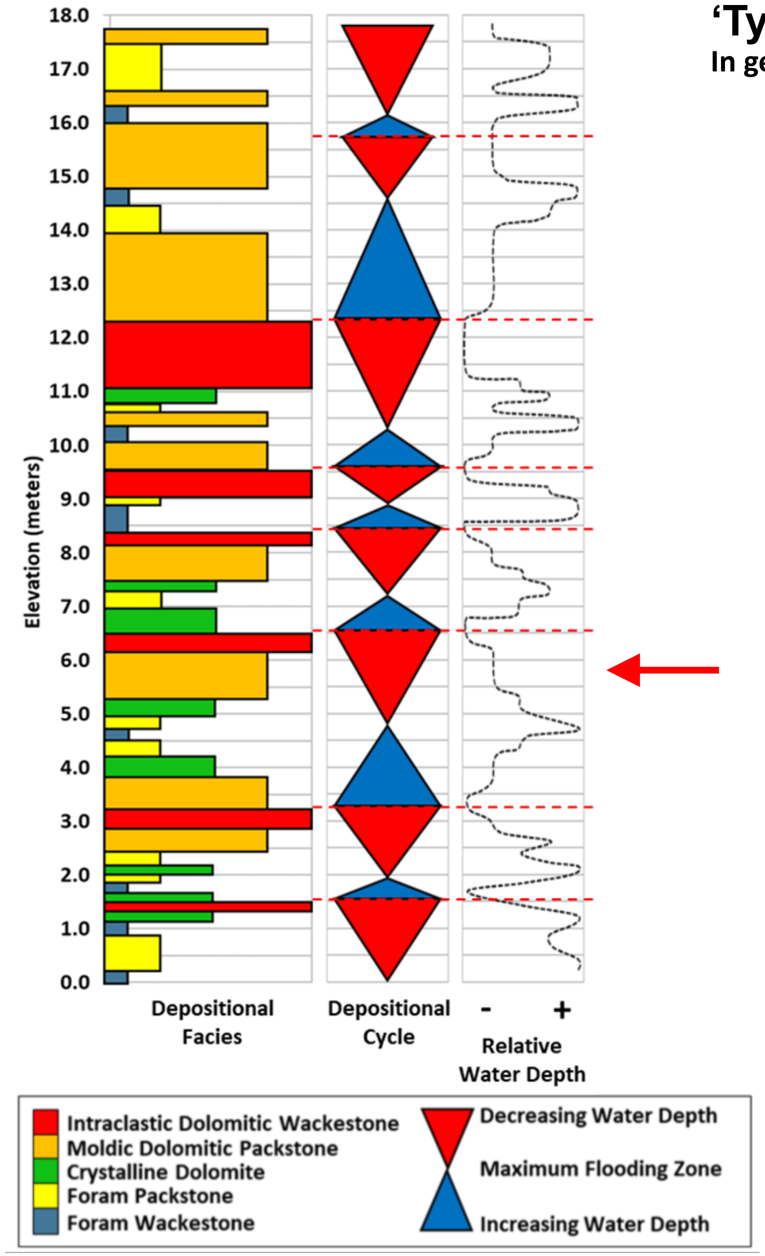
Crystalline Dolomite



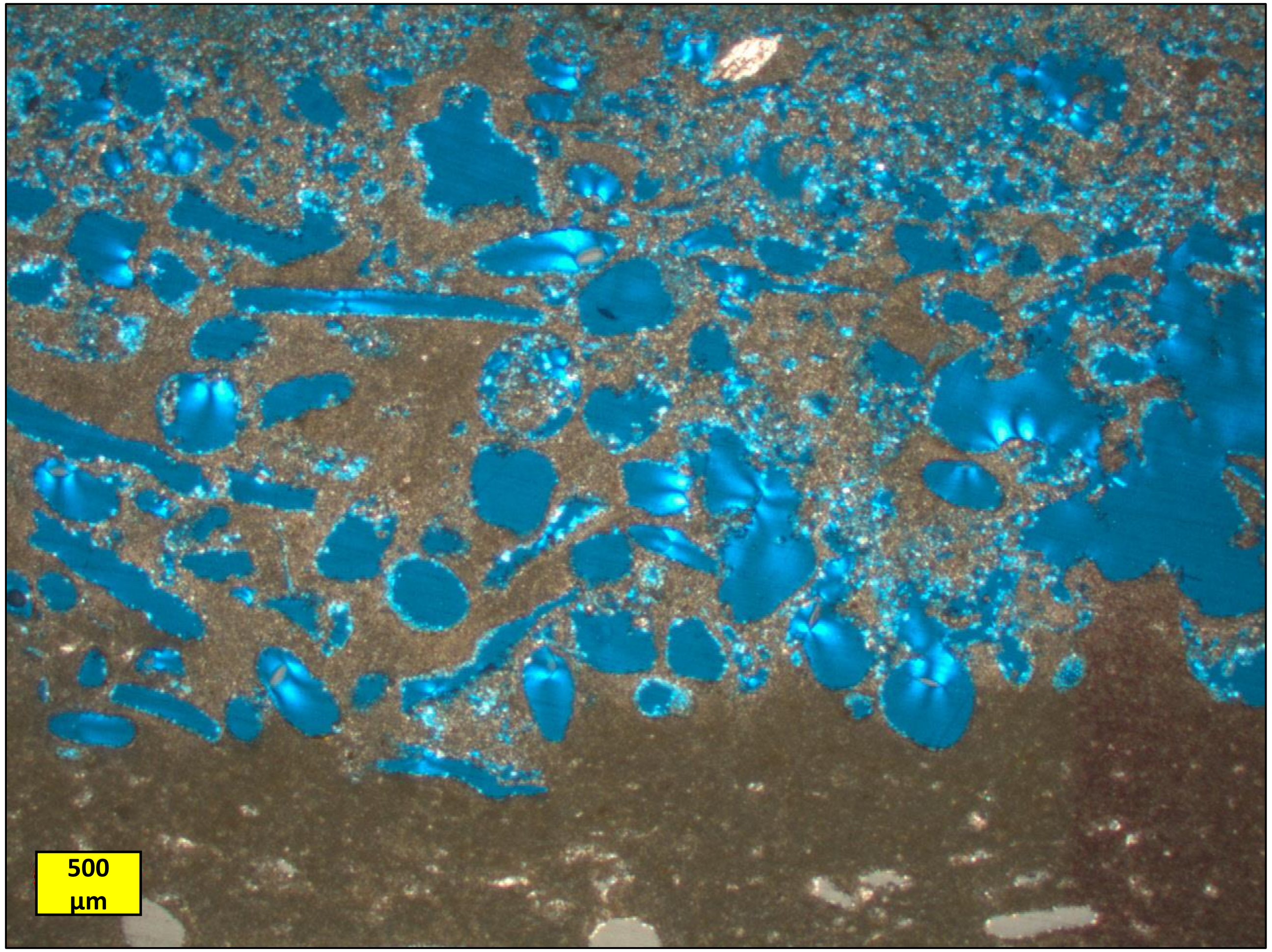
Depositional Facies & Dolomite Mineralogy



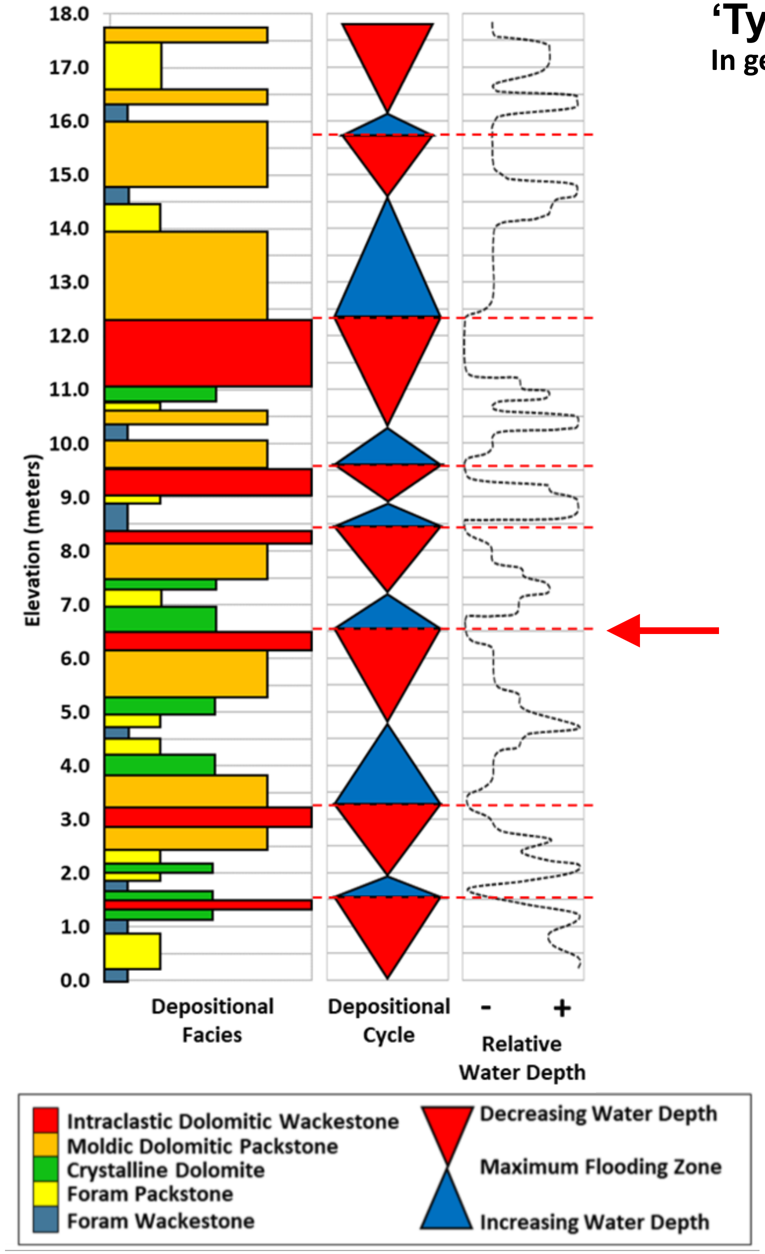
‘Typical’ Cycle

In general agreement with Fullmer (2005); Fullmer and Lucia (2010)

Moldic Dolomite Packstone – Upper Intertidal



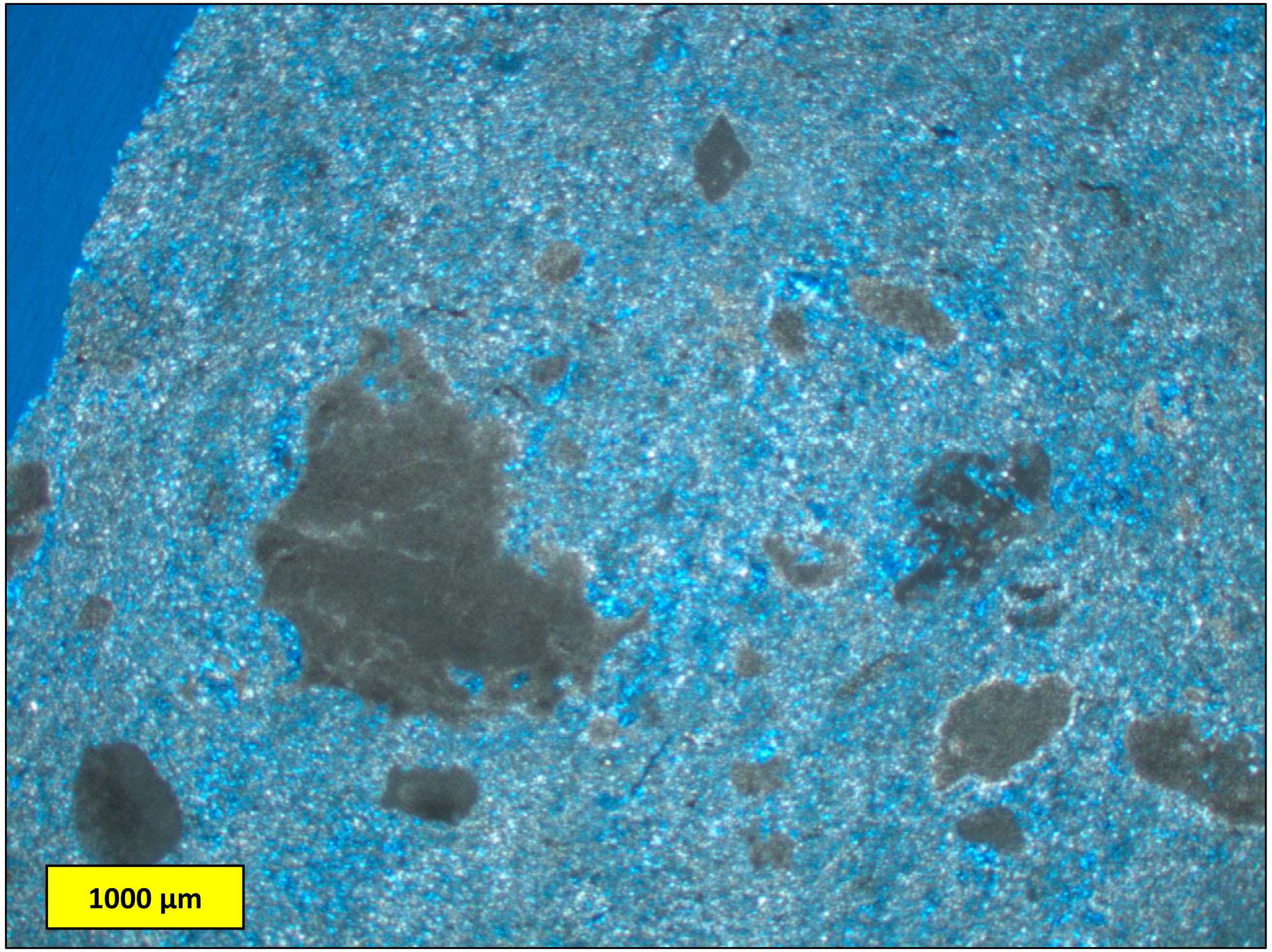
Depositional Facies & Dolomite Mineralogy



‘Typical’ Cycle

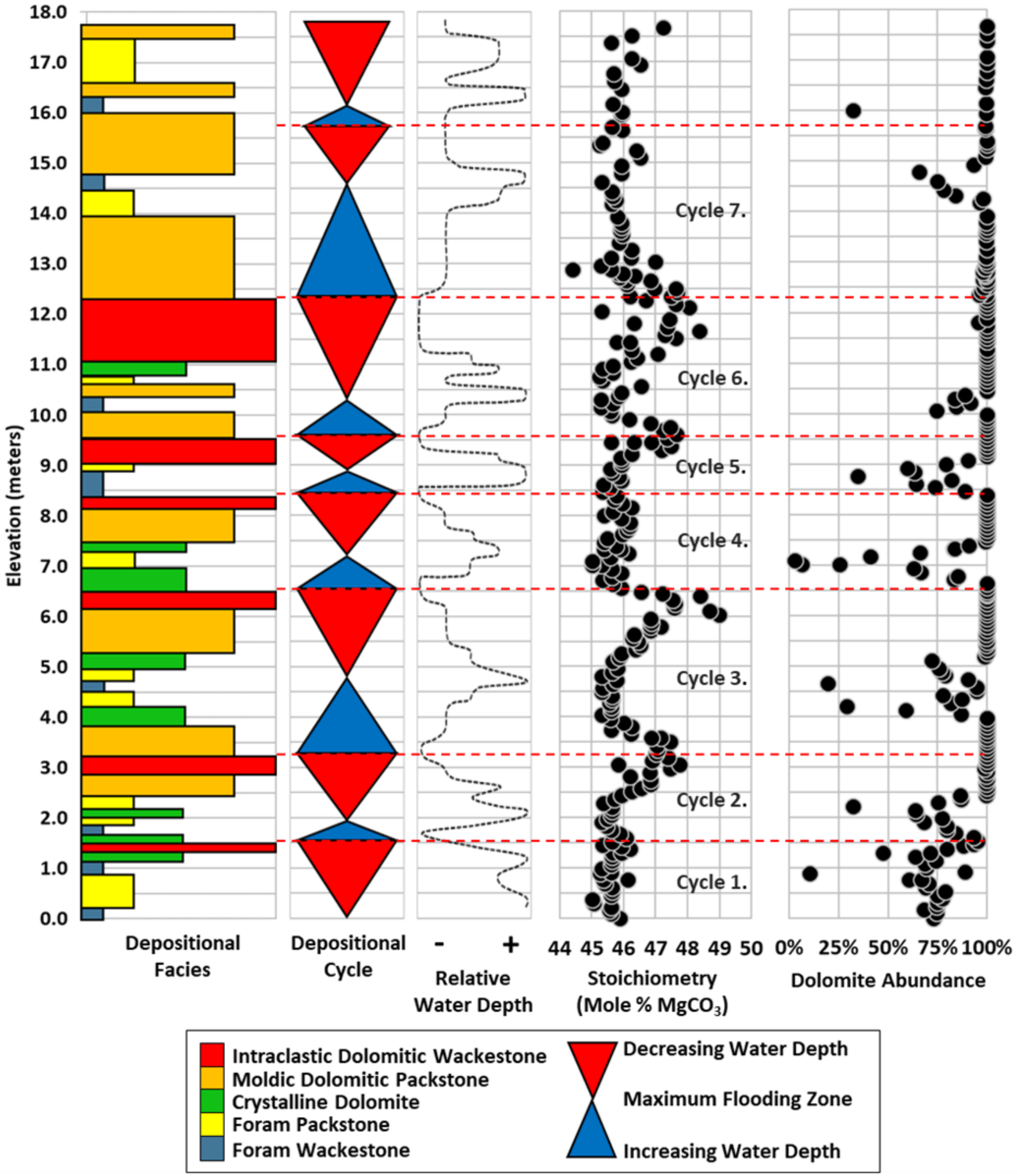
In general agreement with Fullmer (2005); Fullmer and Lucia (2010)

Intraclastic Dolomitic Wackestone - Supratidal



Outcrop Scale Features: Terra rossa and mudcracks

Depositional Facies & Dolomite Mineralogy



Key Point:

- **Fluctuations in dolomite stoichiometry and abundance correspond to changes in facies succession that are interpreted to represent changes in relative water depth.**

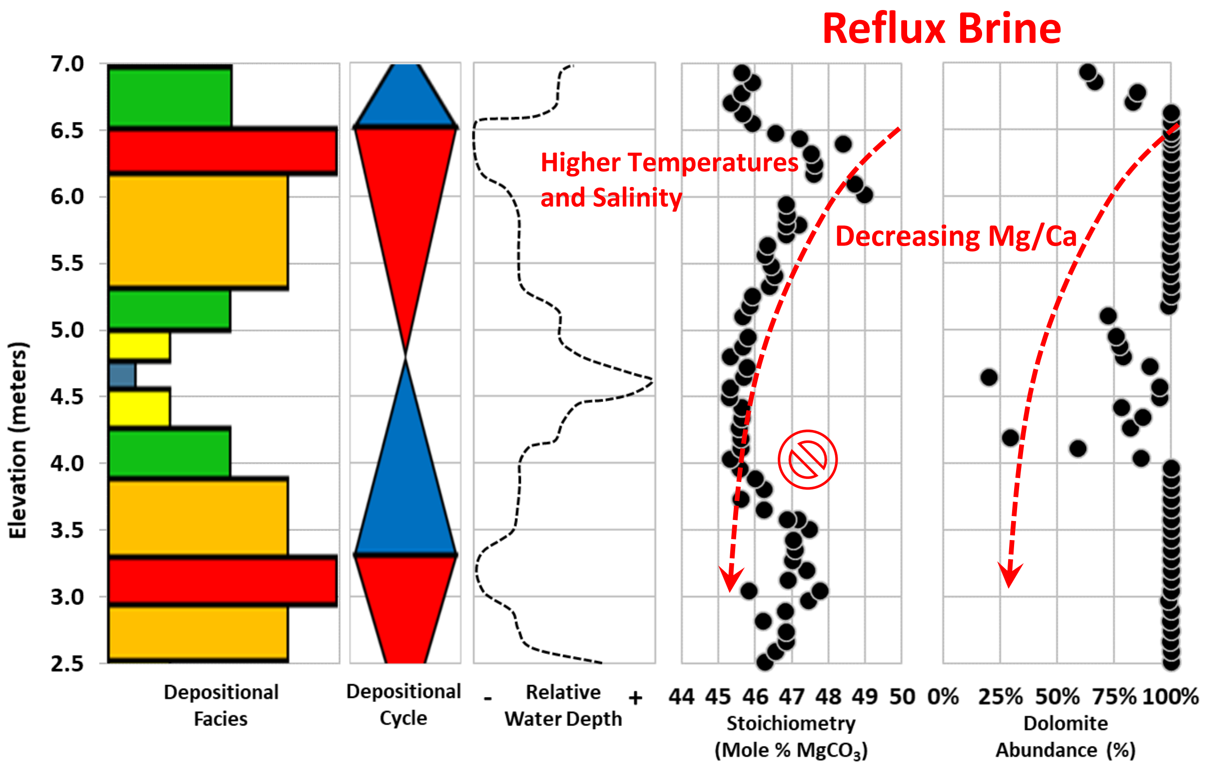
Dolomitization Scenarios & Interpretations

Mechanisms for Dolomitization:

- **Hypersaline Reflux**
- Evaporative Pumping
- Tidal Pumping

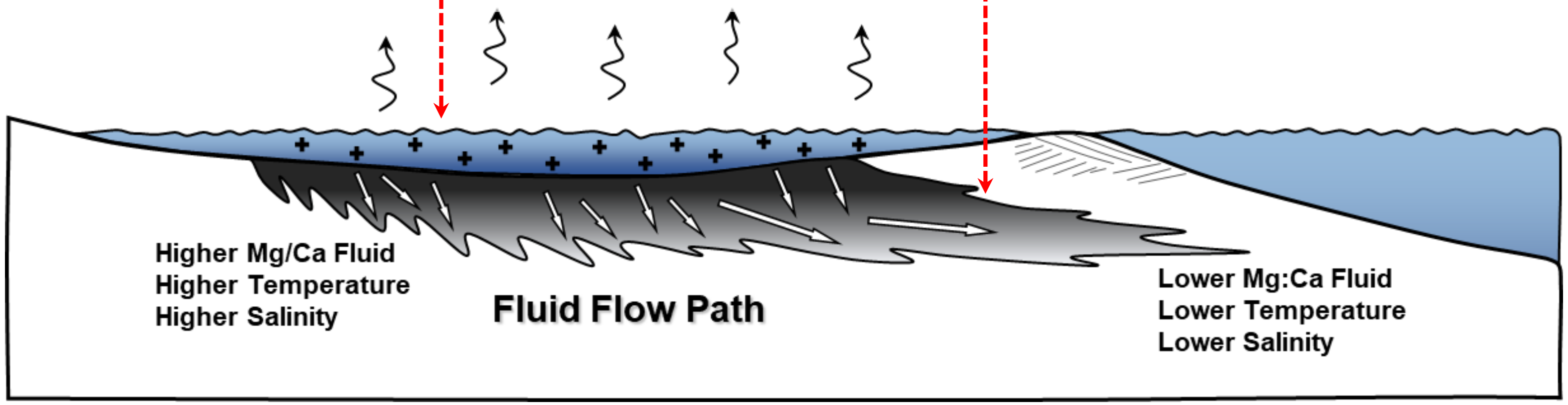
Key Observations:

- ~4 Mole% $MgCO_3$ shift over ~2 meters
- Increasing and decreasing trends in stoichiometry



SAMPLE 1:
- Higher percent dolomite
- Dolomite is more stoichiometric

SAMPLE 2:
- Lower percent dolomite
- Dolomite is less stoichiometric



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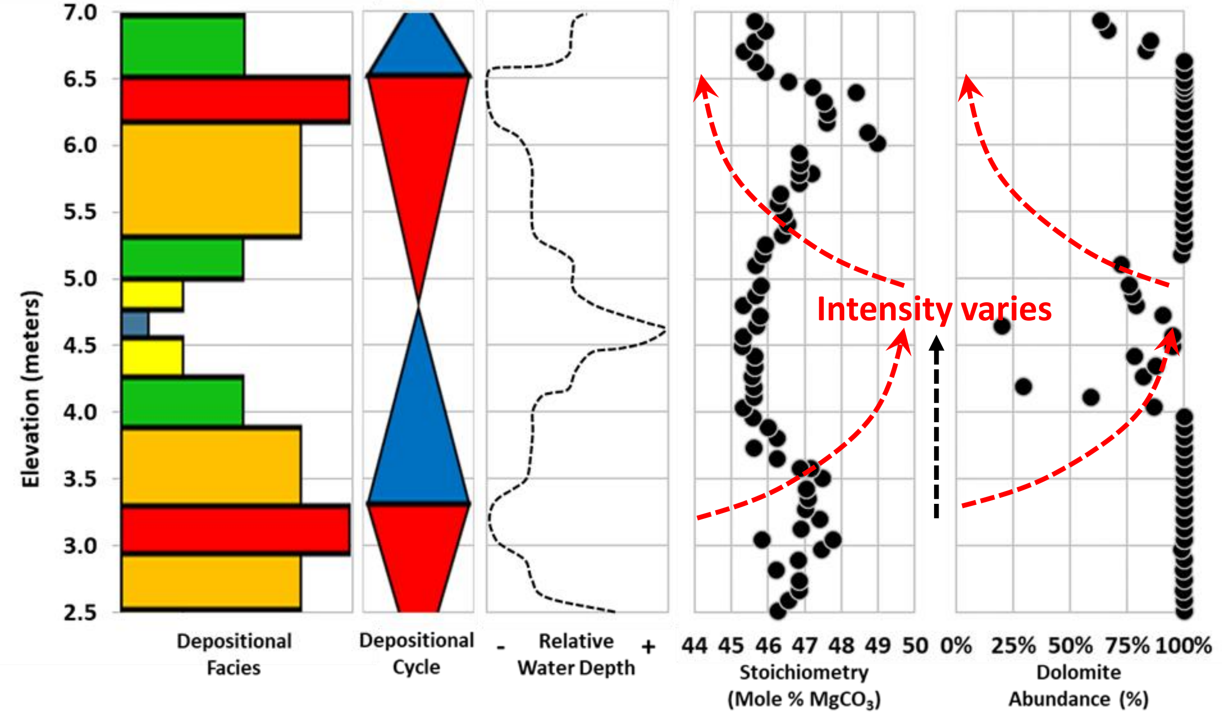
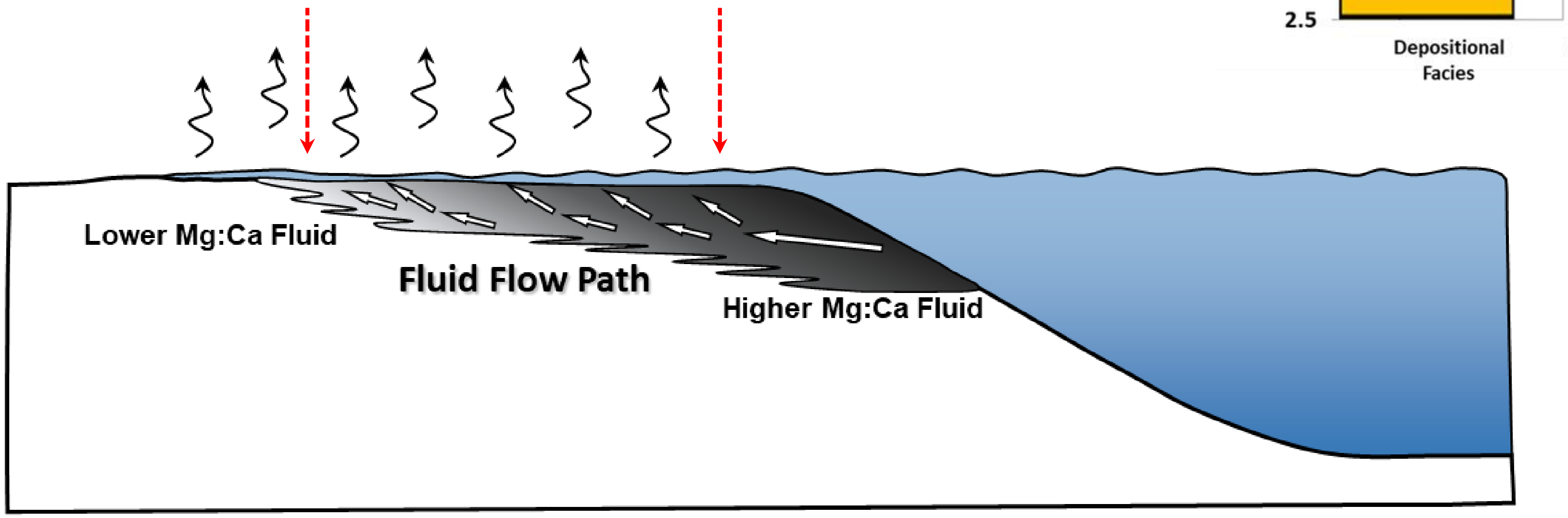
Evaporative Pumping



Decreasing Mg/Ca along flow path

SUPRA/INTERTIDAL:
- Higher temperature
- Higher salinity
- Dolomite is less (?) stoichiometric
- Lower percent dolomite (?)

SUBTIDAL:
- Lower temperature
- Lower salinity
- Dolomite is more (?) stoichiometric
- Lower percent dolomite (?)

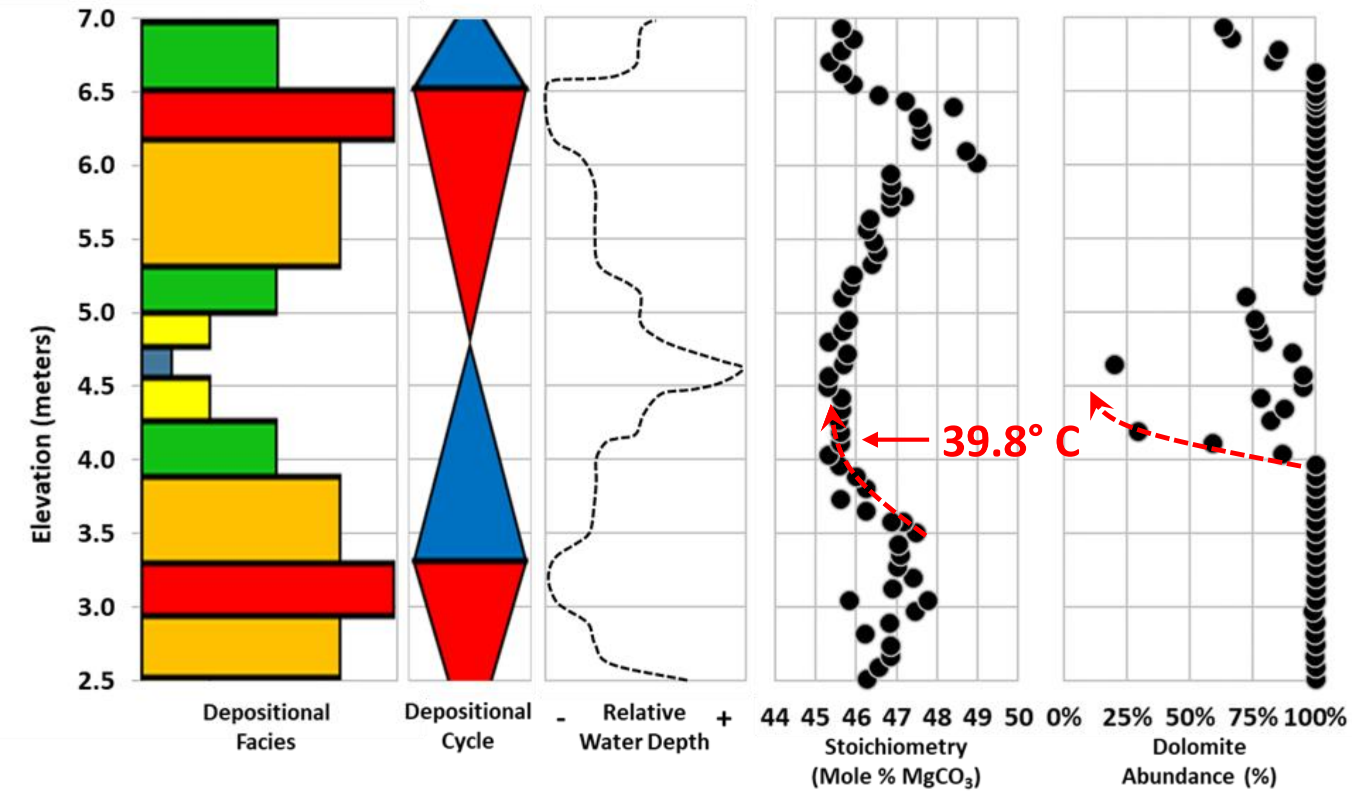


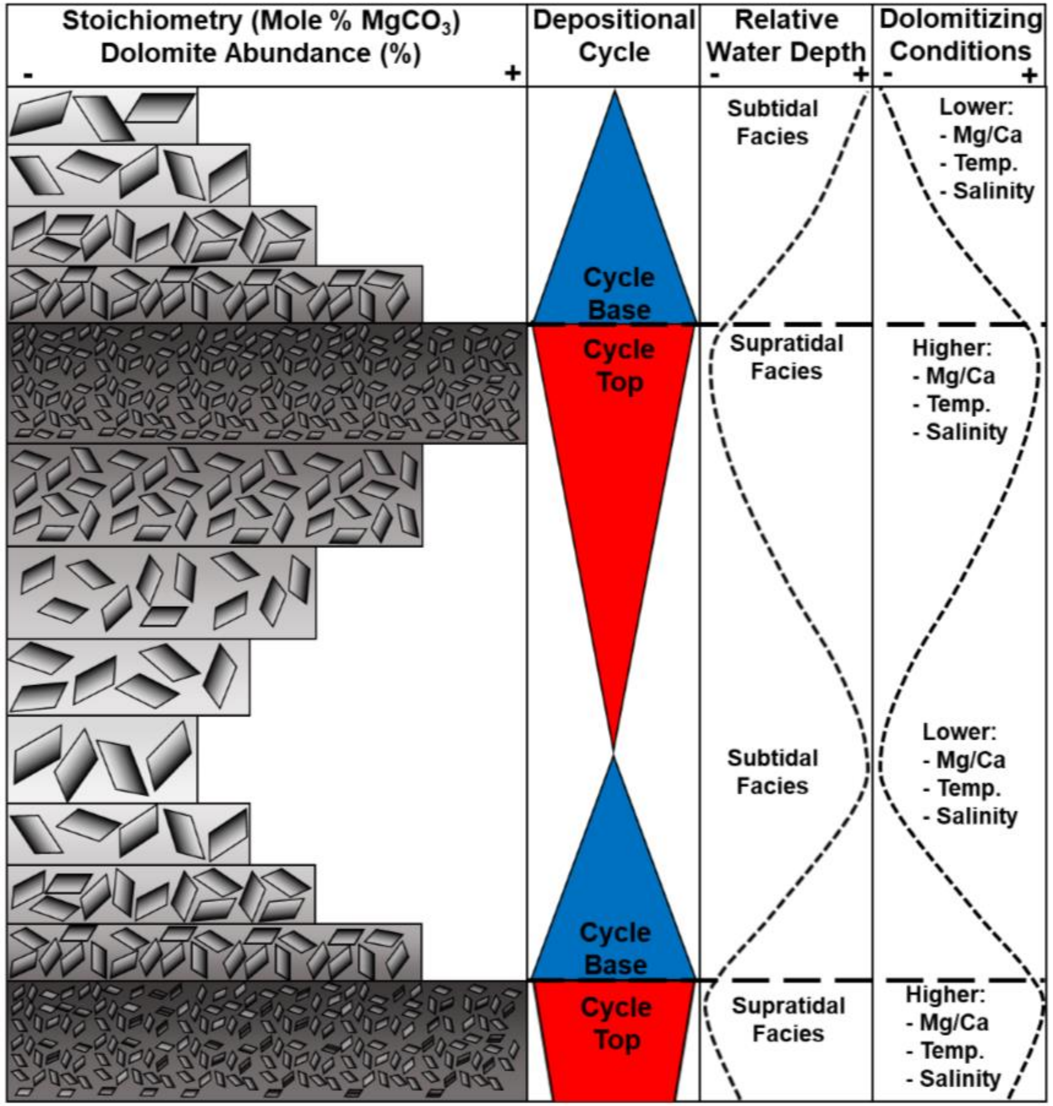
Dolomitization Scenarios & Interpretations

Mechanisms for Dolomitization:

- Hypersaline Reflux
- Evaporative Pumping
- **Tidal Pumping**

Evolving Physicochemical Conditions





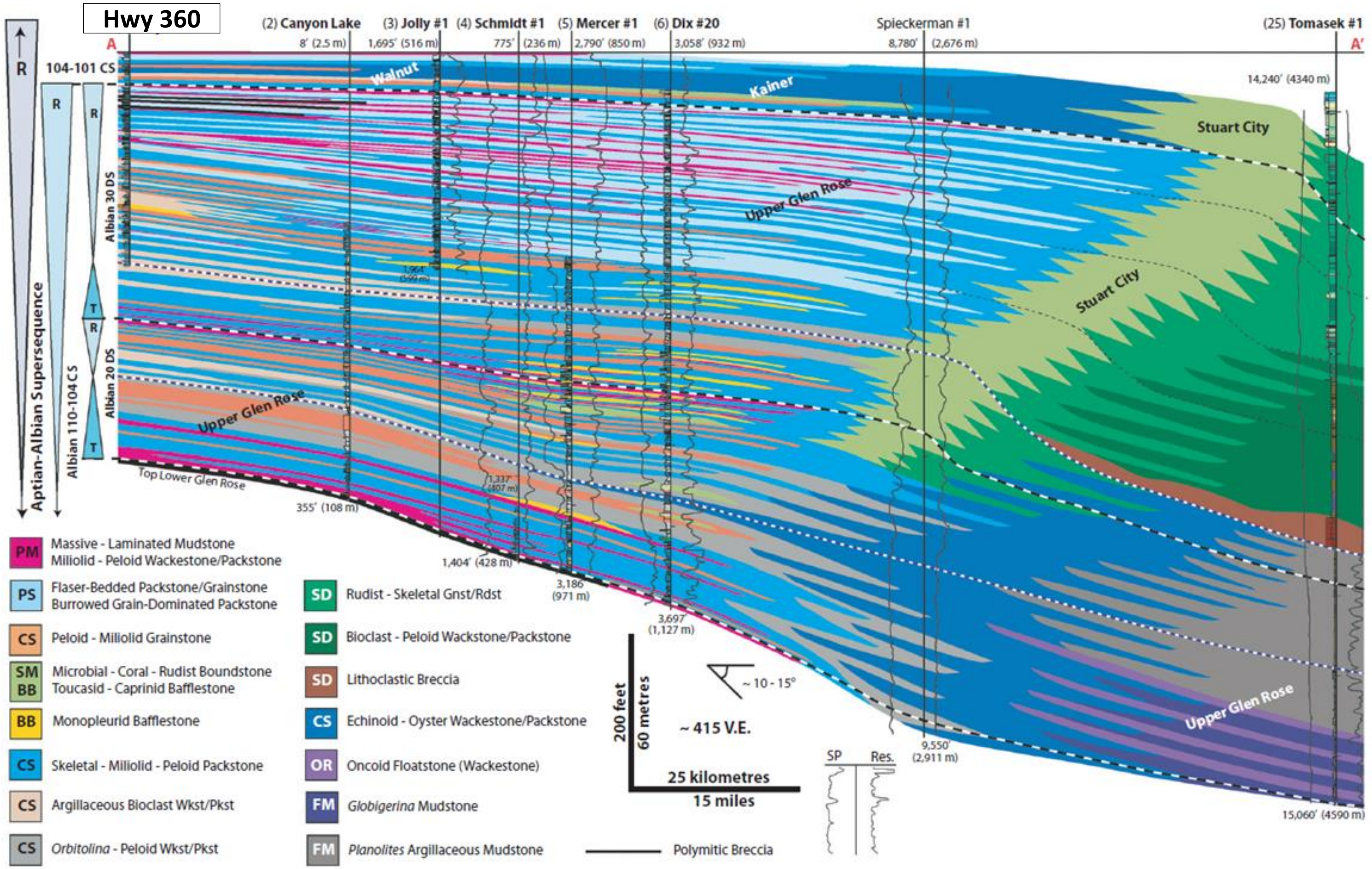
Possible Source of Mg^{2+}

Tidal Pumping:

- Invoked to explain dolomitization of peritidal carbonates.
  - Illing et al., 1965
  - Shinn et al., 1965
  - Carballo et al., 1987
  - Montañez and Read, 1992
  - Mutti and Simo, 1994

Tidal Pumping:

- Comanche Platform:
  - Low relief shelf
  - Peritidal dominated environment
  - High-frequency sea-level changes
- Cretaceous:
  - Hot
  - High pCO_2



Phelps et al., 2014

Key Points

This Study Demonstrates:

- Application of laboratory findings in a coherent and consistent way to examine the causes of temporal stoichiometry variability on the Comanche Platform during the late early Cretaceous.
- High-resolution record of dolomite stoichiometry and abundance in the Upper Glen Rose Formation of central Texas.
- The most commonly invoked model of dolomitization, evaporative reflux, is unable to explain the stoichiometric variability observed within the formation.
- Dolomitization may have occurred continuously as the sediments were being deposited, a scenario that could be more common in the rock record than previously reported.
- The spatial and temporal variations in dolomite stoichiometry may be a valuable new resource for geologists to constrain the genetic origin of sedimentary dolomites.

Acknowledgements

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  - **Carbonate Petrology & Characterization Lab**
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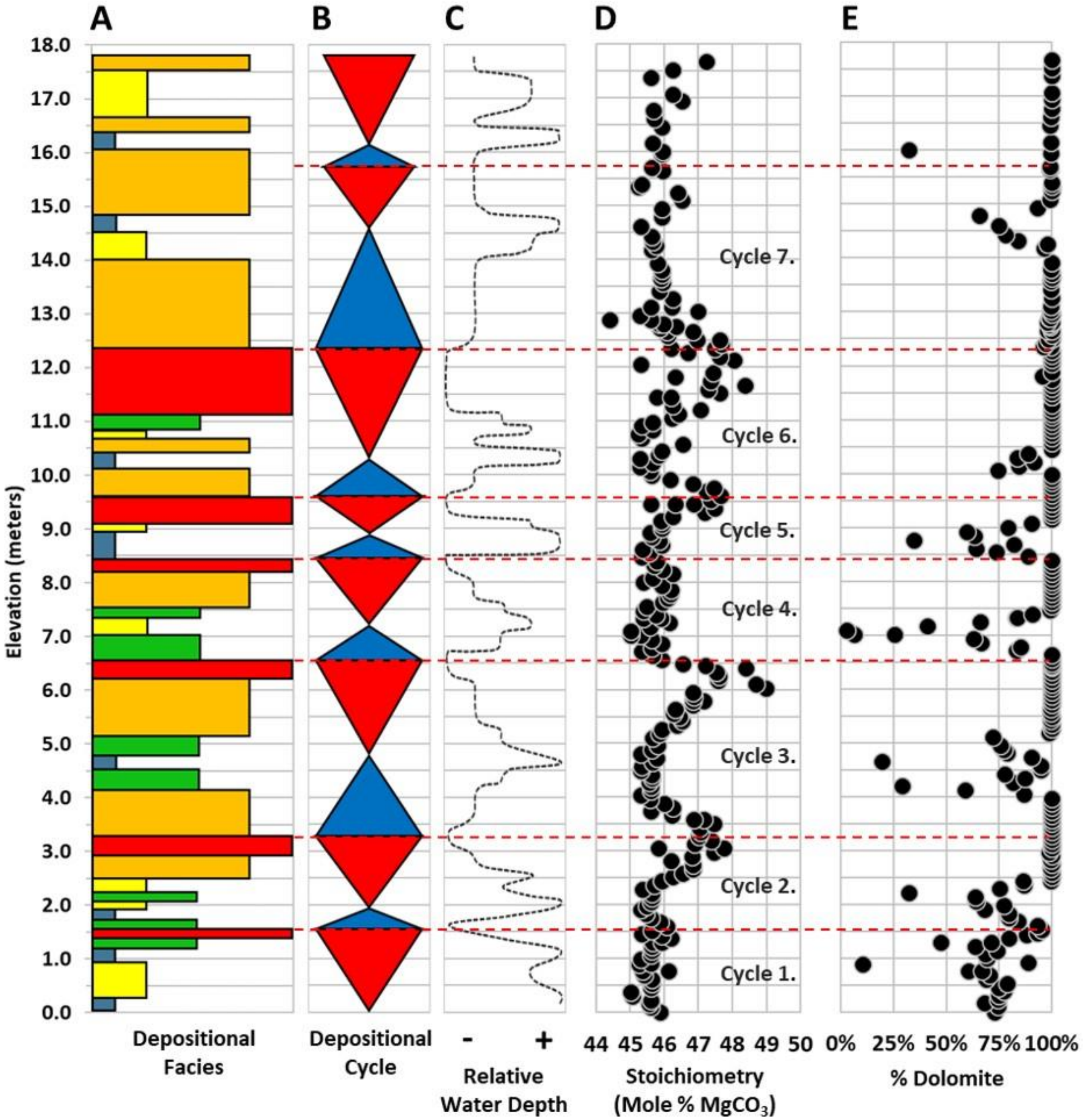
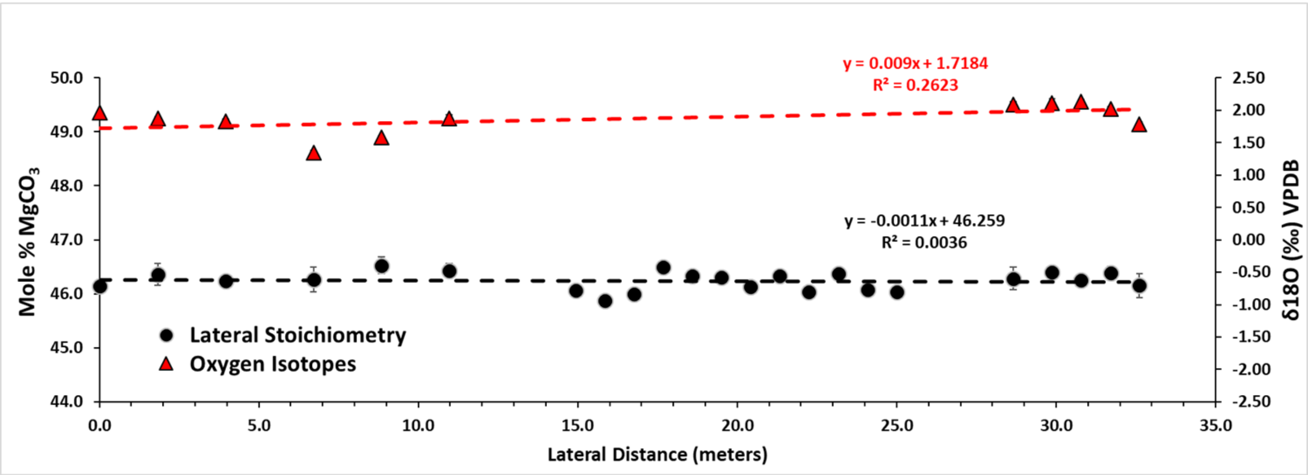
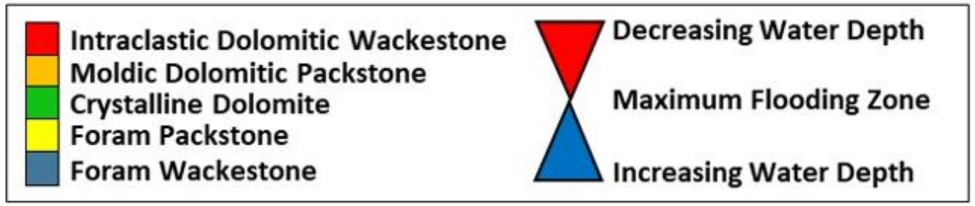
Extra Slide



Lateral Transect



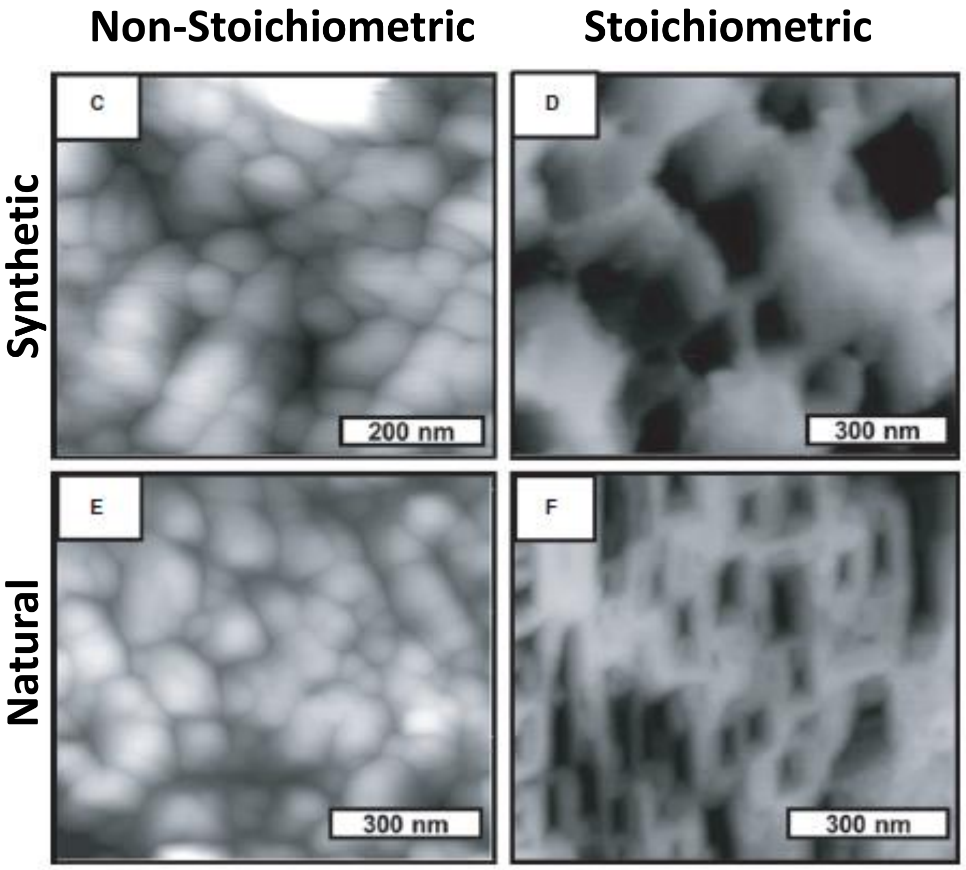
- **Facies Variability**
  - **Mean Mole % $MgCO_3$ – 46.31±0.19 (1σ)**
  - **Mean $\delta^{18}O$ – 1.87 ± 0.23‰ (Marine Conditions)**
- **Data Reproducibility/Analytical Uncertainty**
  - **0.15 Mole % $MgCO_3$**



Extra Slide

Similarities in Natural & Synthetic Dolomites - Growth Structures

Etched surface - Nanotopography



Kaczmarek and Sibley 2007; 2014

Numerous Observations:

1. Rhombic-shaped dolomite crystals;
2. Replacement of allochems;
3. Selective replacement of fine-grained matrix;
4. Limestone-dolomite contacts are usually sharp and involve a decrease in the number of dolomite crystals;
5. Completely dolomitized rocks are more stoichiometric than partially dolomitized rocks.

Many more observations!

Petrographic and geochemical similarities suggest both nucleate and grow in the same way

(1; 3; 4; 5) Sibley et al., 1987; (2) Bullen and Sibley, 1984;
(2) Zempolich and Baker, 1993; (3) Sibley et al., 1994

Extra Slide

Similarities in Natural & Synthetic Dolomites – Fabric Preservation

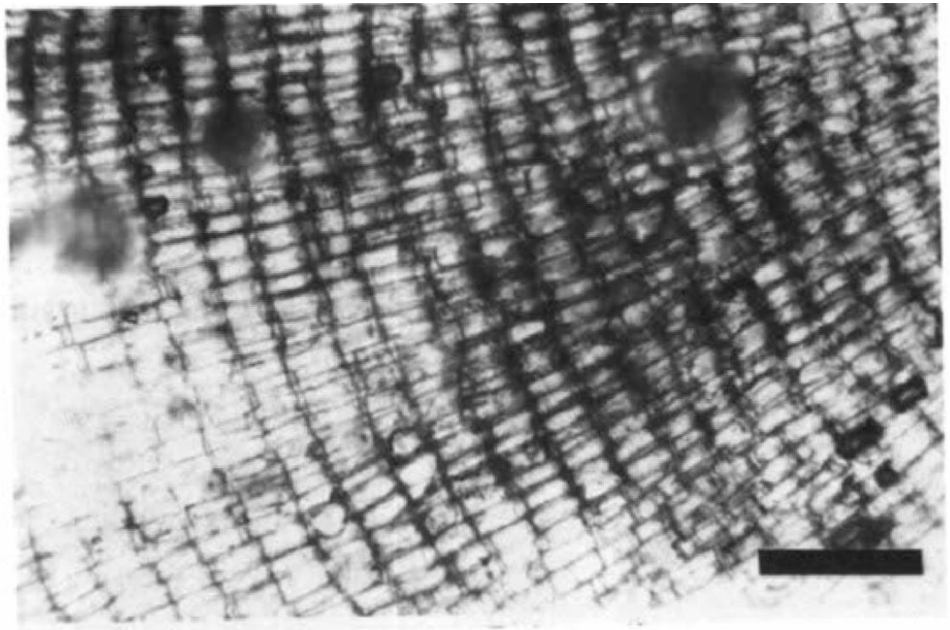
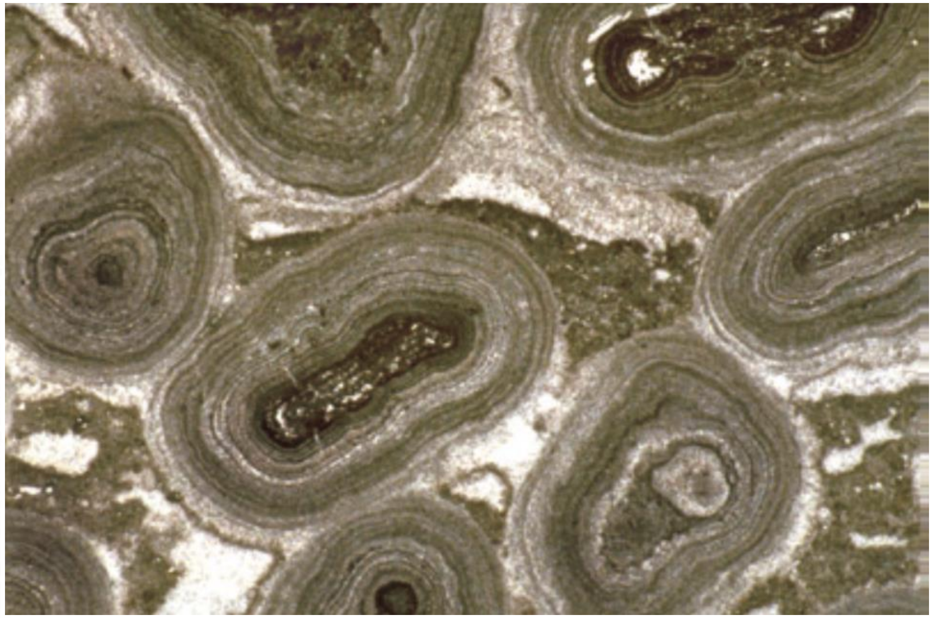


Figure 3. Artificially dolomitized coralline algae with well-preserved skeletal structure. Scale bar = 0.025 mm.



Scholle & Scholle (AAPG Memoir 77)

Bullen & Sibley (1984)