Unravelling Reflux Dolomitization: Why Size Matters*

Chia Pei Teoh1, Juan Carlos Laya1, Fiona Whitaker2, Tatyana Gabellone2, Maurice Tucker2, Cameron Manche3, Stephen E. Kaczmarek3, and Brent Miller1

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1Department of Geology and Geophysics, Texas A&M University, College Station, TX, United States (ct12081@my.bristol.ac.uk)
2School of Earth Sciences, University of Bristol, Bristol, United Kingdom
3Department 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% MgCO₃). 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°C, dolomite geobodies of comparable scale to those at outcrop could form from only marginally evaporated seawater within 200 kyr.

References Cited


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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% MgCO3). 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

- 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 porosity of Seru Grandi clinoforms.

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)).
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Chia Pei Teoh¹, Juan Carlos Laya¹, Fiona Whitaker², Tatjana Gabellone², Maurice Tucker², Cameron Manche², Steve Kaczmarek³, Brent Miller¹

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

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**STABLE ISOTOPES**

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

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**Petrography**

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

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**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.

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**Table 1: Parameters used in simulation.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Porosity</td>
<td>0.40 – 0.25</td>
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<tr>
<td>Permeability X</td>
<td>2.96E+11 – 2.86E+14</td>
</tr>
<tr>
<td>Permeability Y</td>
<td>5.86E+12 – 5.96E+15</td>
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<td>Initial salinity (mg/L)</td>
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<tr>
<td>Temperature (°C)</td>
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</tbody>
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**Fig. 6: Setup of model, with distribution of material properties, dimensions, and boundary conditions.**

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**Fig. 7: Distribution of salinity over time for mesohaline simulation.**

- Note the initiation of reflux at Year 1, and the occurrence of dolomitizing columns, with cliniform-surface controlled flow.

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

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**Fig. 9: Distribution RMS velocity at timestep 10000 years for baseline (mesohaline) simulation run.**

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**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 dolomizing fluids and d18O of dolomite. d18O of dolomitizing fluids calculated using 1000 yrs, 3.2 x 106 Yr = 3.3 (Sheppard & Schwarcz 1970), and an assumed temperature range of 25 – 40. E) Diagram illustrating the d18O evolution on evaporation with humidity of 75%, temperature of 30°C and initial d18O of 2.96E-02 VSMOW. Nonlinear relationship results in 5‰ VSMOW fluids originating from either 20% (44 mg/L) or 85% (236 mg/L).

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

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

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**Fig. 9: Distribution of RMS velocity at timestep 10000 years for baseline (mesohaline) simulation run.**

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**Fig. 10: Panorama of the San Grande clinoforms. Note the conformity and cyclicity of dolomite packages (typical).**

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**Fig. 11: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 12: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 13: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 14: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 15: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 16: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 17: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 18: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 19: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 20: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.

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**Fig. 21: Crystal size (µm) vs Transect Distance (m) for Clino 1, 2, 3.
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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.

IMPLICATIONS

<table>
<thead>
<tr>
<th>Reflux model</th>
<th>Non presence of evaporites</th>
<th>Lower enrichment in δ18O</th>
<th>Non-Stoichiometric Dolomite</th>
<th>Lagoon or Tidal Flat facies association</th>
<th>Subtidal facies</th>
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<tbody>
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<td>✓</td>
<td>✓</td>
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<tr>
<td>Hypersaline</td>
<td></td>
<td></td>
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<td>X</td>
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• 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, mesohaline 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