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Geochemical constraints on the origin of Marinoan cap dolostones from Nuccaleena Formation, South Australia

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ABSTRACT

The geochemistry (including Sr isotope and trace element ratios) of "Snowball Earth" terminal deglacial cap-dolostone from the Nuccaleena Formation, South Australia, is studied. An incremental leaching approach was applied in order to extract the nearest-to-primary chemical composition. Based on the relationship between $^{87}Sr/^{86}Sr$ and Rb/Sr ratios of the leachates, the samples can be categorized into two groups: 1) Group-I dolostones are located 9 cm below to 1.1 m above, and again 4–6 m above a lithologic contact within Nuccaleena Formation marking the end of diamictite (dominantly siliciclastic sediments) and the onset of solid dolostone deposition ("meters above solid dolostones", MASD). In each of these intervals, $^{87}Sr/^{86}Sr$ and Rb/Sr ratios of leachates mostly define a binary mixing relationship and the leaching-sequence-minimum, Rb-corrected $^{87}Sr/^{86}Sr$ ratio is ~0.7077 on average (±0.0003, 1σ, with a minimum value of 0.7073 among all samples); 2) Group-II dolostones define an interval between 1.7 and 4.0 MASD, in which the leaching-sequence-minimum, Rb-corrected $^{87}Sr/^{86}Sr$ ratio is ~0.7092 on average (±0.0004, 1σ). We interpret these minimum $^{87}Sr/^{86}Sr$ ratios in Group-I dolostones to represent Sr isotope compositions of penecontemporaneous seawater, similar to values previously reported for high-Sr limestones under- and over-lying "Marinoan" cap dolostones around the world and permitting an interpretation of no significant long-term seawater $^{87}Sr/^{86}Sr$ variation during Marinoan deglaciation. In contrast, elevated $^{87}Sr/^{86}Sr$ ratios of Group-II cap dolostones indicate later alteration events or formation of samples in a non-marine environment (e.g., the 'glacial lake Harland', Hoffman, 2011). Negative correlation between $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ values can be explained by fluid–rock interaction, either with brine/saline groundwater, ice melt seeps, or hydrothermal fluids as possible alteration fluids, leading to the elevated $^{87}Sr/^{86}Sr$ ratios. Alternatively, the elevated $^{87}Sr/^{86}Sr$ ratios may record the values of 'glacial lake Harland'.

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1. Introduction

Glacial deposits can be found on major continents in the stratigraphic units of late Cryogenian (~850 Ma–635 Ma). Paleomagnetic studies suggest that they formed when most continents were emplaced within low- to mid-paleolatitudes (Hoffman and Li, 2009; Evans and Raub, 2011), implying global "panglacial" events (Hoffman, 2009) often termed "Snowball Earths" (Kirschvink, 1992). Climatically-anomalous units of dolostones ('cap dolostones') are found overlying these glacial deposits, and they are particularly pronounced atop the so-called "Marinoan" glacial deposit ending ~636 Ma (Condon et al., 2005; Hoffmann et al., 2004).

The discovery of ~2–5‰ $\delta^{13}C$ negative shift in Marinoan cap dolostones provides important constraints on the origin of these rocks (e.g., Grotzinger and Knoll, 1995; Hoffman et al., 1998; Kennedy et al., 2001; Shields, 2005; Hoffman et al., 2007; Rose and Maloof, 2010). However, other geochemical proxies, including oxygen (O) and strontium (Sr) isotopes and elemental ratios, have been interpreted to reflect diagenesis, weathering, and/or metamorphism (Jacobsen and Kaufman, 1999; Halverson et al., 2007), or to record depositions in a near-shore environment where high flux of alkalinity was introduced by continental glacial melt (Peng et al., 2011; Romero et al., 2012), rather than to document seawater values. The reported Sr isotope compositions are characterized by relatively more radiogenic values and the lack of systematic variations. For example, the $^{87}Sr/^{86}Sr$ ratios of Marinoan cap dolostones from Canada (0.71065–0.71822, James et al., 2001), Namibia (0.70876–0.71815, Halverson et al., 2007), Brazil (0.70744–0.71129, Nogueira et al., 2003), South China (0.70986–0.71308, Sawaki et al., 2010; Peng et al., 2011), North China (0.71195–0.71364, Xiao et al., 2004), and Central Australia (0.71148–0.71580, Kennedy, 1996) are highly variable, and mostly higher than overlying limestones (e.g., 0.70717–0.71280 in Namibia, Halverson et al., 2007).

The high-Sr (Sr-enriched) Neoproterozoic limestones have been interpreted to record seawater $^{87}Sr/^{86}Sr$ ratios, since they are interpreted to be little affected by later alterations (Halverson et al., 2007). However, $^{87}Sr/^{86}Sr$ ratios are usually considered as alteration signatures in low-Sr

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limestones and dolostones, including cap dolostones (Halverson et al., 2007). As a result, a reliable seawater $^{87}Sr/^{86}Sr$ record is missing precisely during the interval of Marinoan deglaciation cap-dolostones which could document the most extreme climate change (e.g., Hoffman et al., 1998; Hoffman and Schrag, 2002).

In this study, we investigate Sr isotopes and metal concentrations of the parastratotype section of Nuccaleena Fm, at Elatina Creek, South Australia. The onset of cap dolostone deposition at this site is continuous in mixed transition with preceding siliciclastic deglacial sedimentation (Raub et al., 2007), and the Nuccaleena Formation cap dolostone is as completely- and freshly-exposed as dolostones occurring elsewhere in the Adelaide Rift Complex (McKirdy et al., 2001; Raub et al., 2007; Rose and Maloof, 2010). An initial $\delta^{13}C$ value lager than ~−1‰ in this area suggests that cap carbonate deposition may have begun marginally earlier here than elsewhere in the basin (Kunzmann et al., 2013), if carbon isotopic evolution marks basin-wide shoaling of a chemocline (Hoffman et al., 2007).

An incremental leaching test modified after Bailey et al. (2000) is performed to investigate the effect of the diagenesis on $^{87}Sr/^{86}Sr$ ratios of Nuccaleena dolostones. We show that dolostones from the bottom and top of Nuccaleena Fm are most likely to record seawater $^{87}Sr/^{86}Sr$ values. In contrast, samples in the middle section exhibit elevated $^{87}Sr/^{86}Sr$ values, and is interpreted to reflect either that they were altered via water–rock interaction (e.g., Jacobsen and Kaufman, 1999), or that they formed in a high-$^{87}Sr/^{86}Sr$ primary environment, possibly dominated by glacial meltwater (e.g., Shields, 2005; Hoffman, 2011).

2. Sample and geological setting

Nineteen samples from Elatina Creek in the Adelaide Rift Complex (ARC) of South Australia (Fig. 1) were selected for this study. Based on Raub et al. (2007), our samples include one calcareous sample collected from the sub-cap dolostone Nuccaleena Formation sandstone (dolostone interfingering with red siltstone in a mixed transition interval), seventeen carbonates from "solid" Nuccaleena Fm cap dolostone, and one from overlying Brachina Fm (dolostone interbedded with red siltstone).

The ARC is considered as a part of an extended continental margin east of the Stuart Shelf (Fig. 1A, Williams et al., 2008), composed of a 7–12 km thick Neoproterozoic-through-Cambrian sedimentary package overlying the Palaeoproterozoic and Mesoproterozoic cratonic basement (Preiss, 2000). Positioned in the upper part of the ARC sedimentary succession, the Elatina Fm is composed of basal glacial diamictites which grade up into sandstones with lesser diamictite toward the top (Fig. 1). At Elatina Creek, flaser-bedded sandstone, granule conglomerates and muddy siltstone lie on the top of the diamictites, separated from mappable Elatina Formation by a regional-scale truncation surface. Above this unconformity, Nuccaleena Formation siliciclastics exhibit upward increasing calcareous fraction, culminating in a conformable mixed transition into the Nuccaleena Formation cap dolostone (Raub et al., 2007).

Nuccaleena cap carbonate is composed mainly of buff-pinkish allodapic, peloidal dolomicrite of commonly coarse-sand grain size although in thin-section all carbonate phases look to have been recrystallized (Lamb et al., 2012). From the basal part, medium-grained (0.2–0.5 mm), mm-scale laminae construct centimeter-scale swaley, low-angle cross-strata (Rose and Maloof, 2010) and coarsen upward into beds hosting meter-scale pseudo-tepees interpreted as giant wave ripples (Allen and Hoffman, 2005) or early-cemented inherited-topography bedforms in ordinary wave climates moving very coarse dolomite sand grains (Lamb et al., 2012). In the upper half of the megarippled interval, impersistent mm-scale siltstone laminations appear at cm- to dm-scale intervals, and atop the section, a final megaripple is onlapped by fine-grained red siltstones of Brachina Fm, with an upward-diminishing fraction of depositional dolostone lenses diagenetically modified into concretions.

Terrigenous materials are pervasively present in the Nuccaleena Fm, including detrital hematite and rutile, potassic and magnesian clays, quartz and trace apatite (Raub et al., 2007). The whole sedimentary package, from the base of the flaser-bedded sandstone which defines the top of Elatina Fm to the top of solid cap dolostone in Nuccaleena Fm, is interpreted as a transgressive systems tract (e.g. Preiss, 2000).Overlying the cap dolostone lenses, the Brachina Fm consists of a thick succession (>800 m) of upward-shoaling siltstone and minor sandstone, further supporting a flooding surface somewhere immediately above the highest bed of solid cap dolostone (Christie-Blick et al., 1995).

3. Experimental method

Of 124 samples that have been analyzed for C and O isotopes (Raub, 2008), 19 samples were selected for Sr isotope and trace metal concentration measurements. A step-leaching procedure, modified after Bailey et al. (2000), was applied to these samples, in order to extract the elements of interest exclusively (or mostly) from the carbonates. Samples,

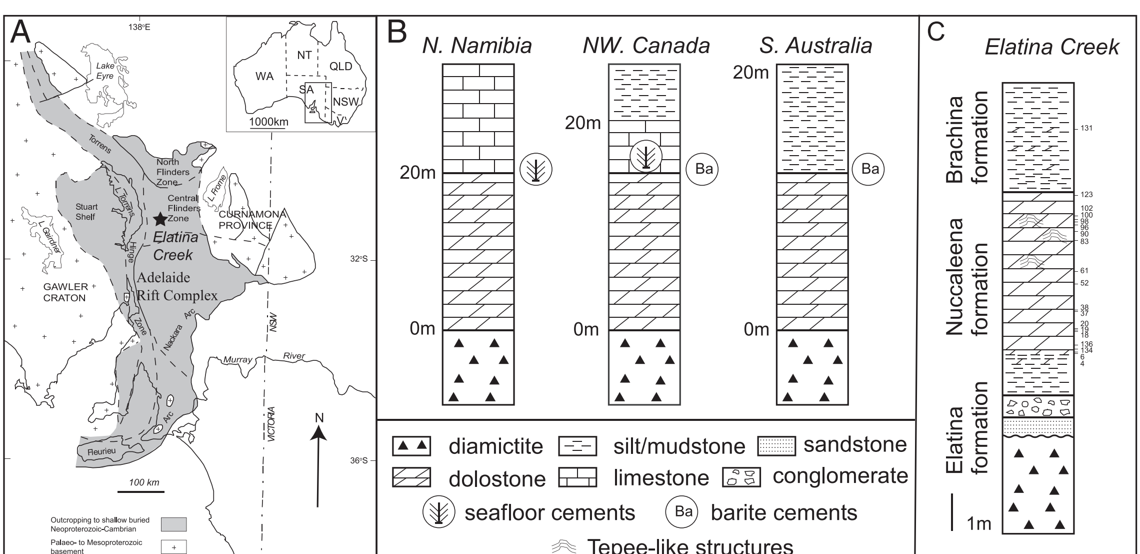

Fig. 1. (A) Tectonic setting of the study area (adapted from Williams et al., 2008). Samples are collected at Elatina Creek, which is within the Central Flinders Zone of Adelaide Rift Complexes; (B) three types of stratigraphic profiles of Marinoan glacial deposits and associated cap carbonates (Hoffman and Schrag, 2002); and (C) stratigraphic profiles of the section in this study (based on Raub et al., 2007). The exact location of each sample is also plotted.