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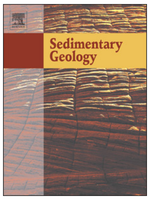

Petrographic and geochemical features of sinkhole-filling deposits associated with an erosional unconformity on Grand Cayman

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ABSTRACT

On Grand Cayman, exposures of dolostones belonging to the Cayman Formation (Miocene) represent an erosional unconformity that has been developing since the late Pliocene (~3.6 Ma). Sinkholes that developed during this time have remained open or become partly to fully filled with various combinations of rootcrete, breccias, loose limestone and dolostone lithoclasts, and white, red and orange limestones. These sinkhole-filling deposits have different geochemical attributes to the Neogene and Pleistocene marine carbonates that form the bedrock of the island. The deposits in the sinkholes formed in response to the variations of sea level, climate, exposure, and vegetation that developed during the period when the erosional unconformity was developing.

The rootcrete, oncoids, red and orange limestones are terrestrial in origin, whereas the limestone and dolostone lithoclasts and white limestones are derived from marine deposits. On the erosional unconformity, intense root activity led to the formation of rootcrete and terrestrial oncoids but also selectively blackening reworked marine carbonates. The red and orange limestone matrices, which formed under more arid conditions, contrast with the other sinkhole-filling deposits that formed during periods when the climate was semi-arid to humid. The distinctive REE signatures of the sinkhole-filling deposits, which are different from those of the bedrock limestones and dolostones, can probably be attributed to trace amount of terra rossa and/or airborne Saharan-derived dust that are present in those deposits.

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1. Introduction

Erosional unconformities in carbonate successions typically represent long periods of subaerial erosion that are accompanied by loss of the rock record, vadose diagenetic and/or pedogenetic alteration, and the formation of surface and subsurface karst (Esteban and Klappa, 1983; James and Choquette, 1990; Tucker, 1990; Clari et al., 1995; Hillgärtner, 1998; Sattler et al., 2005; Alonso-Zarza and Wright, 2010). Assessing the loss of strata is difficult because there is generally no physical record left. In some cases, however, this problem can be partly addressed by examining the lithoclasts and associated sediments that are found in sinkholes and caves that formed during the period of exposure. Studies like those by Daugherty et al. (1987), Smart et al. (1988), Jones (1992b), and C.R. Miller et al. (2012), however, are scarce because there are few examples where sinkholes have been filled by carbonate rather than fluvial siliciclastic sediments (Ford, 1988).

Grand Cayman is a carbonate island that is devoid of surface fluvial systems and lack siliciclastic sediments. On the eastern half of Grand Cayman, dolostones of the Cayman Formation (Miocene) have been exposed since the late Pliocene (~3.6 Ma), when the overlying Pedro Castle Formation was lost to subaerial erosion (Wignall, 1995; Zhao and Jones, 2013; Liang and Jones, 2014). The exposed upper surface of the Cayman Formation, which is an unconformity surface that is still developing, is characterized by numerous sinkholes. Some of these sinkholes, which are up to 30 m in diameter and 10 m deep, remain open whereas others are filled with a variety of deposits that include laminar rootcrete, breccias, loose limestone and dolostone lithoclasts, and white, red and orange limestones. Information derived from these deposits provides some insights into the processes that have been operative over the last 3.6 Ma while this unconformity has developed. Some of these sinkhole-filling deposits have been described in terms of their spatial development and petrography (Jones and Smith, 1988; Jones, 1991, 1992a, 1992b; Alonso-Zarza and Jones, 2007). This study builds on that work by assessing the deposits through the integration of stable isotope analyses, trace element analyses, and examining the distribution of the Rare Earth Elements (REE). Using all of this information, this paper (1) compares the petrographic and geochemical features of the different types of sinkhole-filling deposits, (2) compares the geochemical signatures of the sinkhole-filling deposits with the limestones and dolostones of the bedrock found on the island, and (3) determines the provenance and sequential development of the sinkhole-filling deposits. In particular, it examines the possibility that carbonates that formed in marine or non-marine environments may be characterized by different REE signatures.

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2. Terminology

Calcrete that is associated with roots has been referred as laminar calcrete (Wright et al., 1988; Alonso-Zarza, 1999), rhizogenic calcrete (Wright et al., 1995), calcified root mat (Wright et al., 1988), and rootcrete (Jones, 1992a, 1992c). Wright et al. (1995, p. 144) originally defined rhizogenic calcrete as "… calcretes which are composed largely or wholly of textures which are interpretable as due to the calcification on, in or around roots". In their definition, rhizogenic calcrete includes vertical and horizontal root mats (Wright et al., 1995, 1997). The term rootcrete was used to describe calcrete crusts that covered the surfaces of cavities that had been created by the activities associated with plant roots (Jones, 1992a).

The term "terra rossa", first used in soil science by Kubiëna (1953), has been applied to (1) red, shallow, undifferentiated soils that are associated with carbonate or calcareous material, (2) red material which is transitional between weathered carbonate and new soils, and (3) any red soil in the Mediterranean region (Stephens, 1953; Stace, 1956). In geological situations, "terra rossa" has generally been applied to any reddish, clay-rich soils that lie on limestones or dolostones (e.g., Torrent, 1995; Durn et al., 1999, 2001, 2013; Durn, 2003; Muhs and Budahn, 2009; Muhs et al., 2010), whereas reddish, Al-rich soils are generally referred to as bauxite (e.g., Ahmad and Jones, 1969; Muhs and Budahn, 2009). The chief minerals found in terra rossa are variable, but commonly include clay minerals, such as illite, kaolinites, chlorite, and various combinations of quartz, feldspar, and mica (e.g., Macleod, 1980; Garcia-Gonzalez and Recio, 1988; Moresi and Mongelli, 1988; Boero et al., 1992; Bronger and Bruhn-Lobin, 1997; Durn et al., 1999; Muhs and Budahn, 2009). Calcite and dolomite are present in some of these deposits.

Terrestrial oncoids are laminated coated grains, up to 85 mm in diameter, that develop through microbially-mediated processes in a vadose setting (Wright, 1989; Jones, 1991, 2011). The term "micrite", in this study, is applied to carbonate crystals that are less than 4 μm long (Folk, 1974; Reid and MacIntyre, 1998).

3. Geological setting

The Cayman Islands, comprising Grand Cayman, Cayman Brac and Little Cayman, are isolated oceanic islands located on the Cayman Ridge in the Caribbean Sea (Fig. 1). To the south of these islands lies the Oriente Transform Fault that defines the boundary between the North American Plate and the Caribbean Plate. Grand Cayman is located to the northeast of the Mid-Cayman rise, which is an active spreading center (DeMets and Wiggins-Grandison, 2007). Although located in a tectonically active area, Grand Cayman seems to have remained tectonically stable since the Miocene (Zhao and Jones, 2012, 2013; Liang and Jones, 2014).

The Tertiary carbonate succession on the Cayman Islands was originally assigned to the Bluff Limestone (Matley, 1926), which was subsequently renamed as the Bluff Group by Jones et al. (1994a, 1994b). The Bluff Group is composed of the unconformity-bounded Brac Formation (Lower Oligocene), Cayman Formation (Middle Miocene), and Pedro Castle Formation (Pliocene) (Fig. 2). The Ironshore Formation (Pleistocene) unconformable overlies the Bluff Group (Fig. 2). The Pedro Castle Formation, which used to cover all of Grand Cayman, has been largely removed from the eastern part of Grand Cayman by subaerial erosion over the last 3–4 million years. As a result, the Cayman Formation is widely exposed over much of the eastern half of Grand Cayman (Fig. 1). Dolomitization of the Bluff Group took place during the late Miocene and early Pliocene (Jones and Luth, 2003; MacNeil and Jones, 2003; Zhao and Jones, 2012, 2013).

The Cayman Formation is formed largely of finely crystalline, fabric retentive dolostones that contain numerous fossils, including corals, bivalves, gastropods, red algae, foraminifera, *Halimeda*, and rhodoliths (Jones, 1994; Jones and Hunter, 1994; Wignall, 1995; Der, 2012). The overlying Pedro Castle Formation is formed of limestones and finely crystalline, fabric-retentive dolostones with free-living corals, foraminifera, red algae, and rhodoliths, along with rare colonial corals, echinoids, and bivalves (Jones, 1994; Jones and Hunter, 1994; Wignall, 1995; Arts, 2000; MacNeil, 2001). The Ironshore Formation is formed of friable limestones that contain numerous, well-preserved corals, bivalves, and gastropods (Jones, 1994; Vézina, 1997; Vézina et al., 1999; Coyne, 2003; Li and Jones, 2013).

4. Methodology

Sinkholes are common features of the phytokarst that characterizes much of the eastern part of Grand Cayman and the uplifted core of Cayman Brac (Fig. 3A, B). For this study, attention was focused largely on the southeast corner of Grand Cayman, because that area (1) has numerous open and filled sinkholes (Fig. 3C), (2) has been largely cleared of vegetation, (3) includes a small quarry that provides some vertical sections through the sinkholes (Fig. 3D), and (4) is easily accessible. Similar outcrops at other localities yielded a wide variety of different sinkhole-filling sediments (Fig. 3E–H). During study of the sinkholes and sinkhole-filling deposits in the field, 59 hand samples were collected for detailed study. This included five rootcrete samples that were collected from SQW on Cayman Brac (Fig. 1C). Thirty-three large (7.5 × 5 cm) thin sections were made from samples that were first impregnated with blue epoxy.

Small fracture samples (13 samples) for scanning electron microscope (SEM) analysis were carefully extracted from various samples and mounted on SEM stubs using double-sided tape and/or silver conductive glue and sputter coated with a very thin layer of gold or chrome. SEM analyses were done on a JOEL Field Emission SEM (JOEL 6301F) with an accelerating voltage of 5 kV being used for imaging. The elemental composition of selected spots was determined by Energy-dispersive X-ray (EDX) analysis (Priceton Gamma-Tech X-RAY) with an accelerating voltage of 20 kV.

Powdered samples (75–150 μm) of the different components in the samples, obtained by drilling with a 2 mm diameter drill tip, were used for X-ray diffraction (XRD) analysis and geochemical analyses. Eighty-five samples were analyzed on a Rigaku Ultima IV Powder XRD system that was run at 38 kV and 38 mA using an Ultima IV X-ray generator with a Co tube. All scans were run from 5° to 90° 2θ at a speed of 2° θ/min. Using the same samples, oxygen and carbon stable isotopes were determined for 80 calcite and 21 dolomite samples. Following the method of McCrea (1950), the calcite samples were reacted with 100% phosphoric acid at 25 °C for 1–2 h, whereas the dolomite samples were reacted with 100% phosphoric acid for 2–3 days at 25 °C at the University of Alberta's Stable Isotope Laboratory. The extracted CO_2 gas was introduced into a Finnigan-MAT 252 isotope mass spectrometer for analysis of the $\delta^{13}C$ and $\delta^{18}O$, which are reported relative to the Pee Dee Belemnite (PDB) standard normalized to NBS-18 in the per mil (‰). Analytical reproducibility was 0.05‰ for $\delta^{13}C$ and $\delta^{18}O$. The oxygen isotope values of the dolostones were corrected for the phosphoric acid fractionation.

Powdered samples weighing more than 0.2 g (81 samples) were analyzed for their trace elements contents (such as Mn, Fe, Al and REE) in the Radiogenic Isotope Laboratory at the University of Alberta. Those samples were first digested in 10 ml 8 N HNO_3. Then, 1 ml of the solution was diluted with 8.8 ml deionized water and 0.1 ml HNO_3 and 0.1 ml of an internal standard (Bi, Sc, and In). A Perkin Elmer Elan 6000 quadrupole inductively coupled plasma mass spectrometer (ICP-MS) was used to analyze the trace elements and REE in the diluted solution. The detection limits for the trace elements are from 0.01 ppm for Th to 5 ppm for P. The REE + Y distribution patterns and La/Yb-Sm/Yb parameters in these samples are illustrated by normalizing each REE + Y concentration against Post-Archean Average Shale (PAAS) (McLennan, 1989).

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