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Global perturbation of the marine Ca isotopic composition in the aftermath of the Marinoan global glaciation

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ABSTRACT

Ca isotopic compositions of Marinoan post-glacial carbonate successions in Brazil and NW Canada were measured. Both basal dolostones display $\delta^{44/40}$Ca values between 1 and 0.7‰, overlying limestones show a negative Ca isotope excursion to values around 0.1‰, and $\delta^{44/40}$Ca values rapidly increase up-section to near 2.0‰. In the Brazilian successions, those high $\delta^{44/40}$Ca values rapidly decrease and stabilize to values between 0.6 and 0.9‰. These Ca isotope secular variation trends are unlike those of Sturtian post-glacial carbonate successions, but similar to those of Marinoan post-glacial carbonate successions in Namibia, suggesting that the perturbation of the marine Ca cycle was global. This recommends Ca isotope stratigraphy as a tool to correlate Neoproterozoic post-glacial carbonate successions worldwide.

While the lowermost and uppermost strata have $\delta^{44/40}$Ca values typical of Phanerozoic carbonates, the extremes, 0.1 and 2.0‰, have not been thus far reported for other marine carbonates. These extreme values suggest a short-lived, non-actualistic perturbation in the marine Ca cycle.

Simple box modelling of the Marinoan post-glacial marine Ca cycle can reproduce the extreme values only by postulating a two-step process, with Ca input initially exceeding Ca removal trough carbonate precipitation, followed by precipitation overtaking a decreased Ca input.

1. Introduction

Three different glacial events have been identified in the Neoproterozoic (the *ca.* 0.72 Ga Sturtian, Macdonald et al, 2010; the *ca.* 0.64 Ga Marinoan and the *ca.* 0.58 Ga Gaskiers glaciations; for a recent review see Halverson et al., 2005, 2007). Widespread occurrence of "cap carbonate" successions overlying glaciogenic deposits has been taken as evidence of global glaciation (Hoffman et al., 1998), followed by a rapid change "from icehouse to greenhouse" conditions (Kirschvink, 1992; Hoffman et al., 1998). The post-glacial carbonate successions display sedimentological characteristics and C isotope signatures that have been used to correlate them worldwide (Hoffman and Schrag, 2002; Halverson et al., 2005).

One possible mechanism leading to rapid deglaciation could have been the build-up of volcanically derived atmospheric pCO_2 during glaciation (Kirschvink, 1992; Hoffman et al., 1998). By enhancing continental weathering, the high pCO_2 probably also significantly increased the continental Ca input to the post-glacial oceans, affecting their Ca isotope composition (Kasemann et al., 2005).

Although the mechanisms leading to the precipitation of post-glacial carbonates are contentious (Kennedy et al., 2001; Hoffman and Schrag, 2002; Higgins and Schrag, 2003; Grotzinger and Knoll, 1995; Shields, 2005), investigations of the geochemical response of the post-glacial oceans to the elevated atmospheric pCO_2 levels have focused on cap carbonate successions (Higgins and Schrag, 2003; Kasemann et al., 2005). Here we investigate stratigraphic variations in the Ca isotope composition of two well-preserved carbonate successions overlying Marinoan glacial deposits in Brazil (Mirassol d'Oeste and Guia Formations) and NW Canada (Ravensthroat and Hayhook Formations) as archives of the Ca isotope composition of the post-glacial Neoproterozoic oceans. The Ca isotope-stratigraphic pathways displayed by the studied carbonate successions are similar to those displayed by coeval carbonates in NW Namibia (Keilberg and Maieberg formations; Kasemann et al., 2005). Such similarity suggests a global perturbation of the ocean Ca isotope budget after deglaciation resulting from imbalances in the oceanic Ca input and output. We explore different deglacia-

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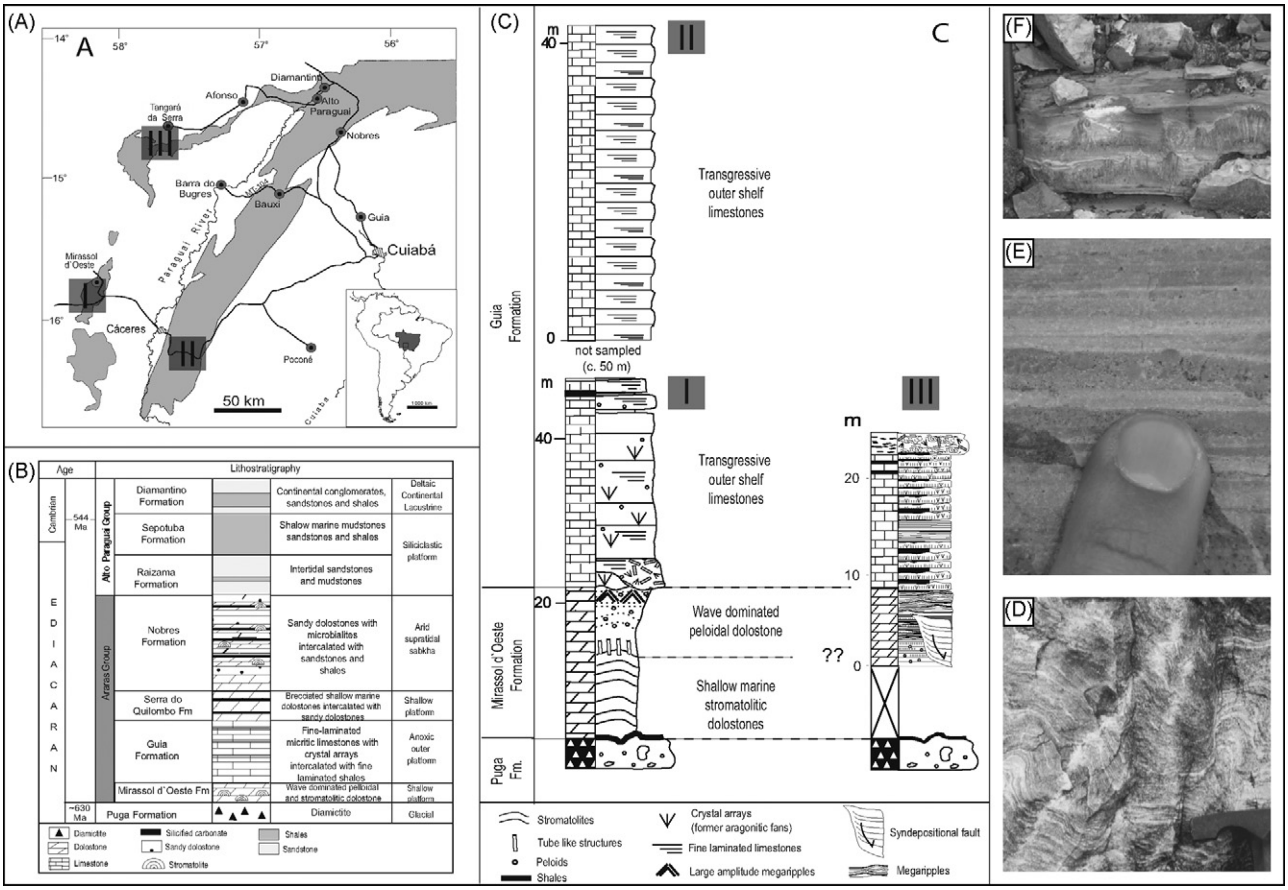

Fig. 1. (A) Schematic map of the Brazilian study area showing the location of the studied stratigraphic sections (modified from Nogueira et al., 2003, 2007). (I) Mirassol d'Oeste locality, (II) Cáceres locality, (III) Tangará da Serra locality. (B) General stratigraphy of the Araras Group and associated units, after Nogueira et al. (2003). (C) Detailed lithostratigraphy of the Mirassol d'Oeste (MOF) and Guia (GF) formations at the studied stratigraphic sections. (D) Basal stromatolitic dolostone from the base of the MOF. (E) Peloidal dolostone from the top of the MOF. (F) Finely laminated micritic limestone crosscut by pseudomorphs of aragonitic crystal fans.

tion scenarios to reconcile the observed Ca isotope signals and sedimentologic features displayed by the post-glacial carbonate successions. A global Ca isotope signal displayed by these Marinoan post-glacial carbonate successions allows us to propose the use of Ca isotope stratigraphy as an additional tool to correlate post-glacial Neoproterozoic carbonate successions.

2. Geological setting, stratigraphy and age

The Mirassol d'Oeste (MOF) and Guia (GF) Formations belong to the late Neoproterozoic Araras Group, Mato Grosso, Central-W Brazil (Fig. 1A and B; for a detailed litho- and sequence stratigraphic framework see Nogueira et al., 2003, 2007). The MOF overlies glacial deposits from the Puga Formation (Fig. 1B and C), which in turn, overlies the crystalline Archean-Mesoproterozoic basement of the southeastern Amazon Craton (Almeida, 1964; Alvarenga and Trompette, 1992). The MOF consists of a basal shallow marine stromatolitic dolostone (Fig. 1C and D), which grades to a wave-dominated peloidal dolostone (Fig. 1C and E). Intertidal to subtidal marine limestones from the GF conformably overlie the MOF. The GF consists of finely laminated micritic limestones, often crosscut by low-Mg calcite crystal arrays (Fig. 1F), which have been interpreted as aragonitic crystal fan pseudomorphs (Nogueira et al., 2007).

The Ravensthroat (RTF) and Hayhook (HHF) Formations belong to the Neoproterozoic Windermere Supergroup, NW Canada, for which a detailed sequence stratigraphic framework was proposed by Narbonne and Aitken (1995). Two post-glacial carbonate successions have been reported for the Windermere Supergroup. The older one, the Twitya Formation, conformably overlies glaciogenic deposits from the Rapitian Group and consists of predominantly shallow marine micritic limestones (Fig. 2). The younger one, comprising RTF and HHF, is the focus of the present study. It overlies diamictites from the Icebrook Formation and consists of a basal shallow marine peloidal dolostone (RTF), which laterally changes to meter-kilometer scale dolomitic bioherms (James et al., 2001). This dolostone is overlain by finely laminated micritic limestones of the HHF, which also present crosscutting aragonitic crystal fan pseudomorphs (Fig. 2).

The Brazilian and Canadian sections are from platform settings. In both sections, outer and inner platform were sampled.

The sedimentological features (e.g. basal stromatolites, large amplitude mega-ripples, aragonitic crystal fan pseudomorphs, Fig. 3) and the C and Sr isotopic signatures displayed by the MOF + GF and RTF + HHF post-glacial carbonate successions can be used to correlate them with other well-dated post-glacial carbonate succession overlying Marinoan glacial deposits (Nogueira et al., 2003, 2007; Alvarenga et al., 2004, 2008; James et al., 2001; Hoffman and Schrag, 2002; Halverson et al., 2005). The post-Marinoan age of the Brazilian carbonate successions is supported by the Pb–Pb age of 627 ± 32 Ma age obtained in carbonates from the GF (Babinski et al., 2006) and the 706 Ma detrital zircon U–Pb SHRIMP ages (uncertainties not reported) obtained from the underlying glaciogenic Puga Formation (Babinski et al., 2008). Palinomorph assemblages also support a post-Marinoan age for the Araras Group carbonates (Gaucher et al., 2003).

For the two Windermere Supergroup successions, a Late Neoproterozoic depositional age has been proposed by stratigraphic