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Distribution and interpretation of rare earth elements and yttrium in Cenozoic dolostones and limestones on Cayman Brac, British West Indies

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ABSTRACT

The Cenozoic carbonate succession on Cayman Brac, a small island (19 km long and 1.5 to 3 km wide) located in the Caribbean Sea, has been dolomitized to varying degrees. The rare earth element (REE) and yttrium (Y) concentrations ($\sum$REE+Y) of 134 carbonate samples (127 from Cayman Brac and 7 supplementary samples from Grand Cayman), vary from 0.2 to 7.5 ppm (average 2.8 ppm, n=134). The shale-normalized REE+Y patterns of the carbonate samples, akin to those of oxygenated seawater, are characterized by: (1) LREE depletion relative to HREE (average Dy_N/Sm_N=1.7, n=125), (2) positive La anomalies, (3) negative Ce anomalies (average Ce/Ce*=0.4, n=133), and (4) superchondritic Y/Ho molar ratios (average Y/Ho=85, n=86). The lack of correlation between the dolomite content of the samples and their $\sum$REE+Y, Dy_N/Sm_N, La_N/Nd_N, Ce/Ce*, or Y/Ho indicates that dolomitization did not have a major impact on REE+Y signatures and that dolomitization was probably mediated by seawater-like fluids.

The shale-normalized patterns (e.g., Dy_N/Sm_N, La_N/Nd_N, Ce/Ce*, and Y/Ho) vary from formation to formation. For samples from the Cayman Formation, the Pedro Castle Formation, and the Ironshore Formation, there are subtle but gradual changes in Dy_N/Sm_N, La_N/Nd_N, Ce/Ce* with depth. In contrast, there are marked changes in La_N/Nd_N, Ce/Ce*, Y/Ho, and Sm/Nd across the Brac Unconformity, which forms the boundary between the Lower Oligocene Brac Formation and the overlying Miocene Cayman Formation. Variations in the REE+Y patterns reflect diagenetic processes (e.g., Dy_N/Sm_N) and possibly secular changes in the REE+Y composition of seawater (e.g., La_N/Nd_N, Y/Ho, and Sm/Nd).

1. Introduction

Many islands throughout the Caribbean Sea and Pacific Ocean are characterized by thick successions of Cenozoic dolostones. Attention has been focused on these "island dolostones" (Budd, 1997) because they are geologically young, have not been buried, and their geological histories are known. In an effort to resolve the long-standing debate on how thick successions of limestones can be pervasively dolomitized (i.e., the "dolomite problem"), these dolostones have been examined from many different perspectives (e.g., Varenkamp and Swart, 1994; Budd, 1997; Warren, 2000; Suzuki et al., 2006). Even so, there is still considerable debate regarding the nature of the dolomitizing fluids, the conditions under which dolomitization took place, and the factors that initiated dolomitization. Much of this debate arises because of uncertainties concerning the interpretation of some of the geochemical proxies, including the stable isotope (O and C) values obtained from the dolostones (cf., Budd, 1997; Zhao and Jones, 2012a,b). Some of these issues might be overcome if other proxies derived from the dolostones could also be used for the interpretation of their origin. In this study, we show that rare earth elements (REE) can provide valuable insights into the origin of island dolostones.

The REE in modern seawater, which include 14 elements (lanthanides) and the pseudo lanthanide yttrium (Y), are well known (German and Elderfield, 1990; Piepgras and Jacobsen, 1992; Bertram and Elderfield, 1993; Sholkovitz et al., 1994; German et al., 1995; Zhang and Nozaki, 1996, 1998; Alibo and Nozaki, 1999; Nozaki and Alibo, 2003). Comparisons of the REE+Y derived from various deposits (including phosphates and carbonates) with the REE+Y of modern seawaters have been used to characterize the composition of ancient seawater (Holser, 1997; Webb and Kamber, 2000; Kamber and Webb, 2001; Shields and Stille, 2001; Miura et al., 2004; Nothdurft et al., 2004; Haley et al., 2005; Bau and Alexander, 2006; Webb et al., 2009; Himmler et al., 2010; Azmy et al., 2011). Such comparisons, however, are commonly problematic because it is not known if the REE+Y patterns derived from the sedimentary rocks are truly representative of the parent seawater. In part, this is because the impact that diagenesis may have had on the REE+Y concentrations in limestones and dolostones is not fully understood.

In this study, attention is focused on the REE+Y distribution throughout the Oligocene to Pleistocene carbonate succession found on Cayman Brac, which is formed largely of dolostones (Fig. 1A). Dolostones in the Brac Formation (Lower Oligocene), the Cayman

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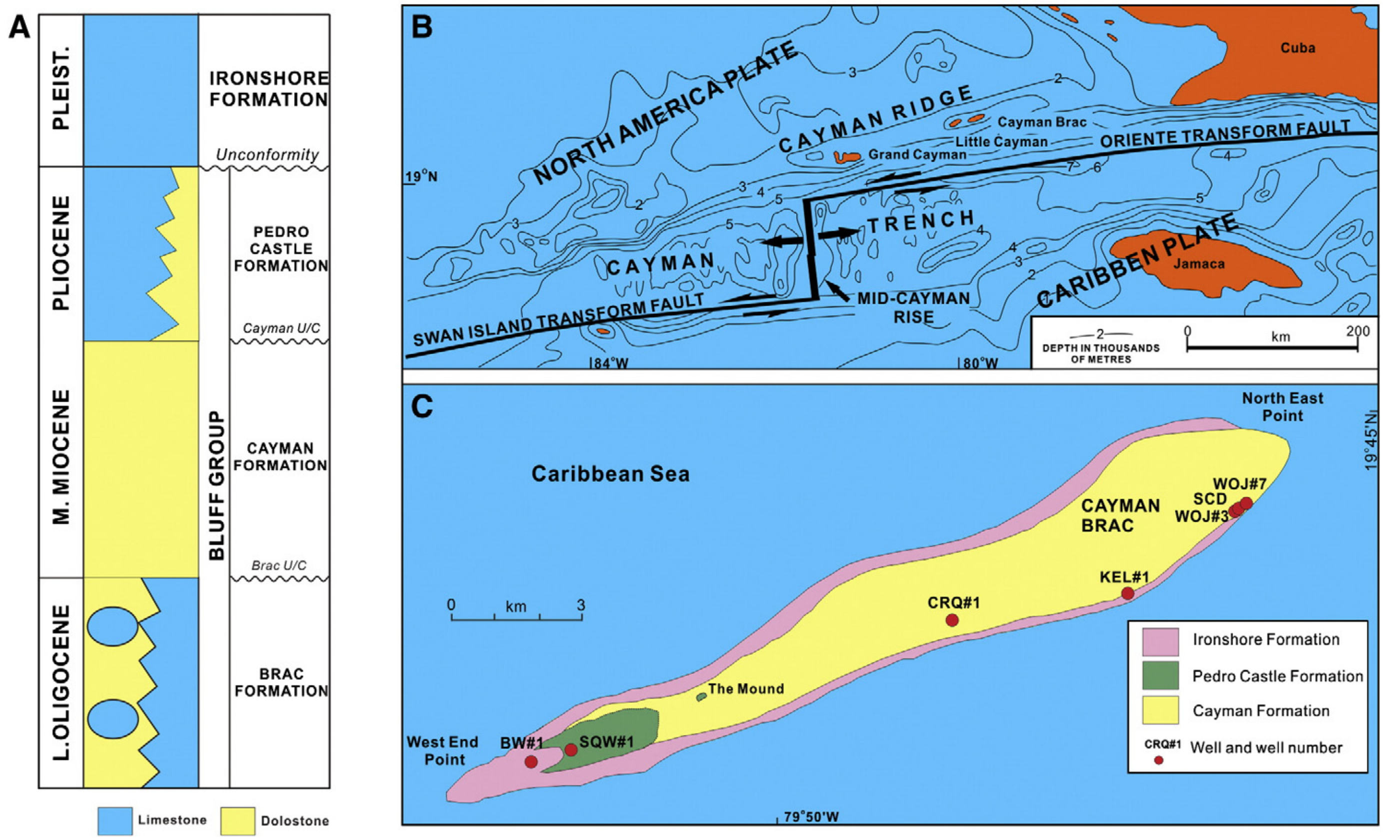

Fig. 1. Location and geology of Cayman Brac. (A) Stratigraphic succession on Cayman Brac (modified from Jones, 1994) showing distribution of dolostones and limestones. (B) Tectonic and bathymetric settings of the Cayman Islands. Modified from Jones (1994) and based on maps from Perfit and Heezen (1978) and MacDonald and Holcombe (1978). (C) Geological map of Cayman Brac (modified from Jones, 1994) showing locations of BW#1, SQW#1, CRQ#1, KEL#1, WOJ#3, SCD, WOJ#7.

Formation (Miocene), and Pedro Castle Formation (Pliocene) have been well characterized in terms of their stratigraphic setting, petrography, stoichiometry, geochemistry, and isotopic signatures (Jones and Hunter, 1994a; MacNeil and Jones, 2003; Jones, 2004, 2005; Zhao and Jones, 2012a,b). Although dolomitization of the Tertiary succession on Cayman Brac has been attributed to slightly modified seawater (Zhao and Jones, 2012a,b), the exact nature of the dolomitizing fluid and the dolomitizing environment remains open to debate. Critically, this study demonstrates that the REE + Y distributions in the limestones and dolostones of Cayman Brac reveal information that brings further focus to the dolomitization processes that transformed much of the limestone to dolostone. Although based on the dolostones of Cayman Brac, the conclusions reached in this study carry important implications for dolostones of all ages.

2. Geological setting

Cayman Brac (19 km long, 1.5 to 3 km wide) is located on the Cayman Ridge, which lies on the north side of the Oriente Transform Fault that separates the North America Plate from the Caribbean Plate (Fig. 1B). Each of the Cayman Islands is an uplifted fault block that rises 2000–2500 m from the seafloor (Perfit and Heezen, 1978; Stoddart, 1980). This area has been tectonically active since the Late Eocene (Rosencrantz and Sclater, 1986; Leroy et al., 2000; DeMets and Wiggins-Grandison, 2007). Today, the Mid-Cayman spreading centre, located southwest of Grand Cayman (Fig. 1B) continues to open at an average rate of 11–12 mm $year^{-1}$ (Rosencrantz and Sclater, 1986; Mann et al., 2002).

The carbonate succession on Cayman Brac (Fig. 1B) is at least 150 m thick (Jones, 1994). Matley (1926) originally assigned the Tertiary carbonates, which are well exposed in the cliffs around the island, to the Bluff Limestone (Fig. 1A). Subsequently, Jones et al. (1994a,b) renamed this succession the Bluff Group, which includes the unconformity bounded Brac Formation, Cayman Formation, and Pedro Castle Formation. The Bluff Group, which forms the uplifted core of the island, is surrounded by a low-lying platform that is formed of Pleistocene limestones that belong to the Ironshore Formation (Fig. 1C).

3. Stratigraphic succession

3.1. The Brac Formation

The Lower Oligocene Brac Formation is exposed in the vertical to overhanging cliffs (up to 45 m high) at the east end of Cayman Brac and was also penetrated by wells CRQ#1 and KEL#1 (Fig. 2). The base of the formation is unknown because it is not exposed and has not been found in any of the wells. It is separated from the overlying Cayman Formation by the Brac Unconformity, which ranges from ~30 m above sea level on the east end of the island to ~47 m below sea level in CRQ #1 (Fig. 2). This range in elevation reflects the karst topography that developed on the unconformity and tectonic tilting of the island to the west.

The Brac Formation is lithologically variable. On the north coast, it is formed of limestone that contains numerous large benthic foraminifera with fewer numbers of other foraminifera, red algae, and echinoid plates (Jones, 1994; Zhao and Jones, 2012a). Jones and Hunter (1994a) suggested that these limestones were probably deposited on a shallow (less than 10 m deep), low energy bank. On the south coast, the Brac Formation is characterized by isolated limestone pods (up to 10 m long and 2 m thick) that are surrounded by coarsely crystalline,