PSUnravelling Reflux Dolomitization: Why Size Matters*

Chia Pei Teoh[1], Juan Carlos Laya[1], Fiona Whitaker[2], Tatyana Gabellone[2], Maurice Tucker[2], Cameron Manche[3], Stephen E. Kaczmarek[3], and Brent Miller[1]

Search and Discovery Article #51519 (2018)**
Posted September 17, 2018

*Adapted from poster presentation given at AAPG 2018 AAPG Annual Convention and Exhibition, Salt Lake City, Utah, May 20-23, 2018
 DOI:10.1306/51519Teoh2018

[1]Department of Geology and Geophysics, Texas A&M University, College Station, TX, United States (ct12081@my.bristol.ac.uk)
[2]School of Earth Sciences, University of Bristol, Bristol, United Kingdom
[3]Department of Geosciences and Environmental Sciences, Western Michigan University, Kalamazoo, MI, United States

Abstract

Refluxing brines have been invoked to explain extensive dolomitization of numerous platform carbonates, including the Permian Basin of West Texas, the Mississippian Madison of the Western US, and the Jurassic Arab Formation of the Middle East. Though orders of magnitude smaller in scale, Bonaire Island in the Netherland Antilles is an often cited, early example of recent reflux dolomitization. Comparisons were drawn between the salt-ponds of the modern Pekelmeer and the fluids forming dolomite bodies in Miocene slope deposits, and the impact of reflux on rock fabric and porosity characterized prior to burial. Using data from a number of new field sites, we re-examine this model for dolomitization of the Mio-Pliocene limestones of Bonaire.

At our type section of Seru Grandi, in the Washington Slagbaai National Park, tongues of replacement dolomite extend down from an erosional unconformity which marks the transition to overlying undolomitized limestone. Dolomite geobodies develop along clinoforms within shallow-marine coral-algal deposits, with preferential alteration of high-Mg calcite red algae. The dolomite is largely 20 to 100 µm sucrosic crystals, with cloudy centers and patchy zonation, and is non-stoichiometric and calcium-rich (45 Mol% $MgCO_3$). This, together with the absence of restricted facies or associated evaporites, supports dolomitization by reflux of mesohaline fluids, rather than dense brines. Stable isotope measurements show significant enrichment relative to precursor limestones, with δ13C values +1 to +4 ‰ VPDB and _δ18O values of +1.5 to +5 ‰ VPDB. Assuming Miocene oceans were δ18O enriched (+1 to +2 δ18O VSMOW) relative to modern oceans, this suggests dolomitizing fluids with salinities of 40-44 ‰.

Several studies have used reactive transport models to better understand dolomitization driven by reflux of brines up to and above gypsum saturation over distances of 10s to 100s of km. Our simulations, constrained by field data from Seru Grandi, indicate that at much smaller scales waters of no more than 44 ‰ can reflux through these permeable bioclastic deposits at 3 to 8 m/yr. These flow rates are comparable with those modeled for high salinity brines suggested to cause dolomitization of larger scale systems. Although the geochemical potential of these

mesosaline fluids is lower, our models suggest that at 40^{o}C, dolomite geobodies of comparable scale to those at outcrop could form from only marginally evaporated seawater within 200 kyr.

References Cited

Bullen, S.B., and D.F. Sibley, 1984, Dolomite Selectivity and Mimic Replacement: Geology, v. 12/11, p. 655-658.

Deffeyes, K.S., F.J. Lucia, and P.K. Weyl, 1965, Dolomitization of Recent and Plio-Pleistocene Sediments by Marine Evaporite Waters on Bonaire Netherlands Antilles, *in* L.C. Pray and R.C. Murray (eds.), Dolomitization and Limestone Diagenesis: Society of Economic Paleontologists and Mineralogists, Special Publication no. 13, p. 71-88.

Enos, P., and L.H. Sawatsky, 1981, Pore Networks in Holocene Carbonate Sediments: Journal of Sedimentary Petrology, v. 51/3, p. 961-985.

Laya, J.C., J. Sulaica, C.P. Teoh, F. Whitaker, T. Gabellone, M. Tucker, P. Tesch, B. Miller, K. Prince, and I. Izaguirre, 2018, Controls on Neogene Carbonate Facie Sand Stratigraphic Architecture of an Isolated Carbonate Platform – The Caribbean Island of Bonaire: Marine and Petroleum Geology, v. 94, p. 1-18. doi.org/10.1016/j.marpetgeo.2018.03.031

Li, Z., R.H. Goldstein, and E.K. Franseen, 2015, Geochemical Record of Fluid Flow and Dolomitization of Carbonate Platforms: Ascending Freshwater – Mesohaline Mixing, Miocene of Spain: Geological Society, London, Special Publications, v. 406/1, p. 115-140.

Lucia, F.J., 1995, Rock-Fabric/Petrophysical Classification of Carbonate Pore Space for Reservoir Characterization: American Association of Petroleum Geologists Bulletin, v. 79/9, p. 1275-1300.

Lucia, F.J., 1968, Recent Sediments and Diagenesis of South Bonaire, Netherlands Antilles: Journal of Sedimentary Petrology, v. 38/3, p. 845-858.

Nash, M.C., B.N. Opdyke, U. Troitzsch, B.D. Russell, W.H. Adey, A. Kato, G. Diaz-Pulido, C. Brent, M. Gardner, J. Prichard, and D.I. Kline, 2013, Dolomite-Rich Coralline Algae in Reefs Resist Dissolution in Acidified Conditions: Nature Climate Change, v. 3/3, p. 268-272. doi:10.1038/nclimate1760

Saller, A.H., and N. Henderson, 2001, Distribution of Porosity and Permeability in Platform Dolomites: Insight from the Permian of West Texas: Reply: American Association of Petroleum Geologists Bulletin, v. 85, 530-532.

Saller, A.H., N. Henderson, 1998, Distribution of Porosity and Permeability in Platform Dolomites: Insight from the Permian of West Texas: American Association of Petroleum Geologists Bulletin, v. 82, p. 1528-1550.

Sheppard, S.M., and H.P. Schwarcz, 1970, Fractionation of Carbon and Oxygen Isotopes and Magnesium between Coexisting Metamorphic Calcite and Dolomite: Contributions to Mineralogy and Petrology, v. 26/3, p. 161-198.

Unravelling reflux dolomitization: Why size matters

ABSTRACT

Refluxing brines have been invoked to explain extensive dolomitization of numerous platform carbonates, including the Permian Basin of West Texas, the Mississippian Madison of the Western US, and the Jurassic Arab Formation of the Middle East. Though orders of magnitude smaller in scale, Bonaire Island in the Netherland Antilles is an often cited, early example of recent reflux dolomitization. Comparisons were drawn between the salt-ponds of the modern Pekelmeer and the fluids forming dolomite bodies in Miocene slope deposits, and the impact of reflux on rock fabric and porosity characterized prior to burial. Using data from a number of new field sites, we re-examine this model for dolomitization of the Mio-Pliocene limestones of Bonaire. At our type section of Seru Grandi, in the Washington Slagbaai National Park, tongues of replacement dolomite extend down from an erosional unconformity which marks the transition to overlying undolomitized limestone. Dolomite geobodies develop along clinoforms within shallow-marine coral-algal deposits, with preferential alteration of high-Mg calcite red algae. The dolomite is largely 20 to 100 µm sucrosic crystals, with cloudy centers and patchy zonation, and is non-stoichiometric and calcium-rich (45 Mol% $MgCO_3$). This, together with the absence of restricted facies or associated evaporites, supports dolomitisation by reflux of mesohaline fluids, rather than dense brines. Stable isotope measurements show significant enrichment relative to precursor limestones, with δ13C values +1 to +4 ‰ VPDB and δ18O values of +1.5 to +5 ‰ VPDB. Assuming Miocene oceans were δ18O enriched (+1 to +2 δ18O VPDB) relative to modern oceans, this suggests dolomitizing fluids with salinities of 40-44 ‰. Several studies have used reactive transport models to better understand dolomitisation driven by reflux of brines up to and above gypsum saturation over distances of 10s to 100s of km. Our simulations, constrained by field data from Seru Grandi, indicate that at much smaller scales waters of no more than 44 ‰ can reflux through these permeable bioclastic deposits at 3 to 8 m/yr. These flow rates are comparable with those modelled for high salinity brines suggested to cause dolomitization of larger scale systems. Although the geochemical potential of these mesosaline fluids is lower, our models suggest that at 40 C, dolomite geobodies of comparable scale to those at outcrop could form from only marginally evaporated seawater within 200 kyr.

GEOLOGICAL SETTING

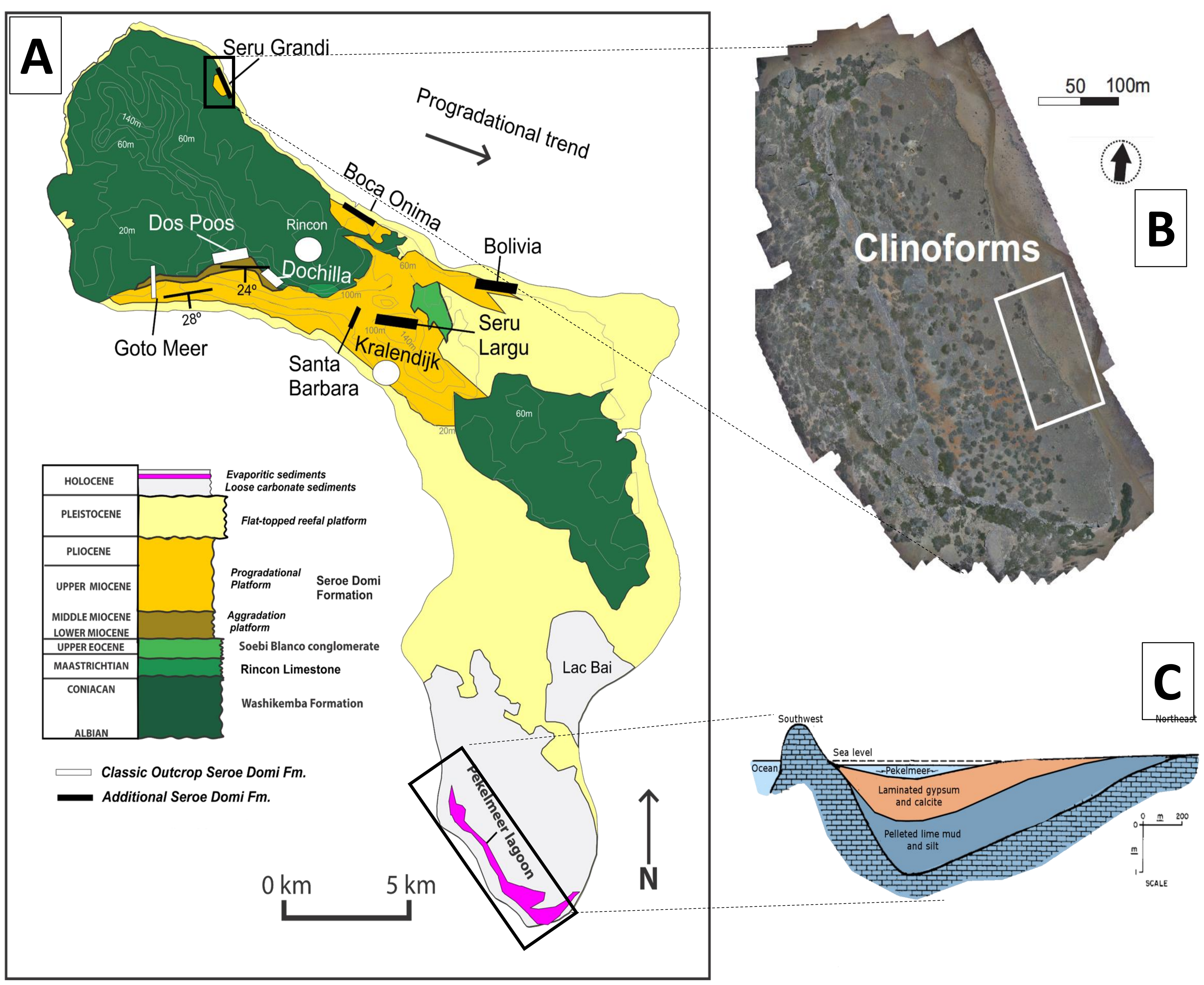


FIGURE 1: A) Simplified Geological Map of Bonaire, with location of Seru Grandi and direction of progradation for clinoforms (modified from Laya et al., 2018). **B)** Plan view of Seru Grandi terraces, with type-outcrop of clinoforms marked. **C)** Schematic cross section of the Holocene hypersaline Pekelmeer lagoon (modified from Lucia (1968)).

- The island of Bonaire is located in the southern Caribbean, 90 km north of the Venezuelan coast. Bonaire is part of the Netherland Antilles island chain. The Miocene age prograding platforms primarily have clinoform geometries, and are chiefly composed of calcareous coralline red algae (up to 70%), with minor components of coral fragments, large benthic foraminifera, volcanic lithic fragments, echinoids, and rare bivalves.
- Replacement dolomitization is extensive in these platforms, and are often concentrated near the more elevated, landward portions of beds with dolomite geobodies developed along clinoforms within shallow-marine coral-algal deposits.
- The Pekelmeer, a Holocene hypersaline lake, is a useful modern day analog for reflux dolomitization within the older units on Bonaire, with rare contemporary dolomitization observed (Deffeyes et al., 1965)

RESEARCH OBJECTIVES

- Re-examine the model for dolomitization for the Mio-Pliocene limestones of Bonaire using stable isotope geochemistry, petrography, and reactive transport modelling.
- Characterize the impact of reflux dolomitization on rock fabric and porosityof Seru Grandi clinoforms.

Unravelling reflux dolomitization: Why size matters

Chia Pei Teoh[1], Juan Carlos Laya[1], Fiona Whitaker[2], Tatyana Gabellone[2], Maurice Tucker[2], Cameron Manche[3], Steve Kaczmarek[3], Brent Miller[1]

E-mail: j.teoh@tamu.edu

1: Department of Geology and Geophysics, Texas A&M University, USA | 2: School of Earth Sciences, University of Bristol, UK

3: Department of Geological and Environmental Sciences, Western Michigan University, USA

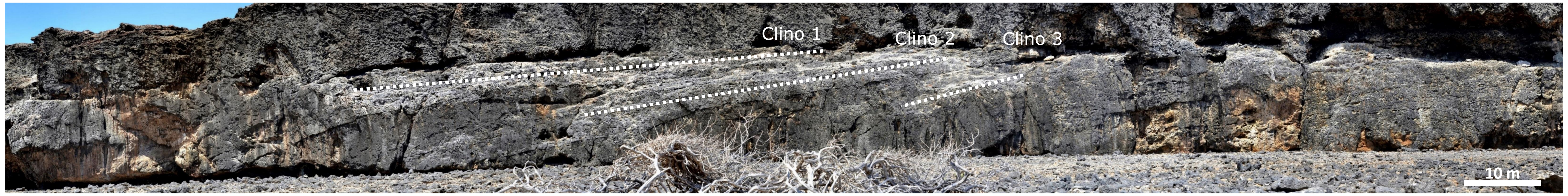
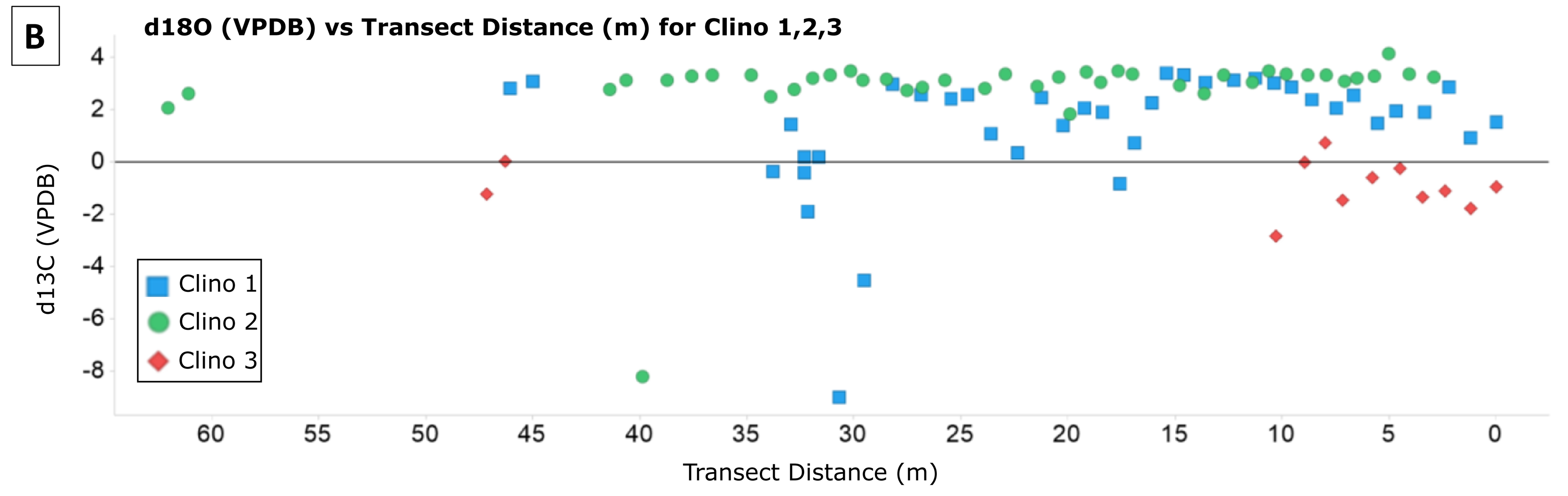
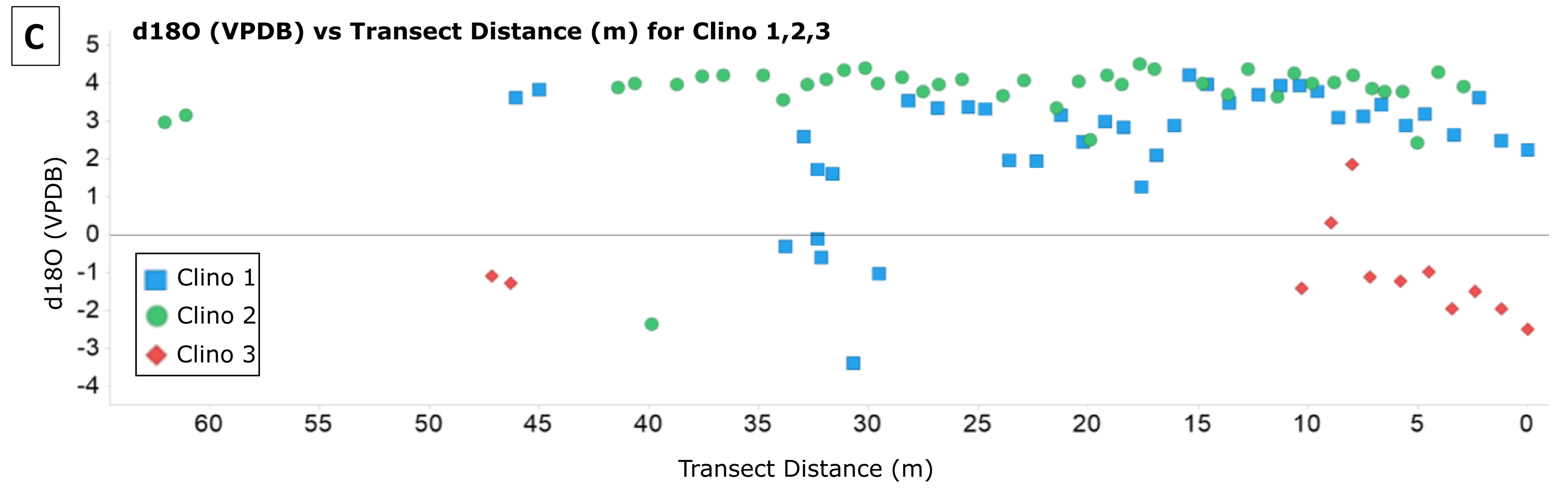


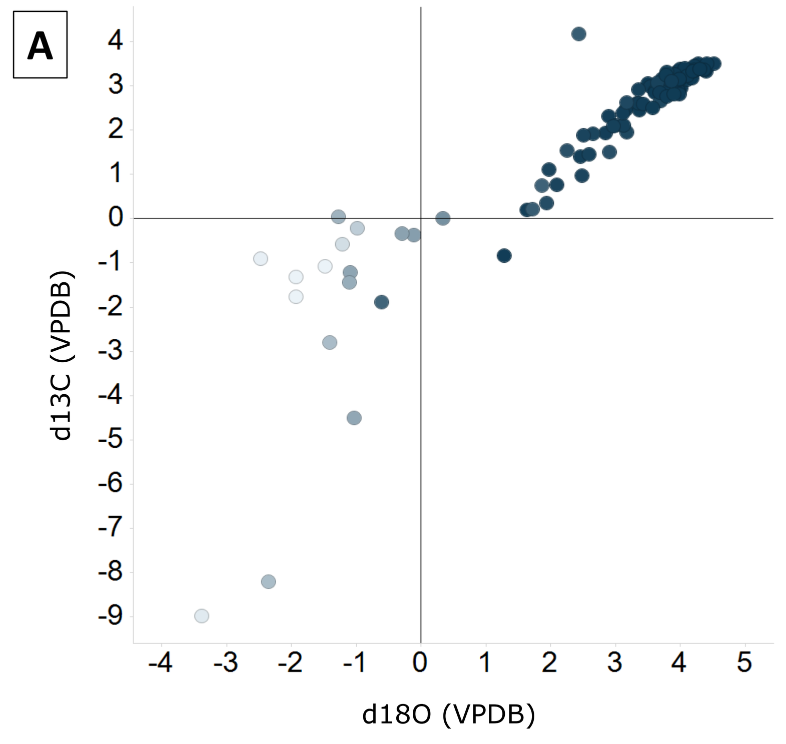
Fig 2: Panorama of the Seru Grandi clinoforms. Note the conformity and cyclity of dolomite packages (lighter)

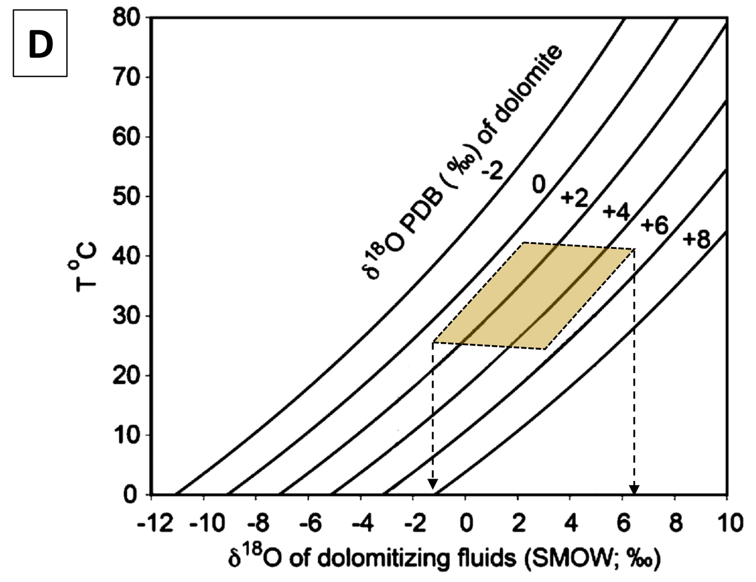
STABLE ISOTOPES

- Stable isotope geochemistry can give clues as to mechanism of dolomitization and salinity of dolomitizing fluids.
- d18O of dolomitizing fluids likely to be at about 5‰ VSMOW, which is likely a result of Miocene seawaters evaporated to 44 mg/L, considering lack of evaporitic minerals and restricted facies.









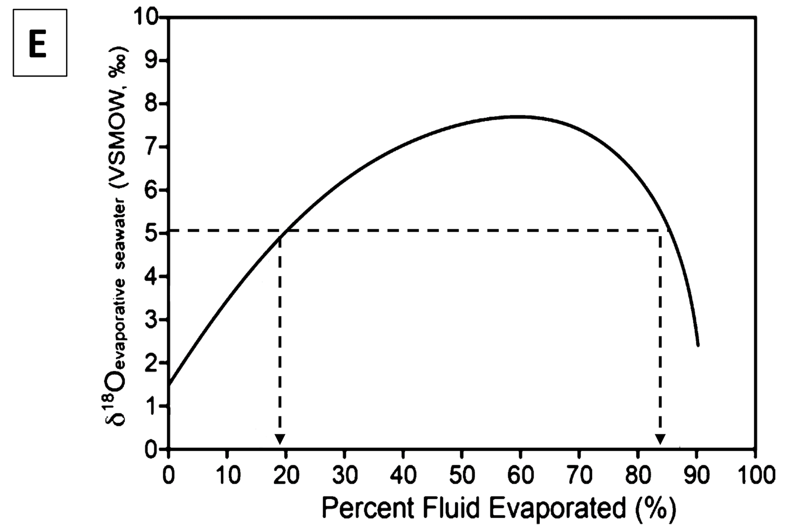


Fig. 3: A) Crossplot of d13C and d18O. Darker markers indicate higher dolomite %. Note the covariance of d13C and d18O **B)** Scatterplot of d18O values along transects Clino 1, Clino 2, and Clino 3. **C)** Scatterplot of d13C values along transects Line 1, Line 2, and Line 3. **D)** Temperature v. d18O of dolomitizing fluids and d18O of dolomite. d18O of dolomitizing fluids calculated using $1000 \ln\alpha = 3.2 \times 10^6 T^{-2} - 3.3$ (Sheppard & Schwarcz 1970), and an assumed temperature range of 25 – 40 C. **E)** Diagram illustrating the d18O evolution on evaporation with humidity of 75%, temperature of 30 C and initial d18O of 1.5‰ VSMOW. Nonlinear relationship results in 5‰ VSMOW fluids originating from either 20% (44 mg/L) or 85% (236 mg/L).

PETROGRAPHY

- Petrography reveals dolomite crystals to morphometrically accord with the classic reflux model suggested by Saller and Henderson (2001), with the largest crystals concentrated towards the upper part of the formation (closest to reflux source).

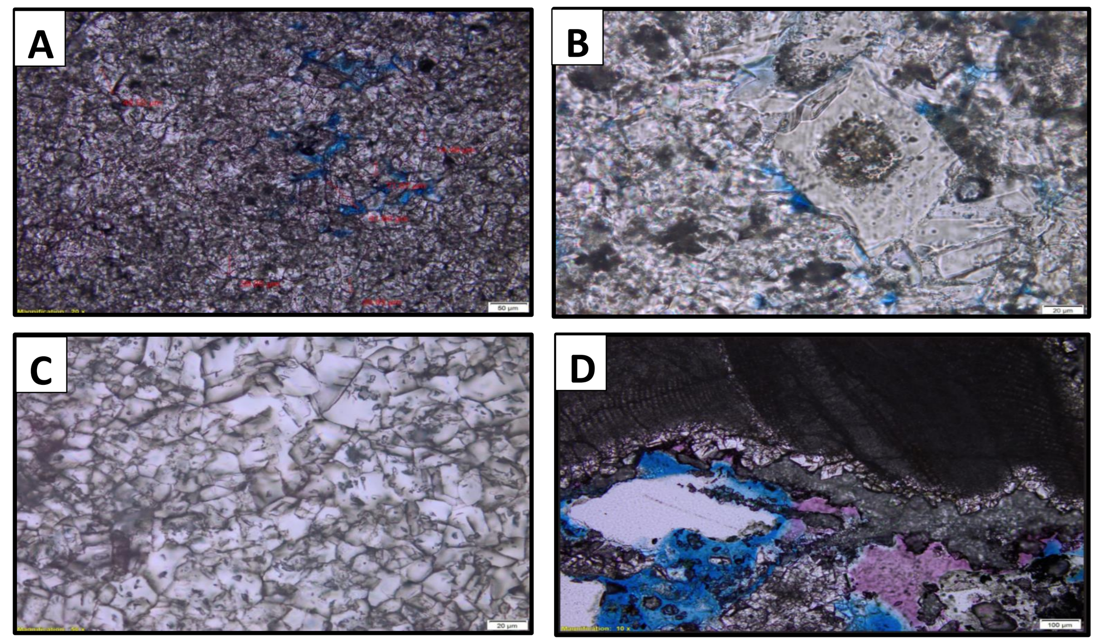
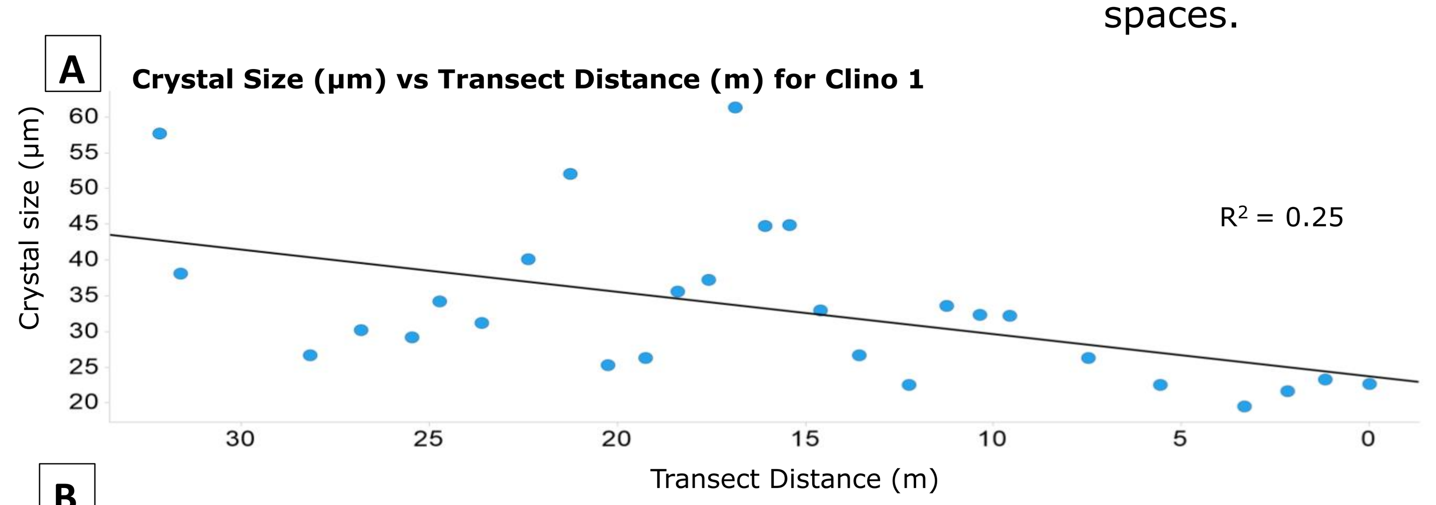


Fig. 4: A) Type 1 dolomite, <30 µm, commonly anhedral. **B)** Type 2 dolomite, 30 – 80 µm, typically clear, unzonated and euhederal. **C)** Type 3 dolomite, 60 to 100 µm, cloudy centers and some zonation. May represent overdolomitization **D)** Type 4, >100 µm, planar euhederal and generally found in pore spaces.



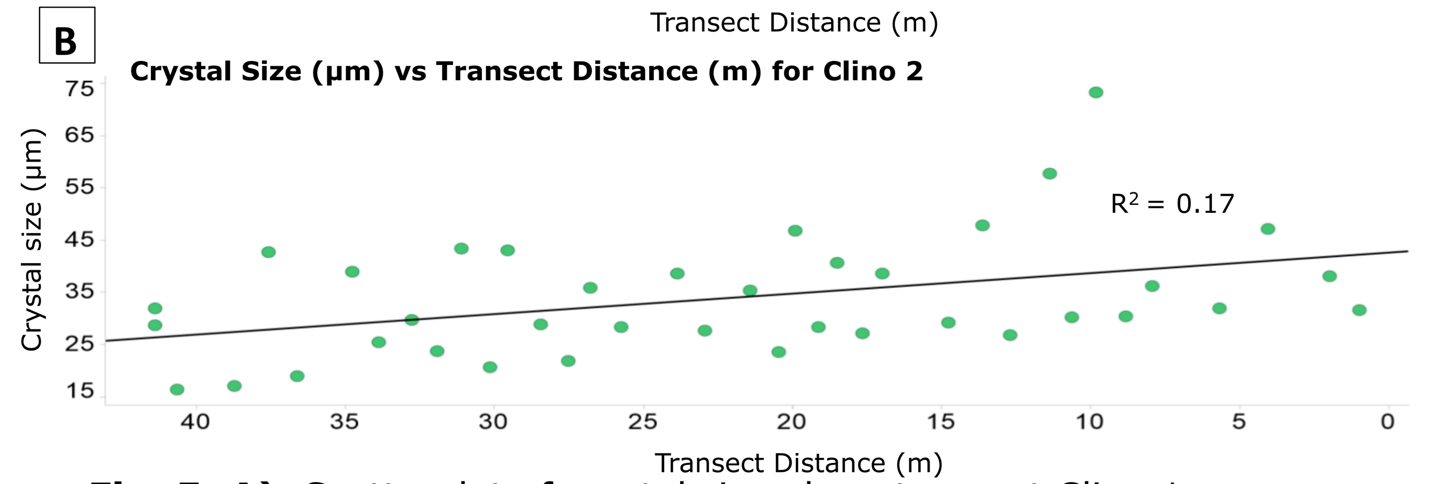


Fig. 5: A) Scatterplot of crystal size along transect Clino 1. **B)** Scatterplot of crystal size along transect Clino 2.

REACTIVE TRANSPORT MODELLING

- Reactive transport modelling provides a numerical approach to understanding the extrinsic and intrinsic controls on dolomitization.
- Dolomite geobodies appear to be initially controlled by permeability differences between clinoforms.

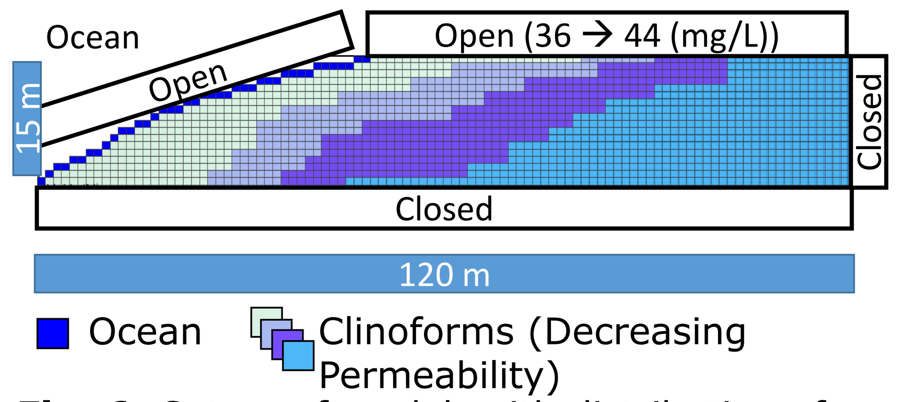


Fig. 6: Set up of model, with distribution of material properties, dimensions, and boundary conditions.

Table 1: Parameters used in simulation.

	Clinoforms
Porosity	0.40 – 0.25
Permeability X (m^2)	2.96E-11 → 2.96 E-14
Permeability Y (m^2)	5.9E-12 → 5.9E-15
Density (kg/m3)	2.71
Anisotropy	5
Reference (poro/perm)	Enos & Sawatsky, 1981, Lucia 1995
Initial Salinity (mg/l)	35.5
Temperature (C)	30

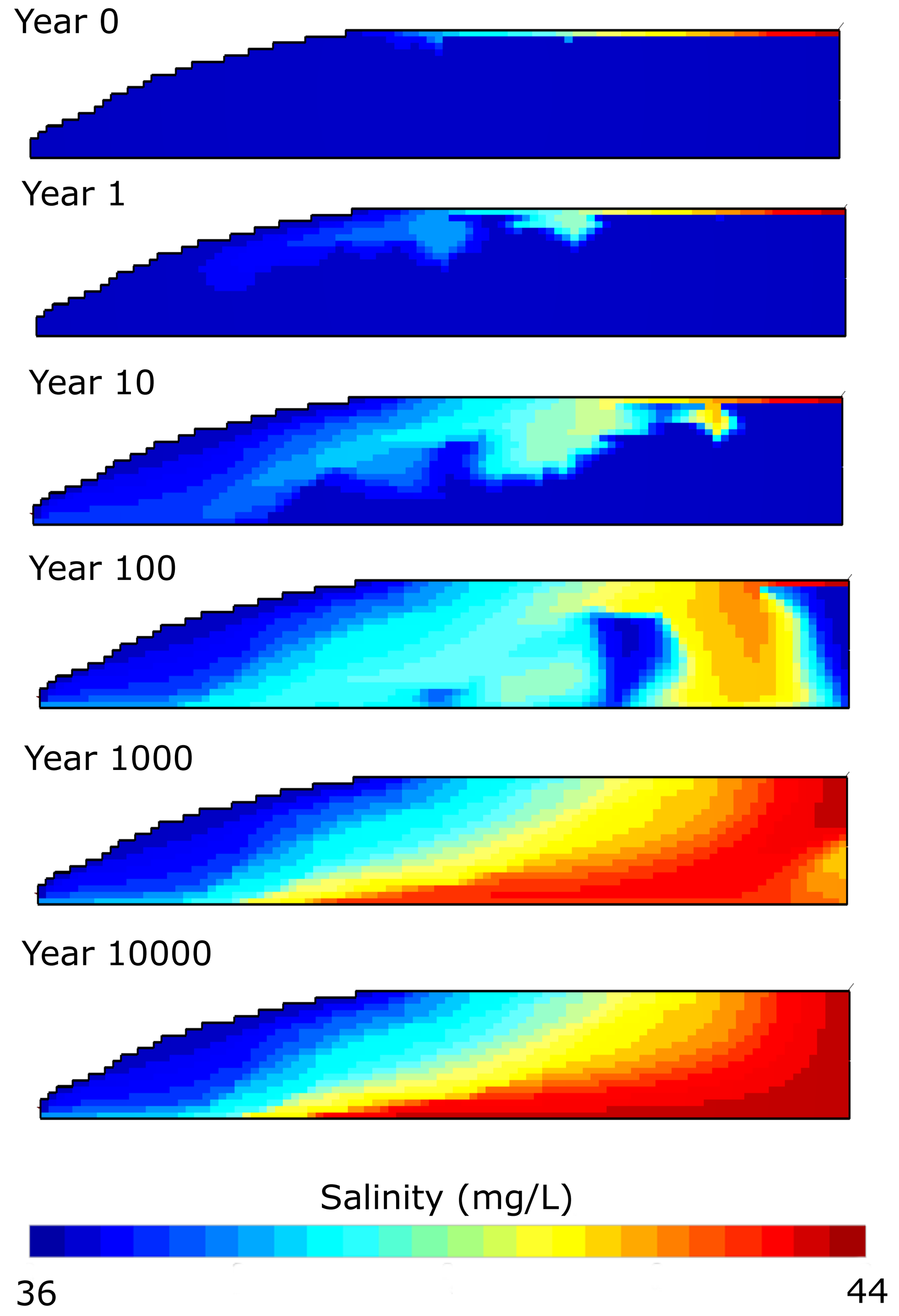


Fig. 7: Distribution of salinity over time for mesohaline simulation. Note the initiation of reflux at Year 1, and the occurrence of refluxing columns, with clinoform-surface controlled flow.

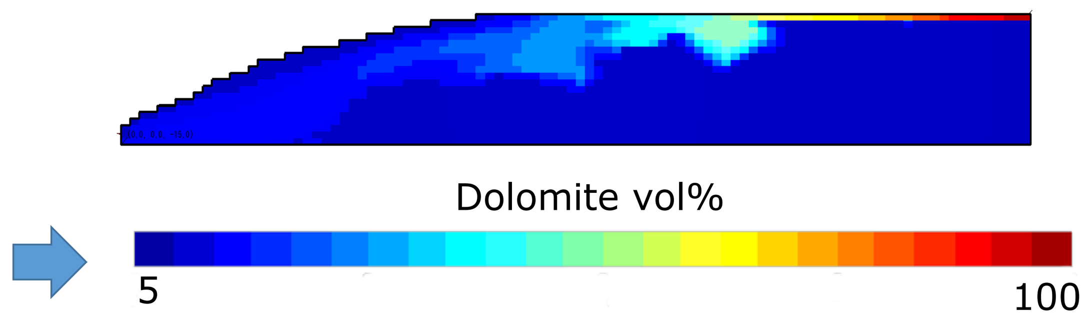


Fig. 8: Distribution of Dolomite at timestep 10000 yr for preliminary simulation run with reactive transport modelling with an initial dolomite of 5%.

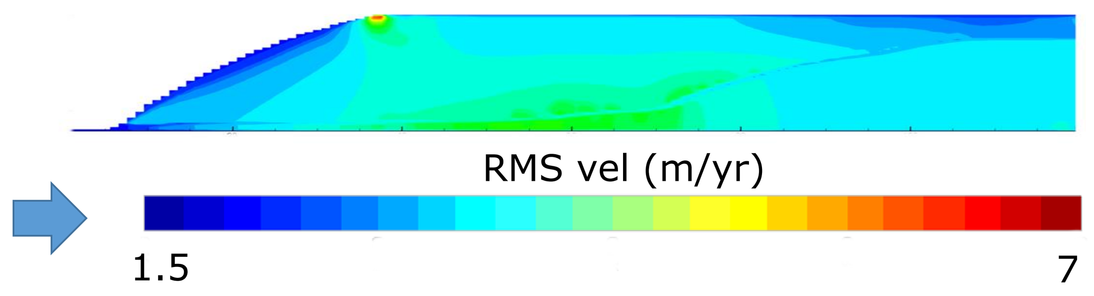


Fig. 9: Distribution RMS velocity at timestep 1000 years for baseline (mesosaline) simulation run.

Unravelling reflux dolomitization: Why size matters

RED ALGAE – ADDITIONAL Mg SOURCE?

The Seru Grandi Miocene prograding clinoforms' dolomite geobodies appear to have preferential alteration of high-Mg calcite red algae. Considering the fairly high Mg content of red algae (up to 30 wt% Mg), and abundance of coralline algae (up to 55% rock volume), red algae potentially can contribute significant amounts of Mg for dolomitization. Additionally, "protodolomite" (non-stoichiometric dolomite) has been observed to directly be precipitated by red algae in studies by Nash (2013), and experimentally demonstrated to be selectively dolomitized by Bullen & Sibley (1984). This "protodolomite" can potentially act as "seed crystals", providing a means to reduce kinetic barriers to dolomitization.

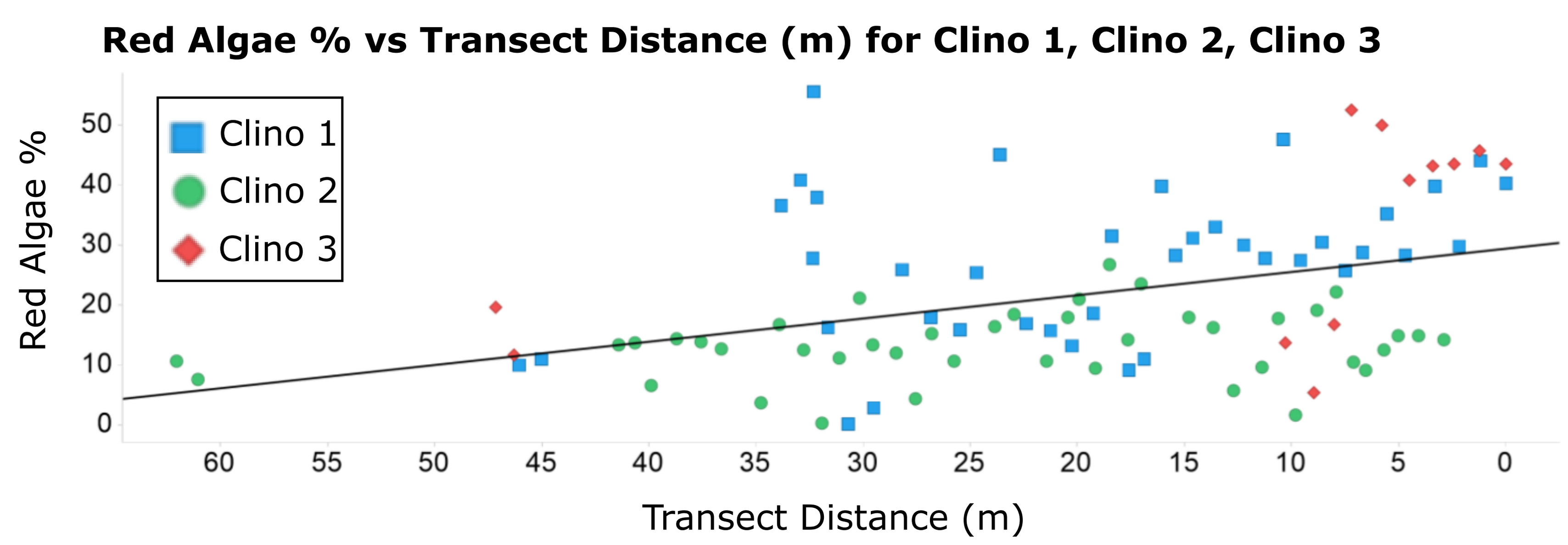


Fig. 8: Scatterplot of red algae % along Clino 1, 2, and 3

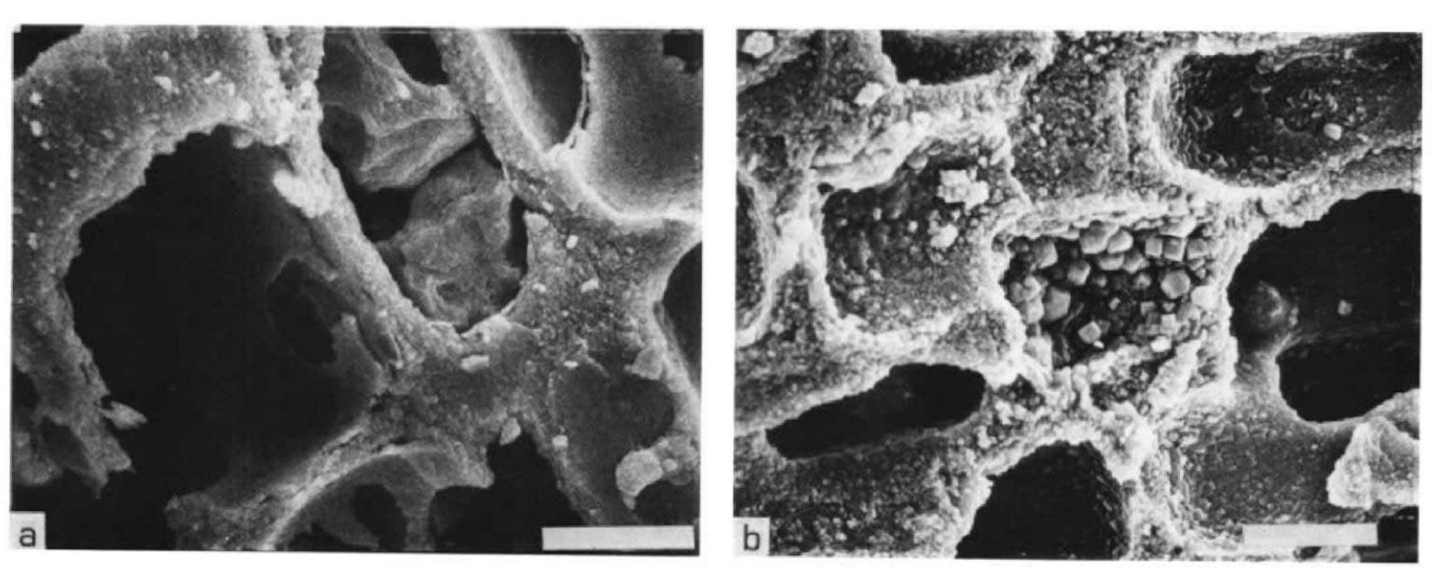


Fig. 9: SEM micrographs of coralline algae. Undolomitized coralline algae fragment (a) composed of cryptocrystalline high-Mg calcite and synthetically dolomitized counterpart (b). Individual crystals are visible in dolomitized algae fragment but are below resolution at this magnification in undolomitized fossil. Scale bars = 0.01 mm. (Bullen and Sibley, 1984).

IMPLICATIONS

Reflux model	Non presence of evaporites	Lower enrichment in $\delta^{18}O$	Non-Stochiometric Dolomite	Lagoon or Tidal Flat facies association	Subtidal facies
Mesohaline	✓	✓	✓	✗	✓
Hypersaline	✗	✗	✗	✓	✗

- Miocene aged reflux dolomitization events within the Seru Grandi were likely driven by mesohaline fluids, with potential Mg contribution from Mg rich bioclasts.

FUTURE WORK

- Further explore the potential role of red algae in rock-derived Mg contribution towards dolomitization.
- Better definition of geobodies within 3D space using geostatistical methods

CONCLUSIONS

- At smaller scales, mesosaline reflux can significantly contribute to dolomitization at magnitudes similar to that of hypersaline reflux.
- The dolomite geobodies of the Seru Grandi likely formed as a result of reflux dolomitization by mesohaline brines, based on the geobody patterns, distribution of dolomite crystal sizes, lack of evaporitic facies, relatively low enrichment of stable isotopes, and non-stoichiometric nature of the dolomite.
- Reactive Transport Models show flow rates of 3 to 8 m/yr., and dolomite geobodies of comparable scale to those at outcrop scale can form within 200 kyr

REFERENCES

Bullen, S. B., & Sibley, D. F. (1984). Dolomite selectivity and mimic replacement. Geology, 12(11), 655-658.
Deffeyes, K. S., Lucia, F. J., & Weyl, P. K. (1965). Dolomitization of Recent and Plio-Pleistocene Sediments by Marine Evaporite Waters on Bonaire Netherlands Antilles.
Enos, P., & Sawatsky, L. H. (1981). Pore networks in Holocene carbonate sediments. Journal of Sedimentary Research, 51(3).
Laya, J. C., Sulaica, J., Teoh, C. P, Whitaker, F., Gabellone, T., Tucker, M., Tesch, P., Miller, B., Prince, K., Izaguirre, I. (2018). Controls on Neogene carbonate facies and stratigraphic architecture of an isolated carbonate platform – the Caribbean island of Bonaire. Marine and Petroleum Geology, 94, 1-18. doi: https://doi.org/10.1016/j.marpetgeo.2018.03.031
Li et Li, Z., Goldstein, R. H., & Franseen, E. K. (2015). Geochemical record of fluid flow and dolomitization of carbonate platforms: ascending freshwater–mesohaline mixing, Miocene of Spain. Geological Society, London, Special Publications, 406(1), 115-140.
Lucia, F. J. (1968). Recent sediments and diagenesis of south Bonaire, Netherlands Antilles. Journal of Sedimentary Research, 38(3).
Lucia, F. J. (1995). Rock-fabric/petrophysical classification of carbonate pore space for reservoir characterization. AAPG bulletin, 79(9), 1275-1300.
Nash, M. C., Opdyke, B. N., Troitzsch, U., Russell, B. D., Adey, W. H., Kato, A., ... & Kline, D. I. (2013). Dolomite-rich coralline algae in reefs resist dissolution in acidified conditions. Nature Climate Change, 3(3), 268.
Sheppard, S. M., & Schwarcz, H. P. (1970). Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite. Contributions to Mineralogy and Petrology, 26(3), 161-198.

GEOSCIENCES TEXAS A&M UNIVERSITY
University of BRISTOL
WESTERN MICHIGAN UNIVERSITY