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Spatial variations in the stoichiometry and geochemistry of Miocene dolomite from Grand Cayman: Implications for the origin of island dolostone

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ABSTRACT

The Cayman Formation (Miocene), ~140 m thick on Grand Cayman, is incompletely dolomitized with the most of the dolomite restricted to the peripheral part of the island. These calcium-rich dolomites, with 50–60 mol%$CaCO_3$ (%Ca), are divided into low-calcium dolomite (LCD, %Ca < 55%) and high-calcium dolomite (HCD, %Ca > 55%). Despite the small size of the island (6.8 km wide), the percentages of LCD and HCD, the %Ca, and the geochemical properties of the dolomites show geographic variations relative to the surrounding shelf edge. Accordingly, the Cayman Formation on the east end of the island is divided into the peripheral dolostone (shelf edge–1.5 km inland), transitional dolostone (1.5–2.7 km inland), and the interior limestone and dolostone (2.7 km to island center). From the peripheral dolostone to the interior limestone and dolostone, there is an increase in the percentage of HCD and %Ca in the dolomite, and decreases in the $\delta^{18}O$ and $\delta^{13}C$ values of the dolomite. Interpretations based on the oxygen and carbon isotopic compositions indicate that seawater is the source of Mg for dolomitization. The concentric pattern of dolomitization on the island reflects the fact that seawater flowed into the island from all directions during dolomitization. The lateral inland variations in the dolomite stoichiometric and isotopic properties reflect the gradual modification of seawater by water-rock interaction along the flow path from the shelf edge to the island center. $^{87}Sr/^{86}Sr$ ratios indicate that two phases of dolomitization (late Miocene–early Pliocene and late Pliocene–early Pleistocene) were responsible for dolomitization of the Cayman Formation. It is very likely that during both phases, the carbonate platform was subaerially exposed and that the pump for circulating the seawater through the island was related to the seawater/freshwater mixing zone. The dolomitization model developed from Grand Cayman may be applicable to many other island dolostones affected by long-term sea-level changes. Given that the diagenetic potential of dolostone is directly linked to its stoichiometry, the distribution of the LCD-HCD will influence the petrographic properties, geochemical signatures, and reservoir potential of the dolostones.

1. Introduction

Dolomite (ideally $CaMg(CO_3)_2$), has received considerable attention because of questions that remain about its origin (Land and Moore, 1980; Budd, 1997; Warren, 2000; Machel, 2004; Gregg et al., 2015). Sedimentary dolomites typically contain excess calcium (48–62 mol%$CaCO_3$, hereafter referred to as %Ca), as is the case for most modern and Cenozoic dolostones (e.g., Vahrenkamp et al., 1994; Budd, 1997; Wheeler et al., 1999; Jones and Luth, 2002; Suzuki et al., 2006). Many Phanerozoic dolomites, despite their antiquity, are still non-stoichiometric (e.g., Lumsden and Chimahusky, 1980; Sperber et al., 1984; Reeder, 1991; Drits et al., 2005; Swart et al., 2005). Calcium-rich dolomites are thermodynamically metastable and more reactive than ideal or near-stoichiometric dolomites (e.g., Reeder, 1991; Chai et al., 1995). Thus, in most geological environments high calcium dolomite (HCD, %Ca = 55–62%) is more susceptible to diagenetic modifications than low calcium dolomite (LCD, %Ca = 48–55%) (Jones and Luth, 2002). This includes the preferential dissolution of the calcium-rich cores found in many dolomite crystals. Dolostones formed of hollow crystals generated by this process have high micro-porosity (Jones and Luth, 2002; Jones, 2007) and may be important reservoir rocks. Later precipitation of calcite or dolomite in the hollow crystals leads to the formation of dedolomite (Schmidt, 1965; Folkman, 1969; Jones, 1989; James et al., 1993) or inside-out dolomite (Jones, 2007). At burial, non-stoichiometric dolomite is prone to recrystallization and transformation to stoichiometric, well-ordered dolomites (e.g., Land and Moore, 1980; Reeder, 1981; Blake et al., 1982; Hardie, 1987;

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Kaczmarek and Sibley, 2014). Such modifications change the petrographic properties, geochemical signatures, and reservoir potential of the dolostones.

Models developed to explain dolomitization have typically regarded dolostones as being compositionally uniform. In many cases, however, two or more dolomite populations, as defined by their composition, are present (Sperber et al., 1984; Searl, 1994; Wheeler et al., 1999; Jones and Luth, 2002; Drits et al., 2005; Suzuki et al., 2006). If variations in stoichiometry have been considered, it is done from a stratigraphic perspective and the possibility of geographic variations have been ignored (e.g., Dawans and Swart, 1988; Wheeler et al., 1999). The Cenozoic dolostones on the Cayman Islands, which are formed of various mixtures of LCD (%Ca = 48–55%) and HCD (%Ca = 55–62%) (Jones et al., 2001; Jones, 2005, 2013), are ideal for testing the notion that lateral variations in the composition of dolostones may be critical for developing a model to explain their origin. On the east end of Grand Cayman, 32 wells drilled and sampled to depths up to 140 m are ideally suited for establishing the stratigraphic and geographic variations in the %Ca of dolostones on an isolated carbonate island. The model developed to explain the formation of these island dolostones is based on the integration of their petrography, %Ca, stable isotopes, $^{87}Sr/^{86}Sr$ isotopes, and stratigraphic relationships with coeval limestones. The model, which also relies on the chemistry of the present-day groundwater, is also used to test some of the basic concepts of dolomite formation that have been derived from laboratory experiments like those described by Kaczmarek and Sibley (2011, 2014). The conclusions reached by this research have far-reaching implications for the development of island dolostones throughout the world.

2. Geological setting

Grand Cayman, located on the Cayman Ridge in the Caribbean Sea (Fig. 1A), is surrounded by a shelf that is <1 km wide (Fig. 1B, C). Sculptured by two submarine terraces at 0–10 m below sea level (bsl) and 12–40 m bsl (Fig. 1D), the shelf formed as a result of reef growth and marine erosion during successive sea-level cycles of the last deglaciation (e.g., Blanchon and Jones, 1995). The island slope, which generally begins at a depth of ~55 m (Roberts, 1994), extends into the deep Cayman Trench to the south and Yucatan Basin to the north. Today, the east end of the island has a N-S width of ~6.8 km. The low-lying interior of eastern part of this island, generally <3 m above sea level (asl), is surrounded by a peripheral rim that is up to 13.5 m asl (e.g., Jones et al., 1994a; Jones and Hunter, 1994; Liang and Jones, 2014).

The carbonate succession on Grand Cayman is divided into the unconformity-bounded Brac Formation, Cayman Formation, Pedro Castle Formation, and Ironshore Formation (Fig. 2). Limestones and dolostones of the Cayman Formation (Miocene) are widely exposed over the eastern part of the island (Fig. 1B). Fossils in this formation include corals, bivalves, red algae, foraminifera, and *Halimeda* (Jones et al., 1994b; Ren and Jones, 2016) (Fig. 2). On the east end, the Cayman Formation has undergone pervasive dolomitization in the coastal areas but minimal dolomitization in the central areas of the island (Der, 2012; Ren and Jones, 2016).

3. Methods

This paper integrates all information from outcrops and 32 wells on the east end of Grand Cayman with focus being placed on 21 wells (Fig. 1C, E; Table 1), which were selected because they are the deepest wells (40 to 140 m with most > 70 m), and are located at various distances from the shoreline. Continuous cores were obtained from wells GFN-2 and RWP-2. Cuttings were collected over 0.76 m (2.5 ft) intervals from all other wells. The depth of each well is accurate to ±1% whereas the depth intervals represented by each sample of cuttings are ±2% with the highest variance being on the deeper samples.

Petrographic descriptions are based on standard thin-section techniques and scanning electron microscopy. Thin sections, made from 120 samples from GFN-2, RWP-2, HRQ-3, and RTR-1, were impregnated with blue epoxy to highlight porosity and stained with Alizarin Red S to indicate calcite. Thicker (40–50 μm) thin sections from selected samples from HRQ-2 were prepared for examination on the SEM. After these epoxy-impregnated thin sections were polished and etched in 30% HCl for 10–15 s following the procedure outlined by Jones (2005), they were then coated with carbon and examined on a Zeiss EVO SEM (LaB_6 electron source, accelerating voltage 15 kV). Backscattered electron (BSE) images were obtained from these samples. Elemental compositions were obtained from spots/lines/areas using a Bruker energy dispersive X-ray spectroscopy (EDS) system with dual silicon drift detectors, each with an area of 60 mm^2 and an energy resolution of 123 eV.

Rock cuttings (one every 1.5 m depth), formed largely of matrix dolostone or limestone (fossils and/or cement were avoided), were ground into a fine powder using a mortar and pestle and then subjected to X-ray diffraction (XRD) using a Rigaku Geigerflex 2173 XRD system with Co Kα radiation from 29° to 38° 2θ at 40 kV and 35 mA following the protocol of Jones et al. (2001). The peak-fitting method of Jones et al. (2001) was used to determine the %Ca of the constituent LCD and HCD (±0.5% accuracy) and the weight percentages of LCD and HCD (±10% accuracy).

Oxygen and carbon isotopes for the dolomite and calcite were determined for every other XRD sample (i.e., at 3 m intervals) from EEZ-1, CKC-1, LBL-1, HMB-1, HRQ-1, HRQ-2, and HRQ-3. These analyses were undertaken by Isotope Tracer Technologies Inc. (Waterloo, Canada) who used a DELTA^{Plus} XL Stable Isotope Ratio Mass Spectrometer (IRMS) coupled with a ConFlo III interface and EA1110 Elemental Analyzer. No phosphoric acid fractionation factor was applied to the dolomite. The isotopes are reported relative to VPDB in per mill (±0.1‰ accuracy).

$^{87}Sr/^{86}Sr$ were measured for 114 samples from RWP-2, FFM-1, HMB-1, CKC-1, RTR-1, and GFN-2 in the Radiogenetic Isotope Laboratory, University of Alberta, using the same procedure as MacNeil and Jones (2003). All results were corrected for variable mass discrimination (0.1194) and normalized to SRM 987 standard (0.710245). The 2 standard errors of the $^{87}Sr/^{86}Sr$ values range from 0.00001 to 0.00003.

Groundwater samples were collected from RTR-1 (2009), GFN-1 (2011), and HRQ-3 (2014); and seawater samples from Spotts Bay (south coast) were also collected in each of these years. Chemical composition and oxygen isotope analyses were performed for 34 groundwater and 3 seawater samples by the Saskatchewan Research Council and Isotope Tracer Technologies Inc., respectively, within 2 months of collection. Saline water is defined using chloride contents (> 19.000 mg/L) following Ng et al. (1992). Ninety-seven groundwater samples were measured for temperature during drilling of GFN-1, HRQ-2, and EEV-2.

4. Results

4.1. Sedimentary facies

The Cayman Formation contains numerous fossils including corals (mainly *Stylophora, Montastrea, Porites*), benthic foraminifera, bivalves, gastropods, red algae, and planktonic foraminifera. Der (2012) and Ren and Jones (2016) recognized the following biofacies: (1) rhodolith-coral-benthic foraminifera, (2) platy and domal coral–benthic foraminifera, (3) branching platy and domal coral–benthic foraminifera, (4) branching coral-benthic foraminifera facies, (5) benthic foraminifera-bivalve, (6) *Halimeda*-benthic foraminifera–coral, and (7) planktonic foraminifera facies (Fig. 3). Facies 1 is found only in two coastal wells (RWP-2 and RTR-1), facies 2, 3, and 4 are found in most wells but are most common in the coastal areas, and facies 6 and 7 are present only in GFN-2 and HRQ-2, which are located in the interior of the island (Fig. 3).