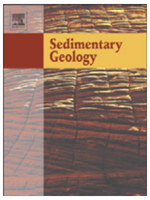
Sedimentary Geology 288 (2013) 66–80

Contents lists available at SciVerse ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo



Microarchitecture of dolomite crystals as revealed by subtle variations in solubility: Implications for dolomitization

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ARTICLE INFO

Article history:
Received 6 January 2013
Received in revised form 29 January 2013
Accepted 31 January 2013
Available online 9 February 2013

Editor: J. Knight

Keywords:
Dolomite
Dolomitization
Diagenesis
Miocene
Cayman Islands

ABSTRACT

Despite their small size, most dolomite crystals in the dolostones of the Miocene Cayman Formation on Grand Cayman are zoned, with a core formed of high-calcium calcian dolomite (HCD) encased by a cortex formed of low-calcium calcian dolomite (LCD). These two different types of dolomite are separated by a sharp, well-defined cortical boundary. Acid etching shows that the HCD cores are characterized by numerous growth defects including twinning, modulations, and dissolution slots whereas the LCD that forms the cortex contains far fewer and less well-developed growth defects. The fact that the HCD is far more soluble than the LCD is attributed to its higher $CaCO_3$ content and greater density of growth defects.

The cortical boundary that separates the HCD core from the LCD cortex is a discontinuity that may have developed as a response to a change in diagenetic regimes or a change in the composition of the dolomitizing fluids. Deciding between these two possibilities, however, is difficult because the small size of the crystals precludes collection of data needed to resolve the issue. Irrespective of the underlying cause, the development of the zoning is critical from a diagenetic perspective because the HCD with its high $CaCO_3$ content and high density of growth defects is far more prone to dissolution than the LCD cortex. Thus, zoned crystals of this type are highly susceptible to diagenetic modifications that will lead to the development of hollow crystals, dedolomite, or inside-out dolomite.

1. Introduction

Models developed to explain the origin of aerially extensive, thick successions of dolostones have typically used geochemical and petrographic data (e.g., Machel and Mountjoy, 1986; Warren, 2000) to identify the Mg source, the mechanism of delivering the Mg to the dolomitization site, and the environmental setting that promotes dolomitization (cf., Morrow, 1982). With a focus on these large scale issues, however, little consideration has been given to the evolution of the constituent dolomite crystals even though subtle mineralogical variations may affect the geochemical and petrographic results (e.g., Searl, 1994) and it is becoming increasingly evident that such crystals commonly evolve through multiple stages of diagenesis (e.g., Jones, 2007; Choquette and Hiatt, 2008; Zhao and Jones, 2012a).

Zoned dolomite crystals defined by systematic variations in trace element concentrations (Katz, 1971), the mol% $CaCO_3$ of the dolomite (Katz, 1968; Jones and Luth, 2003a; Drits et al., 2005), and/or the contrast between a "dirty" core and a clear outer rim (Folk and Siedlecka, 1974) provide the most obvious records of conditions that changed during dolomitization. Variations in the mol% $CaCO_3$, known to be from 48 to 62 mol% $CaCO_3$ in sedimentary dolomites (Jones et al., 2001), are particularly important because the rate of solubility increases as the level of excess Ca increases (Katz, 1968; Navrotsky and Capobianco, 1987; Drits et al., 2005). Relative to stoichiometric dolomite, calcian dolomite is far more energetically unstable (Chai et al., 1995) and therefore prone to more rapid dissolution (Reeder, 2000).

Zoning that is matched by variance in the solubility rates is diagenetically critical because it can lead to the development of hollow dolomite crystals (Folk and Siedlecka, 1974; Weaver and Beck, 1977; Longman and Mench, 1978; Rosen and Holdren, 1986; Randazzo and Cook, 1987; Thériault and Hutcheon, 1987; Jones et al., 1989; Youssef, 1997), leached zones (Jones, 2004), dedolomite (Jones et al., 1989), and inside-out dolomite (Jones, 2007). Similarly, modulated structures, evident in many dolomite crystals, have commonly been attributed to submicron scale variations in mol% $CaCO_3$ concentrations (Reeder and Wenk, 1979; Reeder, 1984, 2000; Van Tendeloo et al., 1985; Wenk and Zhang, 1985; Miser et al., 1987; Schubel et al., 2000).

Controlled acid etching of dolomite crystals exploits the fact that dolomite solubility increases as the mol% $CaCO_3$ increases (cf., Chai et al., 1995; Reeder, 2000). This principle underpins this study, which focuses on the internal architecture of dolomite crystals found in dolostones of the Cayman Formation (Miocene) on Grand Cayman (Figs. 1, 2). Specifically, this study shows that the contrasts between the cores and outer rims of zoned crystals are a reflection of the internal architecture of the dolomites in those zones as well

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http://dx.doi.org/10.1016/j.sedgeo.2013.01.004

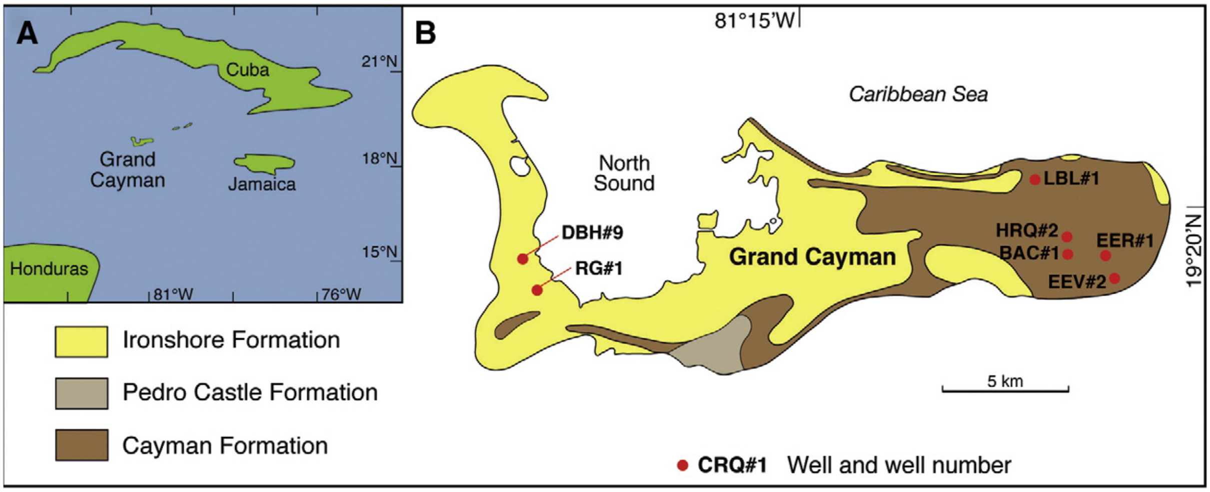

Fig. 1. (A) Location of Grand Cayman in Caribbean Sea. (B) Geology map of Grand Cayman (modified from Jones, 1994, his Fig. 2.3A) showing location of wells used in this study. See Table 1 for location of samples in each well.

as their mol% $CaCO_3$ content. These contrasts in dolomite growth must reflect temporal changes in the dolomitization process that should be taken into account, as models are developed to explain dolomitization.

2. Geological setting

The Cayman Formation (Miocene) on Grand Cayman, which is part of the Bluff Group (Fig. 2), is formed largely of white to off-white, finely crystalline dolostones that contain numerous corals, bivalves, gastropods, red algae, and various other fossils (Jones, 1994, 2005). Fossil-mouldic porosity is high because any skeleton originally formed of aragonite was dissolved. Many cavities in these dolostones contain complex successions of dolomite cement, calcite cement, and various types of internal sediments (Jones, 1992a, 1992b, 2004; Zhao and Jones, 2012b).

3. Methods

Well cuttings (each sample generated over 0.75 m drilling interval) have been collected from numerous wells drilled on Grand Cayman. This study is based on a set of 37 samples that came from seven wells (Fig. 1B). These samples were selected because (1) the dolostones are variable in terms of their mol% $CaCO_3$ contents, (2) each sample has been characterized by XRD and SEM analyses, and (3) they collectively encompass the variability evident in the Ca:Mg ratios of the dolostones from the Cayman Formation. It is important to note, however, that the features documented in this study can be found in virtually any dolostone from this formation.

The mol% $CaCO_3$ (hereafter referred to as %Ca following Lumsden and Chimahusky, 1980; Jones et al., 2001) of each sample was determined by XRD analysis following the procedure of Jones et al. (2001). Such analyses allow calculation of the %Ca in the low-calcium calcian dolomite (LCD: <55%Ca), and the high-calcium calcian dolomite (HCD: >55%Ca), the average %Ca, and the weight percentages of the LCD and HCD.

Backscattered electron (BSE) images were obtained from polished thin sections that had been impregnated with epoxy, cut to a thickness of 50 μm, and coated with carbon. The BSE images were obtained from a Zeiss EOV scanning electron microscope (SEM) operated with an accelerating voltage of 10 to 20 kV. Given that the dolomite crystals from the Cayman Formation contain only trace amounts (collectively<1%) of other elements (Zhao and Jones, 2012b), the zones highlighted on the BSE images reflect variations in the %Ca content of the dolomite (cf., Jones and Luth, 2003a). The samples were mapped with the location of various crystals being carefully noted. The thin section was then etched in HCl (normality = 12.1) for 18 s in order to remove the carbon coating and etch the dolomite crystals. After etching, the thin sections were recoated with carbon and then examined on a JEOL 6301FE SEM under the conditions outlined below.

The internal structures of the dolomite crystals were examined on a JEOL 6301FE SEM that can provide high resolution, high magnification images with an accelerating voltage of 5 kV. Elemental analyses were done using a Dispersive Energy X-ray (EDX) system that is attached to the SEM. Such analyses were done with an accelerating voltage of 20 kV. All samples were mounted on SEM stubs using double-sided tape and/or conductive glue. Many samples were sputter coated with gold before being examined on the SEM. Some problems were encountered with this procedure because the gold commonly migrated, especially if the sample was not examined immediately after coating. With migration, the gold transformed into small beads that became evident on the SEM images once magnifications exceeded 15,000×. This problem was overcome by coating the samples with carbon rather than gold.

The following types of samples were examined on the SEM.

1. Small (3 × 2 cm) thin sections were prepared from dolostone samples that were first vacuum impregnation with epoxy. Once cut to a thickness of ~50 μm, the surfaces of the thin sections were highly polished. Each thin section was then etched in HCl (undiluted) for 12 s (time determined by trial and error), washed in distilled water, and then washed in ethanol before being dried. The latter step was taken so that re-precipitation would not take place as the section dried.
2. Small fracture samples broken from the larger pieces of the well cuttings.
3. Small fracture samples, akin to those used in procedure #2, were etched in HCl (undiluted) for 12 s, washed in distilled water, and then washed in ethanol before being dried.
4. Iterative cycles of acid etching with HCl (undiluted). A small fracture sample (as in #3) was coated with carbon and examined on the SEM. Various parts of the sample were mapped with the exact positions of selected crystals being precisely recorded. The sample was then etched in HCl (undiluted) for 12 s, dried, and re-coated with carbon before being examined on the SEM so that the crystals located in step 1 could be examined once again. For some samples, this process was repeated up to 7 times.