Dolomitization of a Miocene-Pliocene progradational carbonate platform by mesohaline brines: re-examination the reflux model on Bonaire Island

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Abstract

Neogene dolomites are common in island settings, and they have been used to understand the complex processes of dolomitization. The island of Bonaire was one of the first locations where the concept of reflux dolomitization was applied. Given this historical significance, here we re-evaluate the importance and nature of reflux using a previously unstudied set of outcrops in Bonaire. Mio-Pliocene units in Seru Grandi in northwestern Bonaire show well-defined bodies of dolomite that extend along clinoform surfaces beneath a subhorizontal erosional unconformity. The dolomite distribution suggests early dolomitization as a result of fluids moving downwards through a succession of subtidal facies, as expected from the reflux model. However, non-stoichiometric compositions, weak ¹⁸O enrichment, low trace element concentrations and the sedimentological context of the dolomites suggest that refluxing fluid was more likely to be mesohaline in composition rather than hypersaline as previously proposed. In addition, our findings suggest that the fluids did not dolomitize the succession uniformly, but rather elongate
bodies of dolomite were developed within selected clinoforms. This variability may be due to
temporal changes in the flux and chemistry of reactive fluids and textural changes of original
sediment, whereas downdip trends may reflect evolution of magnesium exchange efficiency with
distance from the brine source and reactivity of the rock.

Keywords: Dolomite, Reflux, Bonaire, Mesohaline, Neogene, Caribbean carbonates.

**Introduction**

Dolomite \([\text{CaMg(CO}_3\text{)}_2]\) is an abundant diagenetic mineral in carbonate successions throughout
the Phanerozoic (Given and Wilkinson, 1987). Despite its abundance, the origin of dolomite
remains the subject of considerable debate (Fairbridge, 1957; Machel and Mountjoy, 1986;
Budd, 1997; Warren, 2000; Gregg et al., 2015; Kaczmarek et al., 2017; Petrash et al., 2017).
Contributing to this debate, there are many thermodynamic, kinetic and hydrological models that
have been offered to explain dolomitization in the rock record (Machel, 2004; Whitaker et al.,
2004). Although these models differ in their detail, they generally agree that three fundamental
criteria are necessary for pervasive, platform-scale dolomitization: (1) a precursor limestone, (2)
a sufficient source of Mg, and (3) an efficient hydrological pumping mechanism to deliver Mg
reactants and remove Ca products (Morrow, 1982; Land, 1985). As such, most dolomitization
models represent coupled geochemical-hydrological models that aim to honor these criteria.

One of the most commonly invoked dolomitization models is seepage reflux (Adams and
Rhodes, 1960), which suggests salinity ranges between 72‰ to 520‰. This model is also
commonly referred to in the literature as evaporative reflux, (Deffeyes et al., 1965; Murray,
1969), hypersaline reflux (Lucia and Major, 1994), and simply reflux (Deffeyes et al., 1964;
Melim and Scholle, 2002; Jones and Xiao, 2005; Rivers et al., 2012). Conceptually,
dolomitization by hypersaline reflux proceeds when evaporation of seawater produces a dense
brine, which promotes fluid flow by a density head mechanism, in addition to an elevated Mg/Ca
ratio caused by precipitation of aragonite/calcite and/or gypsum/anhydrite. This dense, Mg-rich
brine then reacts with the underlying limestone as it seeps downward, controlled by many factors
including fluid salinity, density gradient, permeability pathways, time or duration of reflux flow,
topography and depositional facies (reactivity of the sediments). It is argued that the combination
of elevated Mg/Ca ratios and a favorable hydrological flow regime provides an ideal mechanism
to produce platform-scale dolomite dolomitization (Adams and Rhodes, 1960; Deffeyes et al.,
1964; Moore, 1988; Ruppel and Cander, 1988; Saller and Henderson, 1998b; Cantrell et al.,
2004; Garcia-Fresca et al., 2012; Dravis and Wanless, 2018).

Here, we use the term “reflux” to describe a mechanism that can drive fluid flow as a result of
contrasts in fluid density, which can have a wide range of compositions and may, in fact, be very
similar to seawater (Simms, 1984; Whitaker et al., 2004). Salinity classifications vary greatly,
making terminology confusing. Biologists and oceanographers classify salinity based on the
thalassic series (Por, 1972). For example, biologists use the term mesohaline for brackish water
(18-5‰), whereas geologists use the term mesohaline for waters with salinities higher than
seawater, 35-140‰ (Warren, 2006). Incongruent definitions within the sedimentary geology
literature have also led to confusion. Deffeyes et al. (1964); Lucia and Major (1994); Saller and
Henderson (1998b) used the salinity ranges suggested by Adams and Rhodes (1960), which
defines hypersaline fluids as having a salinity of >72‰, and these are divided into penosaline
(72-199‰) and saline (>200‰). In addition, Adams and Rhodes (1960) defined vitasaline as the
salinity between 35 to 72‰, the range where most marine organisms can survive. Here, we
honor Adams and Rhodes’s (1960) definition of hypersaline, which starts from penosaline, since
it is the first reference that classifies salinity range for carbonate geology and reflux
dolomitization. However, we modify salinity ranges based on Warren (2006), which reflect
current terms of saturation stage boundaries for evaporite minerals. We define our ranges:
seawater ~28-38‰, mesohaline ~38 to 140‰, hypersaline, which is divided into penesaline 140
to 350‰ (gypsum/anhydrite-halite) and supersaline >350‰ (halite and bitter salts).

The island of Bonaire is one of the first locations where the concept of reflux dolomitization was
applied and it has been the subject of numerous dolomite studies over the past seven decades
(e.g., Deffeyes et al., 1964; Deffeyes et al., 1965; Lucia, 1968; Murray, 1969; Bandoian and
Murray, 1974; Sibley, 1980, 1982; Major et al., 1992; Lucia and Major, 1994; Budd, 1997; Budd
and Mathias, 2015). After this initial effort, Bonaire became the main study area for a series of
classic studies that have greatly influenced the modern understanding of dolomitization, the
origin of depositional and diagenetic fabrics, and porosity evolution in dolomitized limestones
(Deffeyes et al., 1965; Sibley, 1980, 1982; Lucia and Major, 1994; Budd and Mathias, 2015).
The reason that Bonaire was a target for these studies is that the island provides a rare example
of well-exposed, Neogene dolomitic successions that are geologically young and show a short
diagenetic history, no burial and very limited mechanical compaction (Deffeyes et al., 1965). For
this reason, Bonaire dolomites offer a unique opportunity to constrain environmental conditions
of dolomitization with a higher degree of confidence (Budd, 1997; Warren, 2000; Machel, 2004).

Many of these studies were based on samples collected from a dolomitized succession cropping
out in the northern and central parts of the island in the 1960s and 1980s interpreted to have been
formed by hypersaline reflux. Goto Meer, Dos Pos and Dochilla are considered the classic
outcrops which show a fining-upwards succession of bioclastic deposits formed of coral rudstone
and coralgal grain/packstone. The deposits were partially replaced by dolomite that displayed
various fabrics, including sucrosic texture, cloudy cores/clear rims, and dolomite cement (Sibley, 1982). More recent efforts by Budd and Mathias (2015) focused on understanding the lateral variability of porosity and elemental chemistry of the dolomites using the Dos Pos outcrop (Middle Miocene), which led to the hypothesis of geochemical self-organization of dolomite crystals.

The current study adds to this ongoing conversation about dolomitization on the island of Bonaire. Previously unstudied outcrops (a Mio-Pliocene progradational platform) were compared with the classic Bonaire outcrops (a Middle Miocene aggradational platform) to investigate spatial differences in dolomite distribution on the island (Laya et al., 2018a). We evaluate alternative models, including the role of the underlying volcanic rocks, and the significance of the geometry and dolomite distribution. Collectively, these data reveal new insights into reflux dolomitization in island settings, and the importance of chemical and hydrological controls that operate at different spatial and temporal scales. We use these data to evaluate the degree to which reflux can explain the geometry of the dolomite geobodies, as well as petrographic, mineralogical and geochemical characteristics of the dolomite.

**Geological background and study area**

The island of Bonaire is located in the southern Caribbean Sea, 90 km north of the Venezuelan coast (Fig. 1). Bonaire, together with nearby Curaçao and Aruba, make up the Netherland Antilles island chain. The geology of Bonaire has been extensively described since the 1930’s (Pijpers, 1933; Alexander, 1961; De Buisonjé, 1963; Bandoian and Murray, 1974; De Buisonjé, 1974; Zapata et al., 2014), and comprises five primary lithostratigraphic units: 1) Upper-Cretaceous volcanic basement (Washikemba Formation) made up of folded and deformed
intrusive and extrusive igneous rocks which represent the basement of the succession; 2)
Cretaceous Rincon Limestone; 3) Eocene clastic deposits (conglomerate and sandstone of the
Soebi Blanco Formation); 3) Miocene-Pliocene variably dolomitized carbonates (Seroe Domi
Formation), and 4) Pleistocene-Holocene shallow-marine reefal framework-dominated
carbonates (no formal lithostratigraphic name), with minor evaporite deposits from Holocene-
Recent hypersaline lakes.

The pre-Neogene sequence stratigraphic framework is poorly documented since the stratigraphic
record of Bonaire island is limited. Pre-Neogene sequences include deposits of the Rincon
Limestone, which is the remnant of a Cretaceous transgressive-highstand sequence, but it is
isolated and very limited in thickness (Fig. 1). A sandstone and conglomerate succession
unconformably overlies the basement in the central area of the island and are interpreted as
Eocene continental lowstand deposits (Zapata et al., 2014). There are no stratigraphic sections
preserved between the Eocene and the Early Miocene when a rapid transgression flooded the
Bonaire platform, caused by glacioeustatic response during the Miocene Climatic Optimum
(Laya et al., 2018a). Once the platform was flooded, marine carbonates of Seroe Domi
Formation were deposited.

The Seroe Domi Formation is a succession of shallow-water carbonates that are exposed in a
series of outcrops, offlapping a topographically complex volcanic basement. On the basis of field
description, facies analysis, and Sr isotope dates, Laya et al. (2018a) identified two members of
the Seroe Domi Formation. The older member comprises Middle Miocene calcitic bioclastic
rocks containing gastropods, green algae and bivalve fragments that are mainly exposed on the
northwestern part of the island. This Middle Miocene unit is an aggradational succession
deposited during the initial stage of a third-order transgressive system, which is associated with
rapid sea-level rise during Miocene Climatic Optimum (Laya et al., 2018a). This member includes classic outcrops located in the Goto Meer and Dos Pos areas, show evidence of deformation and uplift.

Between the older member (aggradational platform) and the younger member (progradational platform), an angular unconformity is observed, clearly exposed in the leeward, western area of the island. This unconformity marks the sequence boundary between the transgressive system and the preserved highstand of the progradational platform, and marks a hiatus of approximately 4 My when tectonic deformation and meteoric overprint may have occurred (See Laya et al., 2018a, fig. 15).

The progradational platform is the main focus of the current study. This sequence prograded mainly towards the southeast, following the paleotopography caused by tectonic tilting of the basement (Hippolyte and Mann, 2011; Laya et al., 2018a). This progradation is interpreted as a highstand phase, which is marked by high sedimentation rates and restricted accommodation space, promoting sediment shedding off the platform (Figs. 1 and 2).

The platform margin of the entire progradational platform, as exposed, consists of clinoforms composed of up to 70% calcareous coralline red algae with minor coral fragments, large benthic foraminifera, echinoids, rare bivalves and subordinate volcanic lithic clasts (Laya et al., 2018a). Individual clinoforms exhibit lateral changes in facies, with upslope sections consisting predominantly of encrusting red algae and rhodolite facies, grading downslope over a distance of 30-40 m into bioclastic facies (Laya et al., 2018a) (Figs. 2, 3 and 4).

This study presents a detailed analysis of the Seru Grandi outcrop where Mio-Pliocene progradational platform units consist of concordant clinoforms of dolomitized algal-rich facies
The Miocene-Pliocene strata (progradational platform) at Seru Grandi consist of four facies: 1) large benthic foraminiferal grainstone, 2) coralgal grain/packstone, 3) encrusting red algae-rich and rhodolite grainstone/packstone, and 4) reworked red algal grain/packstone (Table 1; Fig. 3) (Laya et al., 2018a). These facies are notable for the lack of significant reef-building corals, which occur only locally. Most of the facies of the Miocene-Pliocene unit have been dolomitized except for the benthic foraminiferal grainstone; this may reflect the low reactivity of foraminifera tests. The overlying undolomitized Pleistocene section consists of reefal facies made up of coral rudstone with red algal encrustations. The contact between the two units is an erosional unconformity, which shows an irregular lightly karsted surface representing a depositional hiatus of ~1 My. The progradational succession has been interpreted as the shallow subtidal section of a marginal platform (Laya et al., 2018a).

Methods

The study area was characterized by Laya et al. (2018a), with detailed analysis of the stratigraphic architecture and facies. For the present study, only dolomitized outcrops of the progradational carbonate platform were analyzed, but particular emphasis was placed on the outcrop called “Seru Grandi” located in the Washington-Slagbaai National Park, the northern side of the island. The excellent exposures of the Mio-Pliocene dolomite bodies allow detailed studies of the geometries of the dolomite distribution, providing constraints on the dolomitization process. The main outcrop “Seru Grandi” is an excellent representation of the progradational system; there are other examples around the island, but the quality and accessibility of those outcrops are less useful.
To characterize the study area, high-resolution photomosaics were acquired and used for stratigraphic analysis. Drone-based image sets were acquired to construct 3D outcrop models using photogrammetry techniques in Agisoft PhotoScan Professional Edition (version 1.1.6 build 2038, 64 bit). The resolution of the photomosaic reaches 1.2 cm/pixel. Photogrammetry models were calibrated with Trimble r10 and netR9 RTK GPS/Glonass surveying equipment, which was accurate to under 10 cm/pixel. This was supported by traditional field descriptions of the measured sections in order to describe the depositional and diagenetic facies, as well as identify the extent and lateral variability of the dolomite bodies at the bed-scale, as documented by Laya et al. (2018a).

A total of 235 samples (51 hand samples and 184 core plugs) were collected from the outcrops (Table 2). Table 2 presents sampling coverage for different outcrops around the island (for outcrop location, see Fig. 1). The majority (63%) of the samples were collected at the Seru Grandi outcrop (Fig. 2E). For detailed analysis, four clinoforms at the Seru Grandi locality were sampled laterally at 1-m intervals using a Tanaka TED-270PFDH dual-handle gas-powered core drill to collect 5 cm diameter core plugs.

To complement the detailed study of Seru Grandi, we also examined a series of additional outcrops that had not previously been identified as dolomitic, including Bolivia, Fountain, Santa Barbara and Bike Trail (Fig. 1). These were then compared with samples and previous descriptions from a series of Middle Miocene outcrops with dolomite, including Goto Meer, Dos Pos and Dochilla localities (Fig. 1). The intention of this comparison is to determine the difference in dolomitization styles and highlight the findings of this investigation.
Petrographic analysis of 135 polished thin sections of dolomitic samples was completed using an Olympus BX53MTRF microscope and Olympus Stream Essentials 2.1 software. The Dunham (1962) carbonate rock classification, modified by Embry and Klovan (1971), was used to define rock texture; more detailed descriptions of facies and carbonate components can be found in Laya et al. (2018a). Cathodoluminescence (CL) petrography was performed using a Technosyn Cold Cathode Luminescence Model 8200 MKII to analyze the dolomite rim variation and crystal evolution.

215 powdered whole-rock samples were analyzed for stable isotopes of carbon ($\delta^{13}$C) and oxygen ($\delta^{18}$O) in a Kiel IV carbonate device coupled to a Thermo-Scientific MAT-253 isotope ratio mass spectrometer in the Stable Isotope Geosciences Facility at Texas A&M University. From the 215 total sample set, 94 samples came from the Seru Grandi outcrop, which was the main study locality. From this set, only the 72 samples containing >90% dolomite were used to avoid the significant influence of calcite on the isotopic signal; 17 samples of mixed mineralogy were not used for interpretation. Five calcite-dominated samples (>90%) were used as a reference. The results are reported in the VPDB standard with an analytical precision of 0.04‰ for $\delta^{13}$C and 0.08‰ for $\delta^{18}$O.

Whole-rock samples were examined using standard powder X-ray diffraction (XRD) analysis in the Carbonate Petrology and Characterization Laboratory at Western Michigan University. XRD data were collected using a Bruker D2 Phaser Diffractometer with a CuK$\alpha$ anode. All samples were scanned with a 2$\theta$ range of 20° to 60°, a step size of 0.01° and a 1 s count time. Peak positions were calibrated using powdered fluorite (CaF$_2$) as an internal standard. For calibration and more details on these methods see Manche and Kaczmarek (2019). Calibrated XRD diffractogram data were later employed in quantitative analyses to determine stoichiometry and
percent calcite, aragonite and dolomite. A small subset was also analyzed in the Department of Soil and Crops at Texas A&M University with Bruker D8 ADVANCE diffractometer with CuKα radiation collected with a 2θ range of 15° to 50°, a step-size of 0.01°. Standard powder XRD techniques (Graf and Goldsmith, 1956; Milliman, 1974; Tucker, 1988) were used to characterize the stoichiometry (Mg/Ca composition) and abundance of various carbonate minerals.

Examination of XRD diffractograms provided data on the 2θ peak position, d-spacing, and background-subtracted intensities of the dolomite 104, 015, and 110 reflections, as well as the calcite 104 peak. Dolomite composition was calculated based on the calibrated position of the dolomite 104 peak using the peak shift equation derived by (Lumsden, 1979). This equation assumes a linear relationship between dolomite composition and the position of the dolomite 104 peak (Goldsmith and Graf, 1958; Royse et al., 1971; Lumsden, 1979; Lumsden and Chimahuskey, 1980) and can result in inaccuracies of up to 2-3 mol % MgCO₃, particularly at higher MgCO₃ contents (Reeder and Sheppard, 1984). Percent dolomite was calculated using the peak intensity ratio method proposed by Royse et al. (1971). Percent dolomite was calculated using the peak intensity ratio method proposed by Royse et al. (1971). The degree of cation ordering was determined using the ratio of the background-subtracted intensities of the dolomite 015 and 110 reflections following the methods of Goldsmith and Graf (1958).

Samples were dissolved in 5% HNO₃ to measure major and trace elements. 80 dolomite samples were analyzed for calcium (Ca), magnesium (Mg), strontium (Sr), manganese (Mn), iron (Fe), sodium (Na) and aluminum (Al) by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) Element™ Series HR-ICP-MS from Thermo Scientific in the Radiogenic Isotope Geosciences Laboratory of Texas A&M University. Results are reported in parts per million (ppm) with a
precision of 0.007 ppm for Ca, 0.0015 ppm for Mg, 0.001 ppm for Sr, 0.003 ppm for Mn, 0.03 ppm for Fe, 0.03 ppm for Na and 0.03 ppm for Al.

In order to understand the fluid flow behavior of the dolomitized facies, porosity and permeability measures were measured. First, porosity values were obtained using a helium porosimeter from 101 core plugs (1-inch diameter by 1-inch tall cylinders). Helium porosity analysis is based on combining a measurement of grain volume with bulk volume. The process consists of three steps: desiccation overnight, obtaining its bulk volume using digital calipers (Mitutoyo CA–10-8”; precision = 10 µm), and obtaining its grain density using a Micromeritics AccuPyc II 1340 helium pycnometer, based on Boyle’s Law. To maintain a high degree of precision, the maximum standard deviation allowed on the grain volume measurement was 0.0035 cm³. If a higher standard deviation was recorded (assumed to be related to moisture in the sample. In addition, the weight of each core plug was measured using Mettler Toledo ME204E analytical balance to a precision of 0.1 mg. This allowed the calculation of porosity, bulk density (with bulk volume), and grain density (with grain volume). Second, permeability measurements were obtained via a core water flooding permeameter from 27 core plug (1-inch diameter by 1-inch-tall cylinders) in the Texas A&M Harold Vince Department of Petroleum Engineering. The permeability of each sample is acquired by measuring the pressure differential between the upstream and downstream pressures on either sides of the core and utilizing the Darcy equation.
Results

Field observations

Stratigraphic relationship on the type locality Seru Grandi:

At the Seru Grandi locality, the Miocene-Pliocene progradational strata form an outcrop that extends ~800 m along the windward coast (Figs. 1 and 2). This outcrop is largely comprised of reworked encrusting red algal facies showing different progradational geometries (Fig. 3, Table 1). The Seru Grandi outcrop exposes thirty clinoforms with different stratal geometries that dip to the east/southeast at angles up to 12°. Clinoform dimensions were obtained from detailed measurements of base width and clinoform lengths from the digital outcrop model (DOM). The strike azimuth of the clinoforms is 144° ± 14° indicating progradation from northwest to southeast. Individual clinoforms have a base length of 34 ± 13 m, with a maximum vertical thickness of 4 ± 1.5 m measured to the base of the wave-cut platform (Figs. 2D and 2E). Overall, the stacking pattern thickens upwards from the oldest clinoform in the north to the youngest clinoform in the south (Supplementary Material 1).

The prograding strata are overlain by tabular reefal Pleistocene facies up to 10 m thick, separated by a well-defined unconformity. This unconformity shows signs of erosion with brecciated limestone fragments bound by an algal crust approximately 2 cm thick (See Laya et al., 2018a, figs. 6E and 6G), though soil development is clearly absent; there is only light karstification, since the surface is mostly flat (Figs. 2C, 2D, 2E and 3). This surface can be observed all around the island between the progradational platform and the overlying Pleistocene reefal deposits. This surface represents a hiatus of 2-4 My according to reported dating values (Obert et al., 2016; Laya et al., 2018a; Rixhon et al., 2018).
Dolomite distribution at Seru Grandi

Although the carbonate strata are well-exposed at Seru Grandi, the lack of obvious color changes makes it difficult to identify dolomite and limestone contacts. For this reason, identification relied on XRD. The four clinoforms examined in detail (Fig. 2E) do not exhibit clear facies boundaries that can be marked as sharp contacts. Rather they are characterized by a gradational transition from the red algal encrusting facies in the updip area towards reworked bioclastic material downdip (Figs. 3 and 4).

Clinoforms D through A (Fig. 4A) show varying dolomite abundance from XRD measurements. Clinoform D (oldest unit) is variably dolomitized with a significantly lower mean percentage of dolomite (mean 25±21%, n=14) in comparison with other dolomites, excluding a single sample with 80% dolomite located ~15 m down-dip of the unconformity. Clinoform C is dolomitized (mean 86±10% dolomite, n=36), with more samples containing calcite occurring further downdip. Clinoform B is mostly calcite and aragonite (mean 6±5% dolomite, n=3). Clinoform A (youngest unit) consists of a high percentage of dolomite (mean 97±3%, n=43), with a minor decrease in percent dolomite towards the toe of the clinoform (Fig. 4A).

Petrographic observations

Dolomite texture at Seru Grandi

Four texturally distinct dolomite types have been identified at Seru Grandi as well as in other outcrops on Bonaire. Type 1 is a fine-crystalline dolomite (<15 µm), and crystal boundaries are commonly anhedral (Figs. 5A and 5B). This dolomite forms from mimetic replacement of skeletal grains, especially red algal fragments, as well as the original micritic or fine bioclastic matrix. Type 2 dolomite crystals are 15-80 µm in diameter, subhedral in shape and a sucrosic
texture with no zonation (Figs. 5C and 5D). Type 2 is the most abundant dolomite type, followed by type 1 dolomite, and together they are present in 80% of the samples at Seru Grandi (Fig 4B).

Type 3 dolomite has very well-developed euhedral crystals of 50-100 µm size, with cloudy cores and clear rims, as well as bladed calcite inclusions (Figs. 5E, 5F and 6). Crystal zonation is clearly visible under CL (Fig. 6B and 6D). Type 3 dolomites are most commonly located near the unconformity between the Mio-Pliocene and Pleistocene successions; their occurrence decreases dramatically downdip along the dolomite bodies (Fig. 4B). Type 4 dolomite is coarsely crystalline (>100 µm), with euhedral crystal shapes. It occurs as a cement, commonly within fractures, molds and other voids where it lines pore walls (Figs. 5G and 5H). Type 4 dolomite can be observed within 50% of the samples and extends into the lower parts of the clinoforms C and D where the rocks are dominantly calcitic (Fig.4B).

Calcite cements and other diagenetic features

Low-Mg calcite is present at Seru Grandi, and at several other locations around the island, as a constituent of grains and micrite, but no abundant calcite cements were observed. Cements have a bladed texture and occur as rims on reworked red algal fragments, but in other instances, they are drusy spar filling voids (e.g., bivalve molds, coral inner cavities, as well as a few fracture walls and oversized pores). Crystal sizes are between 70-100 µm for the bladed texture and 20-80 µm for the drusy texture. Fibrous and botryoidal cements occur only locally in the lower section of clinoform D presenting a crystal-size range between 100 and 400 µm.

Dissolution features are very common across the succession, including molds of bivalves and large benthic foraminifera as well as micropores within the internal structure of the red algal fragments. These features occur independently of the mineralogy since they appear in both
calcitic and dolomitic facies with no distinction. Pore sizes are varied from a few µm microporosity within the red algal structure to many mm in oversized pores.

**Geochemistry of Seru Grandi Dolomites**

Carbon and oxygen isotopes of samples with >90% dolomite show positive values of both $\delta^{13}C$ and $\delta^{18}O$ (Fig. 7) with an average of $2.7\% \pm 0.8$ (n=72) and $3.6\% \pm 0.7$ (n=72) respectively. There is a strong covariance between carbon and oxygen isotope values (Fig.7). $\delta^{13}C$ and $\delta^{18}O$ range up to 3.5‰ and 4.5‰. Stable isotopes from pure limestones (>90% calcite) in Seru Grandi show values from -2.8 to -0.9‰ $\delta^{13}C$ (n=5) and -3.2 to 1.5‰ $\delta^{18}O$ (n=5), respectively.

Strontium concentrations of dolomites range overall between 29 to 450 ppm, with clinoform A showing a range of 48 - 445 ppm (average 240 ppm, STD 101 ppm) and clinoform C ranging between 29 and 305 ppm (average 134 ppm, STD 49 ppm). The associated limestones in this area show much higher values of Sr, ranging from 187-748, average 371ppm, STD 146 ppm.

Iron and manganese concentrations range from 48 - 1768 ppm, average 487 ppm, STD 366 ppm and 7 - 182 ppm, average 54 ppm, STD 32 ppm, respectively, with the highest values observed nearest to the unconformity. The equivalent limestones in the succession have lower values, iron (38 - 670 ppm, average 264 ppm, STD 207 ppm) and manganese (6 - 64 ppm, average 38 ppm, STD 15 ppm) (Fig. 8).

The dolomites show a broad range of sodium concentrations (94 - 1641 ppm) with no clear relation to the $\delta^{18}O$ values (Fig. 8A). There is a positive relationship between sodium and strontium data, with samples showing a bimodal distribution of Na:Sr (Fig. 8B). Iron and manganese appear to covary at lower Mn concentrations, although scatter around, this
relationship increases at higher Mn values (Fig. 8C), and there is a strong linear relationship between iron and aluminum (Fig. 8D).

**Mineralogy of Seru Grandi Dolomites**

The stoichiometry of the dolomites in the Seru Grandi clinoforms ranges from 43.75 to 46.50 mol% MgCO$_3$ with a mean of 45.2 ± 0.5 mol% MgCO$_3$ (Fig. 9). All samples analyzed have XRD evidence of cation ordering (supplementary material 3). Although the mean stoichiometry varies between the clinoforms, the most stoichiometric dolomites are generally observed in the clinoforms with highest percentage of dolomite (Figs. 9, 10 and 11). In addition, a statistical T-test was performed for stoichiometry values, producing the following results: from clinoform A vs C (T-stat= 3.18; P-value=0.002; t Critical two-tail=2); C vs D (T-stat= 4.78; P-value=0.0001; t Critical two-tail=2.1); A vs D producing (T-stat= 6.6; P-value=0.000001; t Critical two-tail=2.1).

**Porosity and Permeability**

Porosity from core plugs varies from 4-24%, with no clear trend associated with particular facies or sample locations. A similar behavior is shown by the generally low permeability values (most of the values below 1 mD with 17 mD as maximum, (Table 3).

**Characteristics of other Mio-Pliocene dolomites on the Island of Bonaire**

This research describes a number of previously unrecognized Mio-Pliocene dolomite bodies that are mainly located on the windward side of the island and include localities at Bolivia, Fountain, Bike Trail and Seru Grandi, which expose up to 45 m vertical thickness of strata; all of those outcrops belong to the progradation platform (Mio-Pliocene succession). These deposits are characterized by progradational geometries to the east and are overlain by Pleistocene deposits.
with no dolomite. In general, dolomite abundance increases to the northwest. Locally, the
dolomite abundance trends follow stratigraphic surfaces, extending downward from the
unconformity toward the base of the unit (Fig. 4A).

In the Bolivia area, prograding red algal grain/packstones are nearly-completely dolomitized
(>90% dolomite by XRD) and are overlain by a flat-topped Pleistocene reefal section (Table 2).
The dolomite crystals measure <50 µm and are mainly mimetic in texture (type 1). Occasionally
non-mimetic textures are observed, including dolomite types 2 and 3. At the Fountain outcrop,
the equivalent strata are massive, completely dolomitized, showing mimetic replacement of red-
algal facies. South of the Fountain outcrop, discontinuous exposures are present along a
mountain bike trail that crosses the island from the windward to the leeward side, and in the
Santa Barbara area, the dolomite has similar characteristics to dolomite type 2 and 3. The
depositional geometries in this area have been well described by Bowling et al. (2018). The
strata are characterized by 20-25 m thick prograding clinoforms consisting of partially
dolomitized red algal facies that have been cemented by late calcite.

In Santa Barbara area, dolomite crystals range in size from 20-100 µm and exhibit cloudy centers
and clean rims, i.e., dolomite type 3, and thus display similar features to the dolomite crystals
described by Sibley (1980, 1982). These are conformably overlain by an aeolianite facies
containing no dolomite (Seru Largu outcrop). Northwest from the bike trail and 2 km north of
Rincon Town, a small outcrop about 3 m high and 10 m wide (identified locally as “Rock of
Bonaire”) display fully dolomitized beds of massive red algal facies. The dolomites have a
crystal size of ~ 40-50 µm and clear crystal appearance, dolomite type 2. All the outcrops
described above were sampled to observe the extent and nature of the dolomite bodies. However,
sampling in other outcrops was limited to selective beds and representative facies (Table 2).
Discussion

Based on geological and geochemical data from the Mio-Pliocene progradational platform on Bonaire, we discuss the nature of the dolomitizing fluids as well as the timing of dolomitization. To understand those topics, we initially consider the geochemical signatures of the dolomites and the possible dolomitization fluids, then we present the paragenetic reconstruction. Subsequently, we analyze the stratigraphic relationships and timing of dolomitization. Finally, we propose the most likely dolomitization model and discuss alternative models for this succession.

Geochemistry of the dolomites and dolomitization fluids.

$\delta^{18}O$ values, +2 to +4‰ VPDB or higher, in carbonates are normally interpreted as the result of evaporative $^{16}O$ depletion. Isotopic fractionation ($\delta^{18}O$) between dolomite and calcite has been reported in many studies, indicating that dolomite values are typically +1 to +4‰ VPDB more positive than coeval calcite (Land, 1983; Major et al., 1992; Vasconcelos et al., 2005). If we apply this fractionation factor from Upper Miocene sea-surface $\delta^{18}O$ values from calcitic planktic foraminifera, that range from -2‰ to 0‰ VPDB (Grossman, 2012), this suggests that dolomite formed from seawater would yield values of -1 to +3‰ VPDB, using the minimum fractionation factor, and +2 to +4‰ VPDB, with the maximum factor. This range corresponds to values measured in this study, which vary from +1.2 to +4.5‰ VPDB, and also of many other island dolomites listed by Budd (1997). In summary, the Bonaire dolomite isotopic values indicate precipitation from fluids that are closer to sea-water composition or slightly modified.

In addition, if we calculate the $\delta^{18}O$ value of the dolomitizing fluids using the dolomite-water fractionation factor of Land (1983) at 25°C and Bonaire dolomite $\delta^{18}O$ +1.2 to +4.5‰ VPDB, values from 0.1 to +3.4‰ SMOW are obtained. These values imply that the dolomitizing fluids for
the Bonaire carbonates were not highly evaporative, but rather were close to seawater composition or perhaps only slightly evaporated. This interpretation is supported by the strong positive correlation between $\delta^{18}O_{\text{SMOW}}$ and salinity reported by Rivers et al. (2019), which suggests that dolomitizing fluids on Bonaire would range between 34‰ and 52‰, that is falling in the range of normal-marine to mesohaline fluid as we defined above (Fig. 7). This calculation indicates the nature of the dolomitizing fluids.

The Sr concentration is controlled by the Sr/Ca ratio of the dolomitizing fluid and the distribution coefficient (Vahrenkamp and Swart, 1990; Budd, 1997; Lu and Meyers, 1998). Though the distribution coefficient $D_{\text{Sr}}$ is still a matter of debate, Vahrenkamp and Swart (1990) proposed that $D_{\text{Sr}}$ is controlled by the stoichiometry of the dolomite using 0.00118 for ideal dolomite and 0.00507 for high-calcium dolomite (HCD). Using the latter value for our non-stoichiometric dolomite yields a parent fluid Sr/Ca mole ratio of 6.6 – 15 mmol/mol (mean 8.4 ± 0.3). These values are comparable to present-day seawater values presented by De Villiers (1999) and Busch et al. (2015), which range between 8.4 and 9.6 mmol/mol.

The sodium content of dolomite has been examined as a possible proxy of dolomitizing fluid salinity (Budd, 1997; Lu and Meyers, 1998). The Seru Grandi dolomites show a moderately high concentration of Na reaching up to 1800 ppm, which is surprisingly high given the other evidence suggesting mesohaline parent fluids. However, examples of dolomite with high Na concentrations (up to 3000 ppm) have been reported by Rivers et al. (2012) in southern Australia attributed to mesohaline fluids with up to 50‰ salinity. In addition, the use of Na as a proxy for salinity has been criticized in view of the lack of a valid distribution coefficient for sodium (Budd, 1997). Na does not coprecipitate with Ca and Mg, and it may occur as solid or fluid
inclusions within crystal defects which may affect the concentration without a significant meaning for the interpretation of the salinity of dolomitizing fluids (Budd, 1997).

For Seru Grandi dolomites, sodium and strontium show two trends of covariation (Fig. 8B). The first group of samples presents a cluster of values with lower sodium (mostly below 400 ppm) and Na:Sr of c. 2:1, and the second group extends towards high values of sodium (up to 1600 ppm) with a Na:Sr of c. 4:1. There is no particular relationship between the Na/Sr ratio and the facies, dolomite type, stoichiometry or stable isotope composition. Also, there is no apparent link with dolomite stoichiometry. The most likely interpretation is that the signal is a geochemical memory from the precursor mineralogy or incorporation of micro-inclusions during dolomitization as explained above.

The elevated trace element concentrations provide additional constraints on the dolomitizing fluids. The source of iron, manganese, and aluminum in the Mio-Pliocene dolomites may have been prior interaction with basalts and other igneous rocks that are in direct contact with the Miocene carbonates in Bonaire (Fig. 1) or alternatively, these elements may have been transported via aeolian dust (Prospero and Nees, 1986). However, incorporation of Fe and Mn into dolomite requires that these elements be in a reduced and divalent state; this is common within marine porewaters as a result of decomposing organic matter (Swart, 2015). These elements co-vary within the whole succession (Fig. 8C); however, the values are higher in clinoform A than C, supporting the suggestion for dolomitization of these two clinoforms by different fluids.

The non-stoichiometric nature of the dolomites argues against formation from highly concentrated brines, which are typically associated with more highly stoichiometric
compositions (e.g., Sass and Bein, 1988; Cohen and Kaczmarek, 2017). In fact, the
stoichiometry values observed here are consistent with other shallow-water dolomites interpreted
to have been formed in near normal to mesohaline marine fluids (e.g., Budd, 1997; Manche and
Kaczmarek, 2019).

Paragenesis at Seru Grandi locality.

We propose that the Mio-Pliocene Bonaire succession has had a relatively short diagenetic
history starting on the seafloor in a shallow-marine setting (Fig. 12), although evidence of marine
cementation is limited to local thin bladed rims of cement and micritization of grains are rare.
After this initial marine diagenesis, dolomitization occurred through a series of stages, forming
dolomite types 1 (the earliest) through to type 4 (latest) as described above. Subsequently,
through the Plio-Pleistocene, an extended period of subaerial exposure resulted from a fall in
relative sea-level and was responsible for a major unconformity across the island (Laya et al.,
2018a). As a result of the exposure, meteoric fluids affected the whole succession dissolving
grains and matrix as well as limited dolomite, which is observed in some dolomite crystal cores
in type 3. Dissolution and LMC precipitation alternated during the Pleistocene and Holocene,
perhaps controlled by water-table fluctuations. Evidence of this process is observed in dolomite
cores, which in some cases are dissolved and others are filled by meteoric LMC. Finally, some
calcite cements filled voids and fractures with a more drusy texture, with one exception of a
fibrous-bladed late cement located down-dip of clinoform D, which suggests a late marine
incursion promoting seawater cementation in the lower section of the clinoforms.
Stratigraphic relationship and timing of dolomitization

Our observations suggest that dolomite types 1 and 2 were precipitated early and were directly related to the depositional facies, which is composed of subtidal platform-margin facies, giving mimetic textures, especially in replacing the high-Mg calcite red algal grains. Despite detailed mapping carried out by Laya et al. (2018a) there is no evidence of tidal-flat facies, evaporites, or any other clearly littoral deposits, although there are observations of small aeolian deposits conformable with the subtidal facies in the central part of the island (See Laya et al., 2018a, Fig. 7). These observations could suggest that there are no links between early dolomitization and any shoreline process involving restricted conditions. However, the absence of coastal sediments could be explained by erosion during subaerial exposure, which is evident on the upper stratigraphic boundary of the dolomitized clinoforms, as Lucia and Major (1994) suggested.

Another possibility is that sea-level fluctuations were relatively rapid and high amplitude so that the platform was either completely flooded during highstands or completely exposed during lowstands, leading to rapid transitions between those stages preventing the developing of coastal environments. This could indicate that the dolomitization processes occurred under marine conditions at a relatively shallow depth.

Dolomite type 3 developed later in the paragenesis, producing growth zones on pre-existing dolomites and creating a more euhedral crystal habit. Finally, dolomite type 4 occurs as cement filling voids and microfractures. All of those dolomites occurred before the major exposure event, which led to the unconformity with the overlying Pleistocene limestones, as confirmed by the Sr-isotope dating (Laya et al., 2018a).
Although different stages of dolomitization are recognized in the clinoforms at Seru Grandi, Sr isotope dating suggests that this episodic dolomitization is limited to within a relatively short time-interval in the Mio-Pliocene, ranging from 3.5 to 7 Ma (Laya et al., 2018b). However, two of the four investigated clinoforms are calcite-rich and the dolomite is not distributed uniformly (Figs. 4). These observations indicate that the fluids did not dolomitize the whole succession homogeneously but rather bodies of dolomite developed locally downdip within selected clinoforms (Figs. 4 and 13). This variability may be due to short temporal changes in differences in the flux and chemistry of reactive fluids, whereas downdip trends may reflect evolution of magnesium exchange efficiency with distance from the brine source and reactivity of the rock (Garcia-Fresca et al., 2012).

In addition, boxplots, histograms and T-test results of dolomite stoichiometry data from Seru Grandi suggest that each clinoform is comprised of a distinct dolomite population, with an associated variation in stoichiometry in the prograding strata (Figs. 9 and 10). These differences argue against a model whereby the clinoforms were first deposited in a succession and then dolomitization took place through a single event of reflux. Rather, the data suggests that the dolomite in each clinoform formed independently of each other, as each limestone sequence was being deposited, probably by a series of reflux episodes (Fig. 13).

Mass balance calculations (Kaczmarek and Sibley, 2011) and reactive transport models (Jones and Xiao, 2005) suggest that the Mg/Ca ratio of downward refluxing brine should decrease during dolomitization as Mg is consumed and Ca is released. Given that the fluid chemistry evolves down-gradient, dolomite stoichiometry and abundance would be expected to decrease down the fluid flow path as the conceptual model suggests (Saller and Henderson, 1998a; Manche and Kaczmarek, 2019). However, the absence of any clear lateral trends in
stoichiometry within individual clinoforms suggests that fluids did not evolve laterally downdip within clinoforms, assuming the predominant flow path is downdip (Fig. 11). This assumption is based on our observations of the dolomite distribution where dolomite bodies are interbedded within non-dolomitized rocks following the clinoform geometries downdip. This observation suggests that the dolomitization fluids should have taken the most permeable path, which is the sigmodal route of the clinoforms, and have dolomitized those sediments. However, there are uncertainties relating to the flow path, such that more complex fluid flow patterns could have occurred within the clinoforms, although we did not encounter the evidence to suggest this.

The observation that dolomite stoichiometry varies between individual clinoforms is consistent with temporal changes in chemistry of the seawater-derived dolomitizing fluids. Thus, for example, this could explain the increase in dolomite stoichiometry and abundance from clinoform D (oldest) to clinoform A (youngest). A multitude of geochemical factors such as Mg/Ca ratio, temperature and salinity of the seawater likely evolved in concert (Manche and Kaczmarek, 2019). This hypothesis is consistent with laboratory experiments that have demonstrated that an elevated Mg/Ca ratio (Kaczmarek and Sibley, 2011), temperature (Gaines, 1968; Kaczmarek and Thornton, 2017), and salinity (Medlin, 1959; Glover and Sippel, 1967; Cohen and Kaczmarek, 2017) result in more stoichiometric dolomite.

In addition to fluid properties, the distribution of dolomitization is controlled by variations in sediment permeability (via its effect on fluid flux) and the reactivity (effective reactive surface area and mineralogy) (Whitaker et al., 2012). Permeability is inherently highly variable (Fig.14), ranging from <1mD to 800mD over a distance of 60 m, as measured in the Middle Miocene of Seroe Domi at Dos Pos (Lucia and Major, 1994; Budd and Mathias, 2015). In fact, the permeabilities measured in samples from Seru Grandi after dolomitization are uniformly quite
low, mostly <1mD, with only a few samples up to 17mD. It seems that the dolomitization process has produced a tight arrangement of fine crystals leaving only isolated moldic pores, which are likely a product of over-dolomitization. Initially, based on the depositional facies (Laya et al., 2018a), moderate to high permeability values were expected, but in fact, they are highly variable and do not show any particular trend.

Proposed dolomitization model

For the Bonaire Mio-Pliocene succession, we suggest that dolomitization by mesohaline reflux supports our mineralogical and geochemical observations and is consistent with geological context of the island. In addition, based on our set of evidence, we suggest that the mesohaline reflux model occurred in separate time steps following after deposition of the individual clinoform, as we describe in the Figure 13. We limited our interpretation to four-stage reconstruction of the clinoform formation and dolomitization process, because we are restricted to our interrogated clinoforms.

The mesohaline reflux model is supported by previous workers who have suggested that there is no need for an additional source of magnesium for mesohaline reflux to drive dolomitization, nor do fluids need to be evaporated to the point of hypersalinity (salinity in excess of 140‰ as we defined above), not even the lower boundaries of 72‰ defined by Adams and Rhodes (1960). This model is confirmed by Simms (1984) who proposed the possibility of reflux of mesohaline water (salinity 37-42‰) on the basis of experimental data and analytical models and suggested that mesohaline reflux could be taking place in the shallow and semi-restricted waters of the Great Bahama Bank. This appeared to be confirmed by the presence of Mg-depleted mesohaline brines and associated sparse dolomites in the carbonates beneath the adjacent island (Whitaker et
Subsequently, groundwater flow models have been used to explore the controls on this circulation system (Jones et al., 2002, 2004); however, reactive transport simulations suggest mesohaline reflux has limited potential to rapidly dolomitize large areas (Al-Helal et al., 2012).

As an alternative, mixing-zone dolomitization was invoked on Bonaire by other authors including, Sibley (1980) and more recently for similar Miocene-Pliocene dolomites on Curaçao by Sumrall (2019), who cited a contribution of magnesium from meteoric water interacting with volcanic bedrock exposed in the center of the island. Also, $\delta^{18}O$ and $\delta^{13}C$ values in the Seru Grandi dolomites co-vary. Although, some authors (e.g., Ward and Halley, 1985; Meyers et al., 1997; Humphrey, 2000) have suggested that such isotopic covariance is associated with mixing-zone environments, strong arguments have been made against the mixing-zone model, including the absence of dolomite and the widespread evidence of dissolution in modern mixing-zones (Machel and Mountjoy, 1986; Smart et al., 1988; Machel, 2004; Swart, 2015). Additionally, spring water extracted from the volcanic deposits that underly the majority of the Washington-Slagbaai National Park show minor evidence of magnesium enrichment, and geochemical modelling suggests that mixing with seawater generates no significant potential for dolomitization (Whitaker, unpub. data).

Furthermore, the Seru Grandi dolomite bodies do not accord with the geometry expected for a product of mixing-zone diagenesis, confirming isotopic evidence and textural indications (lack of associated dissolution features) that argue against mixing-zone dolomitization. Finally, there is no isotopic evidence for dolomitization from fluids more dilute than seawater, nor do we see textural evidence for associated dissolution or elevated values of porosity-permeability, which are widely recognized features of mixing-zone diagenesis (Swart, 2015). For all these reasons, this model is considered very unlikely.
There are other alternative models that could be considered. However, the elongate geometries of the dolomitized rock following the clinoform-shaped strata at Seru Grandi (Figs. 4, and 13) are inconsistent with hydrological models suggesting subsurface lateral inflow of Mg-bearing seawater. Such mechanisms, which include evaporative pumping, sub-mixing-zone circulation, and geothermal convection, would preferentially tend to alter more distal sediments (Warren, 2000; Whitaker et al., 2004; Gabellone et al., 2016). Rather, this distribution would indicate a source of Mg-rich fluids proximal to the margin of the island and a flow direction which is towards this margin. This rationale underlies Figure 13, which shows representative stages of progradation and episodes of reflux, which we propose, are responsible for the present-day dolomite distribution in the succession.

Summary and Conclusions

Non-stoichiometric compositions, weak $^{18}$O enrichment, low trace-element concentrations and sedimentological context of the Mio-Pliocene dolomites of Bonaire, together suggest that refluxing fluids were more likely to be mesohaline and close to seawater in composition.

Detailed characterization of the progradational bioclastic units at the Seru Grandi outcrop shows well-defined tongues of dolomite that extend along clinoform surfaces beneath a sub-horizontal unconformity, which is overlain by Pleistocene limestones. The Seru Grandi clinoforms display a dolomitization pattern, which suggests early replacement of HMC and aragonite as a result of fluids moving down dip along the clinoforms through a succession of subtidal facies. These geobodies are morphometrically consistent with dolomitization by refluxing fluids, as suggested by many other studies. However, these Mio-Pliocene dolomitized clinoforms have individually small volumes and they do not require large density contrasts to trigger fluid flow and activate dolomitization. We suggest that a succession of individual mesohaline reflux events affecting the
clinoforms soon after their deposition could have been responsible for the distribution of the
dolomites across the island, especially in the Mio-Pliocene units.

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**Figures**

Figure 1: Geological map and stratigraphy of Bonaire Island. Location of the ‘classic’ outcrops and new study areas. Modified from Laya et al. (2018). Inset shows location of Bonaire within
the Netherland Antilles. Schematic cross-section (below) showing stratigraphic relations between major lithostratigraphic units Modified from Laya et al. (2018).

Figure 2: Key features of the Seru Grandi outcrop. A) Orthomosaic presenting the areal extension of the Seru Grandi outcrop, with arrows showing a perspective of oblique image in C and D. B) Digital Terrain Model (DTM) of the Seru Grandi outcrop showing elevation (white squares show values of the contour lines in meters). C) Lateral view of the southern end of the Seru Grandi outcrop showing the major unconformity and stratigraphic relations between the lower progradational platform and the overlying flat-topped platform. (note this view is oriented in strike direction of the clinoform). D) Panoramic view of the eastern face of the Seru Grandi outcrop showing clinoform development within the progradational platform, and location of the section shown in detail in Figure 2E (apparent thickness variation is an artifact of the image perspective). E) Detailed clinoform morphology of the Seru Grandi outcrop showing four sampled geobodies (color squares = sample sites) and contact with overlying flat-topped platform.

Figure 3: Main facies and facies distribution at the Seru Grandi outcrop. A) detailed clinoform image showing a relative facies distribution. B, C) Encrusting red algal (ERA) rich grainstone/packstone; D, E) Coralgal grainstone and packstone facies with abundant large benthic foraminifera and red algae; F, G) Reworked red algae (RRA). Relative facies distribution within the clinoform architecture (above).

Figure 4: Mineralogy distribution of the interrogated clinoforms at Seru Grandi. A) XRD-determined bulk mineralogy, pie charts show the relative volumes of dolomite, calcite and aragonite. Note that in clinoforms A and C, the samples are largely dolomite below the
unconformity and dolomite tends to decrease in abundance with depth and/or distance downdip.

Dolomite is less abundant in samples from clinoforms B and D, but in the latter it is higher beneath the dolomitic C clinoform. B) Relative dolomite type distribution within the clinoform architecture, (see explanation on the text).

Figure 5: Features of dolomite types. A) Dolomite type 1 has a crystal size <15 µm, and crystal boundaries are commonly anhedral. Mimetic textures are shown replacement of red algal skeletons. B) SEM image dolomite type 1. C) Dolomite type 2 has clear crystals ranging in size from 15µm to 80µm, with subhedral crystal boundaries and a sucrosic texture. D) SEM image dolomite type 2. E) Dolomite type 3 has very well-developed crystals from 50 µm to 100 µm, with cloudy centers and some zonation (white arrows). F) SEM image dolomite type 3. G) Dolomite type 4 is coarsely crystalline (>100µm) with euhedral crystal boundaries and where present occurs as a cement partially filling void spaces. H) SEM image dolomite type 4.

Figure 6: Thin-section images of dolomite. A) Crystals of dolomite type 3 showing cloudy cores and clear rims under plane-polarized light. B) CL image of A showing alternations of bright and dull bands and bright crystal cores. C) Late calcite cement following euhedral dolomite type under plane polarized light. D) CL image of C showing that calcite is not luminescent, whereas dolomite shows a bright core and alternating luminescent and dark bands.

Figure 7: Stable isotope cross-plot for limestone (triangles) and dolomite (circles) for samples from Seru Grandi. Dolomites show positive oxygen and carbon isotope values whereas limestones are all negative and more variable. Blue dashed line represents the interval of δ¹⁸O values of well-preserved planktic foraminifera showing a tropical sea-surface signal (Grossman,
Black arrows show +3‰ calcite-dolomite fractionation factor suggested by Land (1983) and used to infer the normal seawater values as shown by the orange dashed line.

Figure 8: Trace-element content of dolomites from clinoforms A and C. A) No relationship between sodium and $\delta^{18}$O. B) Bimodal distribution of samples with high (ratio approx. 4:1) and low (ratio approx. 2:1) ratio between strontium and sodium. C) Positive correlation between iron and manganese (ratio approx. 10:1) and D) between iron and aluminum (ratio approx. 2:1). Sr, Fe, Mn and Al are higher and oxygen isotopes are heavier in clinoform A than clinoform C though there is no difference in sodium values.

Figure 9: Histogram of stoichiometry variation in four clinoforms. Note the increase in mole % MgCO$_3$ from lowest values in Clinoforms B and D, to intermediate values in Clinoform C and highest (but still non-stoichiometric) values in Clinoform A. Dashed vertical line represents maximum for each clinoform.

Figure 10: Boxplots showing stoichiometry of samples from each clinoform. All dolomites are non-stoichiometric, but stoichiometry is highest in clinoforms A and C and lower in the smaller number of samples of dolomite from clinoforms B and D.

Figure 11: Lateral variability in stoichiometry of the interrogated clinoforms. Upper clinoform A shows the highest stoichiometry values (yellow circles). In contrast, light blue circles represent clinoform D, which is the most calcitic with the lowest stoichiometry values.

Figure 12: Paragenesis of Seru Grandi deposits showing relative timing for diagenetic events. Note that Seru Grandi deposits show a very simple diagenetic history.
Figure 13: Seru Grandi mesohaline reflux dolomitization model. Four-stage reconstruction of the
clinoform formation and dolomitization process. Red shadow represents dolomite concentration
within the clinoforms based on data shown in Figure 4. A) Represents the basinward shedding of
reworked red algal facies during the formation of clinoform C; B) A pulse of refluxing
mesohaline fluid dolomitizing clinoform C and partially clinoform D, prior to, or, as shown,
before deposition of clinoform B; C) Additional progradation, with deposition of clinoform B at
low sea level with no evidence of reflux, followed by deposition of clinoform A. D)
Dolomitization of clinoform A via reflux across a wider area. E) Present-day setting of the
outcrop with dolomite distribution and clinoform architecture, and the erosion to form the
unconformity that separates the clinoform units from the overlying flat-topped platform.

Figure 14: Porosity and permeability distribution for Bonaire dolomitized carbonates and those
from similar-aged successions. Bonaire Middle Miocene data from Lucia and Major, 1994 and
Budd and Mathias, 2015. Seru Grandi values are at the lower end of the porosity-permeability
ranges.

Tables

Table 1: Carbonate facies descriptions with interpretations of depositional environment.

Table 2. Dolomite characteristics of the outcrops sampled on Bonaire showing, number of
samples, dominant dolomite type, average values of stable isotopes carbon and oxygen, and
dominant facies.

Table 3. Porosity-permeability data for samples from the Seru Grandi outcrop.
The diagram illustrates the variation of δ¹⁸O and δ¹³C values for limestone and dolomite samples. The δ¹⁸O values range from -4 to 4‰ (PDB), while δ¹³C values range from -5 to 4‰ (PDB). The fractionation factor calcite-dolomite is +3. Normal seawater values are indicated, with mesohaline and marginally enriched conditions shown on the right side. Well-preserved planktic foram tropical sea surface signal is marked on the left side of the graph. Limestone samples are represented by blue triangles, and dolomite samples are represented by orange circles.
A. 

\[ \delta^{18}O \% (VPDB) \]

B. 

\[ R^2 = 0.764 \]

\[ R^2 = 0.526 \]

C. 

\[ R^2 = 0.5134 \]

D. 

\[ R^2 = 0.9197 \]
<table>
<thead>
<tr>
<th>Facies</th>
<th>Brief description</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Large benthic foraminifera grainstone</strong></td>
<td>Fine-grained, well-sorted grainstone with abundant large benthic foraminifera <em>Amphistegina sp.</em>. Also, <em>Cycloclypeus</em> and <em>Miogypsinids</em> present. Brachiopod fragments common and rounded peloids. This facies is mostly calcitic with no evidence of dolomite cementation or replacement. High-angle cross-stratification common as well as limited low-angle planar cross-bedding.</td>
<td>High-energy environments, driven by coastal and aeolian processes. Shoreline sand-body of shoreface-foreshore-aeolian backshore facies.</td>
</tr>
<tr>
<td><strong>Coralgal grainstone/packstone</strong></td>
<td>Fine to medium-grained bioclast fragments of red algae (<em>Spongites</em> sp. and <em>Lithothamnion</em> sp.), corals (<em>Acropora</em> sp., <em>Porites</em> sp., <em>Montastrea</em> sp.), echinoids, bivalves, gastropods and large benthic foraminifera (<em>Amphistegina sp.</em>). Most grains coated by micrite, probably a microbialite crust. This facies is calcitic with locally bladed and drusy cements. Some fine-sand brownish volcaniclastic fragments.</td>
<td>High-energy conditions dominated. Coralline red algae abundant and limited coral fragments indicate slightly deeper and cooler conditions. Increasing large benthic foraminifera content and fine-grained skeletal component suggest reworking by waves and currents moving away from the platform margin.</td>
</tr>
<tr>
<td><strong>Encrusting red algae-rich and rhodolite grainstone/packstone</strong></td>
<td>Facies dominated by different taxa of encrusting coralline red algae including <em>Sporolithon</em> sp., <em>Spongites</em> sp., <em>Lithothamnion</em> sp., and <em>Neogoniolithon</em> sp., as well as encrusting foraminifera and large benthic foraminifera which are commonly dissolved out. This facies partly to completely dolomitized in mimetic, non-mimetic and sucrosic textures. Dolomite cements with zoned crystal habit and cloudy centres as well as clean crystal rhombs.</td>
<td>Although red algae can live in slightly deeper water, combination with large benthic foraminifera and possible hard substrates suggest shallow-marine upper platform within the upper photic zone with low-moderate energy at 0-30 m depth.</td>
</tr>
<tr>
<td><strong>Reworked red algae-rich grainstone/packstone</strong></td>
<td>Variety of calcareous algae with high degree of fragmentation, abrasion and micritization. Skeletal grains mostly well-sorted and subrounded to rounded; some angular. This facies partly to completely dolomitized with microcrystalline dolomite cements and replacement dolomite within the algal internal structure. Bladed and drusy calcite also present.</td>
<td>High degree of fragmentation and abrasion indicate high-energy setting. Low diversity of bioclasts and abundant red algae suggest sediment supplied from shallow shelf.</td>
</tr>
</tbody>
</table>
Table 2. Dolomite characteristics of the island outcrops showing, number of samples, dominant dolomite type, average values of stable isotopes carbon and oxygen, and dominant facies.

<table>
<thead>
<tr>
<th>Localities</th>
<th>Dominant dolomite type</th>
<th>$\delta^{13}$C</th>
<th>$\delta^{18}$O</th>
<th>Dominant facies</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seru Grandi (Mio-Pliocene)</td>
<td>1 and 2</td>
<td>2.7</td>
<td>3.6</td>
<td>Encrusting red algal facies</td>
<td>72</td>
</tr>
<tr>
<td>Bike Trail and Santa Barbara</td>
<td>3</td>
<td>-1.5</td>
<td>0.6</td>
<td>Reworked red algal facies</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>(Mio-Pliocene)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bolivia (Mio-Pliocene)</td>
<td>1 and 2</td>
<td>1.8</td>
<td>3</td>
<td>Encrusting red algal facies</td>
<td>24</td>
</tr>
<tr>
<td>Fountain (Mio-Pliocene)</td>
<td>1 and 2</td>
<td>1.7</td>
<td>2.5</td>
<td>Encrusting red algal facies</td>
<td>3</td>
</tr>
<tr>
<td>Rock of Bonaire (Mio-Pliocene)</td>
<td>1 and 2</td>
<td>2.6</td>
<td>2.3</td>
<td>Encrusting red algal facies</td>
<td>2</td>
</tr>
<tr>
<td>Goto Meer (Middle- Miocene)</td>
<td>3</td>
<td>0.7</td>
<td>2.7</td>
<td>Coralgal facies</td>
<td>12</td>
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</table>
Table 4. Porosity-permeability data of Seru Grandi outcrop.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Facies</th>
<th>Clinoform</th>
<th>Permeability (mD)</th>
<th>Porosity (%)</th>
<th>Dolomite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1 SG1</td>
<td>Encrusting</td>
<td>C</td>
<td>0.04</td>
<td>9.1</td>
<td>86.8</td>
</tr>
<tr>
<td>Line 1 SG6</td>
<td>Reworked</td>
<td>C</td>
<td>0.03</td>
<td>9.1</td>
<td>87.6</td>
</tr>
<tr>
<td>Line 1 SG12</td>
<td>Encrusting</td>
<td>C</td>
<td>0.6</td>
<td>7.3</td>
<td>99.1</td>
</tr>
<tr>
<td>Line 1 SG18</td>
<td>Encrusting</td>
<td>C</td>
<td>0.01</td>
<td>10.9</td>
<td>93.8</td>
</tr>
<tr>
<td>Line 1 SG24</td>
<td>Reworked</td>
<td>C</td>
<td>0.01</td>
<td>11.4</td>
<td>88.7</td>
</tr>
<tr>
<td>Line 1 SG28</td>
<td>Reworked</td>
<td>C</td>
<td>4.87</td>
<td>14</td>
<td>97.5</td>
</tr>
<tr>
<td>Line 1 SG32</td>
<td>Encrusting</td>
<td>C</td>
<td>17.67</td>
<td>24.6</td>
<td>96.3</td>
</tr>
<tr>
<td>Line 1 SG34</td>
<td>Encrusting</td>
<td>C</td>
<td>0.07</td>
<td>10</td>
<td>80.9</td>
</tr>
<tr>
<td>Line 1 SG36</td>
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<tr>
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<td>Encrusting</td>
<td>C</td>
<td>0.06</td>
<td>10.4</td>
<td>99.1</td>
</tr>
<tr>
<td>Line 1 Wed2</td>
<td>Encrusting</td>
<td>B</td>
<td>0.06</td>
<td>6.2</td>
<td>12.1</td>
</tr>
<tr>
<td>Line 2 SG6</td>
<td>Reworked</td>
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<td>0.41</td>
<td>5.3</td>
<td>80.6</td>
</tr>
<tr>
<td>Line 2 SG10</td>
<td>Reworked</td>
<td>A</td>
<td>0.01</td>
<td>13.2</td>
<td>99.0</td>
</tr>
<tr>
<td>Line 2 SG16</td>
<td>Encrusting</td>
<td>A</td>
<td>0.01</td>
<td>6</td>
<td>92.3</td>
</tr>
<tr>
<td>Line 2 SG23</td>
<td>Reworked</td>
<td>A</td>
<td>0.004</td>
<td>5.9</td>
<td>99.2</td>
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<td>Line 2 SG39</td>
<td>Reworked</td>
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<td>0.01</td>
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</tr>
<tr>
<td>Line 2 SG42</td>
<td>Reworked</td>
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