

Neoproterozoic ice ages, boron isotopes and ocean acidification: Implications for a “snowball Earth”

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Material and Methods

1. Samples

Samples were obtained from four sections of the Neoproterozoic Otavi Group in NW Namibia (Fig. 1, Tables DR1 and DR2). These sections consist of marine carbonate rocks deposited along the southern margin of the Congo craton prior to Pan-African orogenesis (Miller, 1983) and contain a record of the two glacial-to-greenhouse transitions that occurred <746 (“Sturtian”) and 635 (“Marinoan”) Myr ago (Hoffman et al., 1996; Hoffmann et al., 2004). The older Sturtian aged glaciogenic Chuos Formation is overlain by the Rasthof Formation cap carbonate, a dark to medium grey micritic dolostone and limestone rhythmite (Hoffmann et al., 1996). The Ombaatjie Formation comprises micritic limestones and dolostones. The carbonate sequence which post-dates the 635 Ma glaciogenic Ghaub Formation (Hoffmann et al., 2004) starts with the post-glacial Keilberg cap carbonate, a micritic dolostone consisting of a variably developed basal laminated unit typically overlain by an interval containing sheet-cracks, soft-sediment deformation features and/or stromatolites, and then a thin-bedded dolostone. This passes transitionally upward into rhythmite limestone and thin-bedded dolostone-limestone of the Maieberg Formation and the overlying dolomitic grainstones of the Elandshoek Formation (Hoffman et al., 1996). The targeted sections include three that record deposition on a shallow-marine platform (“Entrance”, “Ombaatjie” and “Khowarib” localities) and one (“Fransfontein” locality) that records a deeper-marine slope setting. This permits establishing and assessing the pattern and character of these isotopic trends for coeval

but paleogeographically and paleoenvironmentally distinct settings. The chosen sample localities have not experienced metamorphism, the rocks are only moderately deformed in broad, open folds, and they preserve exquisitely detailed evidence for original sedimentary textures and structures. The Entrance and Fransfontein sections start in the basal Rasthof Formation, the cap carbonate sequence of the older-Cryogenian (Sturtian) Chuos glaciation, and continue through much of the Keilberg-Maeiberg cap sequence of the younger Cryogenian (Marinoan) Ghaub glaciation. The Ombaatjie and Khowarib sections span the upper part of the Ombaatjie Formation, which includes the Trezona anomaly presaging the Ghaub (Marinoan) glaciation (Halverson et al., 2002), through various levels of the Keilberg-Maeiberg cap sequence. Thus, each section captures the meltback phase through to climatic normalcy of both of the glacial epochs. Samples were taken in dcm- to dkm-scale spacing from micritic limestones and dolostones, covering about 45 m of the basal Rasthof and 80 m of the Ombaatjie Formation. Samples were taken in cm- to dcm-scale spacing from the post-glacial Keilberg cap carbonate (*sensu stricto*) and the fine-grained limestones and dolomitic grainstones of the Maeiberg and Elandshoek Formations; sampling spanned as much as 300 m of stratigraphic thickness. Samples selected for isotope analyses were screened macroscopic (in the field) and microscopic (scanning electron microscope) and selected because of their uniformity in texture (micrites); they contain no evidence of secondary alteration or recrystallisation (i.e. no veining, or spar/microspar components even as viewed by SEM) and all display well-preserved original and finely detailed sedimentary lamination and features. In addition, CL (cathodoluminescence) examination showed no significant intrasample variations. Secondary ionisation mass spectrometry (SIMS) revealed similar trace element pattern as initially described by Kasemann et al. (2005). The boron concentration for both the Chuos and the Ghaub postglacial carbonate profiles is on average $1 \mu\text{g g}^{-1}$ and ranges independent on the Mg/Ca ratio between 0.5 and $2.5 \mu\text{g g}^{-1}$. The B concentration for

carbonate samples with optical (SEM) evidence of recrystallisation is $< 0.1 \mu\text{g g}^{-1}$. The Mn concentration for the younger preglacial carbonates of the Keilberg and Maieberg Formation is typically $< 250 \mu\text{g g}^{-1}$, with only some samples (OBTJ 58, KW1 64, 67, FF1 28, 29, 30) showing $\sim 400 \mu\text{g g}^{-1}$. The Sr concentration in these samples generally clusters around $80 \mu\text{g g}^{-1}$ with three samples (KW1 77, OBTJ 65, 67) showing values between 500 and $900 \mu\text{g g}^{-1}$ but no indication of Sr contamination. The measured Mn/Sr ratio for the younger postglacial carbonates is < 2.7 suggesting no influence of meteoric fluid. Trace element and SEM analyses in the older postglacial carbonate rocks from the Rasthof and Ombatjie Formation showed a greater dissemination of detrital feldspar and clay minerals. However, the Mn/Sr ratio in these samples is still < 3 with Mn concentrations typically $< 400 \mu\text{g g}^{-1}$ and Sr concentrations around $200 \mu\text{g g}^{-1}$. High Sr concentrations are regularly coupled with elevated concentrations of elements typically found in feldspars (e.g. high Ba concentration) reflecting the detrital input rather than the carbonate composition. Mn/Sr is generally used as a geochemical criterion for assessing the degree of alteration of ancient carbonates: high Mn/Sr is taken as indicative for meteoric diagenesis (i.e. Jacobsen and Kaufman, 1999). However, high Mn/Sr may also indicate carbonate precipitation from anoxic waters and low Mn/Sr can regularly be found in Neoproterozoic carbonates which show clear optical evidence for recrystallisation. Consequently, the main criteria for samples selected for isotope analyses were uniformity in micritic texture, no optical (SEM) evidence for recrystallisation and a B concentration $\geq 0.5 \mu\text{g g}^{-1}$.

2. Analytical methods

Carbon isotope ratios were determined by a modification of the phosphoric acid method of McCrea (1950) at the Scottish Universities Environmental Research Centre. Analyses were performed on an Analytical Precision automated carbonate analyzer on-line to an AP 2003

triple collector mass spectrometer. Isotope data are reported in the conventional δ per mil (‰) notation relative to V-PDB. Calibration to international reference material was through NBS 19 and the precision and accuracy for pure standards are better than 0.2‰ (2 σ). Boron isotope ratios were determined in the Isotope Laboratories at the University of Bristol using the Finnigan TRITON thermal ionisation mass spectrometer, following the method of Kasemann et al. (2001). B-isotope ratios are given relative to NIST SRM 951 in the conventional $\delta^{11}\text{B}$ (‰) notation. The $n(^{11}\text{B})/n(^{10}\text{B})$ ratio of the reference material for each analytical session was reproduced better than 0.8 ‰ (2 σ standard deviation). The uncertainty on the isotope ratios of the samples is 1‰ (2 σ_{mean}). The total boron blank was 1 ng. For further information on the preparation and analytical method see Kasemann et al. (2005).

3. Constraints on the boron isotope-seawater pH relationship

Atmospheric $p\text{CO}_2$, concentration of dissolved inorganic carbon, and carbonate alkalinity influence seawater pH and these in turn influence the B-isotope composition of marine carbonates (Pearson and Palmer, 2000). The application of B-isotope values in marine carbonates as a proxy for seawater pH is based on the fractionation factor for isotope exchange between boric acid and borate in solution ($\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$), and the primary incorporation of $\text{B}(\text{OH})_4^-$ into marine carbonates (Hemming and Hanson, 1992). To accurately constrain how the B-isotopic composition of borate changes with pH requires a precise knowledge of the fractionation factor for isotope exchange between boric acid and borate in solution ($\alpha_{\text{B4-B3}}$) and the equilibrium constant for the dissociation of boric acid (pK_b). Until recently, most B-isotope-based pH reconstructions applied the theoretical $\delta^{11}\text{B}$ -pH curve of Kakihana et al. (1977) with a calculated $\alpha_{\text{B4-B3}}$ of 0.981 at 25°C. In a recent evaluation of the B-isotope-pH proxy, Pagani et al. (2005) estimated an empirical fractionation factor from inorganic carbonate precipitation experiments (Sanyal et al., 1995) of 0.974 at 22°C, which is

significantly different than the α_{B4-B3} value of Kakihana et al. (1977), but similar to previous theoretical results ($\alpha_{B4-B3} = 0.975$) of Oi (2000). This lower value has since been supported by an experimental study of B-isotope fractionation in seawater that yielded an α_{B4-B3} value of 0.974 at 25°C (Klochko et al., 2006) and recently gained acceptance by researchers interested in using the B-isotope-pH proxy in Holocene biogenic carbonates (e.g. Foster, 2008; Kasemann et al., 2009). In view of these arguments, and considering that pH variations would be smaller given the steeper curve over the studied pH range and, thus, more realistic, we use $\alpha_{B4-B3} = 0.974$.

4. Environmental uncertainties on the boron isotope-seawater pH relationship

Environmental factors that could have influenced the $\delta^{11}\text{B}$ -ocean pH relationship throughout Neoproterozoic carbonate precipitation include temperature, salinity and bathymetry. Based on heuristic estimates of the Neoproterozoic icehouse-to-greenhouse conditions (Pierrehumbert, 2004), initial ocean temperature was likely to be -1.5°C followed by a rapid increase in the surface ocean to 30°C (Higgins and Schrag, 2003) and mean air temperatures of potentially up to 60°C during deglaciation. In general, the dissociation constant of boric acid (pK_B) decreases with increasing temperature, but the effect on pK_B and the resulting $\delta^{11}\text{B}_{\text{Borate}}$ -pH relationship for a temperature range between 0° and 60°C is described to be either indifferent (Kakihana et al., 1977) or minor (Dickson, 1990; Klochko et al., 2006). Using the pK_B data from (Dickson, 1990), a potential temperature dependence on our pH calculation of a given $\delta^{11}\text{B}$ would produce higher pH values at lower temperature and vice versa. Consequently, it could be argued that our calculated pH variations could be either too small or the transient pH decrease could be the result of high greenhouse temperatures. However, the potential temperature effect on the $\delta^{11}\text{B}$ -ocean pH relationship is asymmetrical and strongest at a pH of approximately 8.6. Therefore, cold seawater conditions at the start of

the deglaciation could have potentially decreased the B isotope composition of the basal cap carbonates deposition by up a maximum of $\sim 3\text{‰}$ which in turn would increase the calculated seawater pH by up to 0.3 units. In contrast, integrating a rise in seawater temperature during the greenhouse state would theoretically produce lower ocean pH values and hence more acidic conditions. However, due to the nature of the $\delta^{11}\text{B}$ -ocean pH relationship, the rising temperature does not have a significant effect on our transient ocean acidification calculations. It neither increases the calculated acidity of the ocean any further nor does it generate the transient ocean acidification pattern. Similar to temperature, the pK_B increases with decreasing salinity (Dickson and Millero, 1987). However, even considering a drastic decrease in salinity ($S < 21$) due to meltwater influx (Shields, 2005), salinity-associated isotope variations are negligible.

It is assumed that the depth at which carbonate was dominantly precipitated in Neoproterozoic oceans was restricted to the euphotic zone because of the dominance of phototrophic and microbially mediated precipitation, *i.e.* primarily cyanobacterial communities (Riding, 2000; Ridgwell et al., 2003). However, the potential high saturation state of the deeper seawater might have stimulated benthic carbonate precipitation directly on the seafloor (Higgins et al., 2009) as observed in lower Maieberg Formation seafloor cements. Modern seawater pH-depth profiles from the tropics show that pH values can decrease by up to ~ 0.2 units in the first 300 m (World Ocean Database 2005), thus the B-isotope composition of carbonates precipitated at depth could be offset (*i.e.* be more negative) by up to 2.5‰ compared to surface precipitates. Though, simultaneously colder seawater conditions with depth would counterbalance the isotope offset. Consequently, the uncertainties in the $\delta^{11}\text{B}$ -ocean pH relationship introduced by changes in temperature, salinity or bathymetry are at most $\pm 3\text{‰}$ or 0.3 pH units.

5. Secular boron isotope variation

The average B-isotope composition of the Neoproterozoic carbonates deposited during inferred climatic normalcy is $\sim 4\text{‰}$ and that of the seawater assumed to be in equilibrium with those carbonates $\sim 25\text{‰}$ (see Figures 2, 3). These are lower than the values of modern marine carbonates and seawater of $\sim 22.1\text{‰}$ and $\sim 39.5\text{‰}$, respectively (Hemming and Hanson, 1992). However, recent work on brachiopod calcite (Joachimski et al., 2005) has shown that the B-isotope composition of marine carbonates was considerably lower at times in the geological past, with values as low as 7‰ . This has been attributed mainly to variations in the global boron budget influencing the B-isotope composition of seawater during Earth history (Joachimski et al., 2005). Such secular changes can explain the overall more negative B-isotope composition of the Neoproterozoic carbonates, as well as the scatter in the older Cryogenian glacial-cap, sequence but would not produce the sharp negative Keilberg cap carbonate excursion, especially given the long residence time of boron (14 Ma; Lemarchand et al., 2000) compared to the rapidity of cap carbonate precipitation ($<10^5$ years; Kennedy, 1996).

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TABLE DR1. Boron and carbon isotope data, post-Marinoan Neoproterozoic carbonate sections, Namibia.

| unit | lithology | sample | height (m)* | $\delta^{13}\text{C}_{\text{CC}}$ (‰) | $\delta^{11}\text{B}_{\text{CC}}$ (‰) ⁺ |
|---|--------------------|--------|-------------|---------------------------------------|--|
| FRANSFONTEIN (20° 11' 57.00"S 15° 00' 58.19"E) | | | | | |
| Elandshoek | med-bd dolostone | FF1-46 | 252.2 | 0.69 | -0.5 |
| Fm | " | FF1-41 | 142.2 | 1.34 | 2.0 |
| | thin-bdd dolostone | FF1-40 | 132.2 | 1.37 | -0.2 |
| | " | FF1-39 | 122.2 | 1.39 | 4.7 |
| | " | FF1-37 | 102.2 | 1.61 | 6.7 |
| | " | FF1-36 | 92.2 | 1.57 | 4.5 |
| | " | FF1-34 | 72.2 | 1.52 | 2.0 |
| | " | FF1-32 | 52.2 | 0.58 | -1.0 |
| | " | FF1-31 | 48.2 | -0.34 | -4.3 |
| | " | FF1-30 | 42.7 | -4.19 | -2.5 |
| | " | FF1-29 | 42 | -4.37 | -2.0 |
| | thin-bdd limestone | FF1-28 | 14.7 | -4.13 | -3.6 |
| | dolomicrite | FF1-20 | 4.6 | -3.25 | -3.5 |
| | " | FF1-12 | 2.2 | -2.97 | -2.2 |
| | " | FF1-9 | 1.6 | -2.25 | 1.0 |
| | " | FF1-6 | 1 | -2.60 | -2.6 |
| | " | FF1-5 | 0.8 | -1.74 | -1.2 |
| | " | FF1-4 | 0.6 | -2.17 | -0.5 |
| | " | FF1-3 | 0.4 | -1.82 | 1.2 |
| | " | FF1-2 | 0.2 | -1.56 | 3.0 |
| KHOWARIB (19° 18' 10.64"S 13° 59' 44.19"E) | | | | | |
| Elandshoek | med-bd dolostone | KW1-82 | 300.3 | -1.49 | 6.5 |
| Fm | " | KW1-80 | 264.3 | -2.57 | 4.5 |
| | thin-bdd dolostone | KW1-79 | 260.3 | -4.09 | 6.5 |
| | " | KW1-78 | 245.3 | -3.60 | 5.0 |
| | thin-bdd limestone | KW1-77 | 225.3 | -3.63 | 6.8 |
| | " | KW1-75 | 185.3 | -4.18 | 0.2 |
| | " | KW1-67 | 80.3 | -5.19 | 2.5 |
| | " | KW1-64 | 57.3 | -5.24 | 3.2 |
| | " | KW1-58 | 31.3 | -5.24 | 0.2 |
| | " | KW1-55 | 21.3 | -5.13 | 2.2 |
| | dolomicrite | KW1-45 | 14.8 | -4.19 | 0.5 |
| | " | KW1-37 | 10.8 | -3.25 | -1.2 |
| | " | KW1-32 | 8.3 | -3.03 | -0.1 |
| | " | KW1-29 | 6.8 | -2.77 | 2.7 |
| | " | KW1-24 | 4.3 | -2.98 | 1.5 |
| | " | KW1-21 | 2.7 | -2.90 | 2.0 |
| | " | KW1-18 | 1.4 | -3.07 | 1.7 |
| | " | KW1-18 | 1.4 | -3.10 | 1.5 |
| | " | KW1-15 | 0.8 | not run for C | 3.5 |
| | " | KW1-14 | 0.6 | -2.96 | 2.8 |
| | " | KW1-12 | 0.2 | -3.23 | 3.2 |
| | " | KW1-11 | 0.1 | -3.17 | 6.7 |
| | " | KW1-10 | 0.0 | -3.21 | 9.7 |

OMBAATJIE (19° 15' 23.63"S 13° 59' 54.63"E)

| | | | | | |
|-------------|--------------------|---------|-------|-------|------|
| Elandshoek | med-bd dolostone | OBTJ 74 | 241.0 | -1.94 | -0.5 |
| Maieberg Fm | thin-bdd dolostone | OBTJ 70 | 181.0 | -3.02 | 0.0 |
| | thin-bdd limestone | OBTJ 67 | 126.0 | -4.31 | 0.2 |
| | " | OBTJ 65 | 106.0 | -4.08 | -0.2 |
| | " | OBTJ 58 | 36.0 | -5.78 | -2.4 |
| Keilberg Fm | dolomicrite | OBTJ 55 | 10.5 | -3.87 | -6.0 |
| | " | OBTJ 52 | 5.6 | -3.04 | -6.2 |
| | " | OBTJ 47 | 2.5 | -3.01 | -4.8 |
| | " | OBTJ 46 | 1.6 | -2.56 | -5.5 |
| | " | OBTJ 45 | 1.5 | -2.63 | -3.3 |
| | " | OBTJ 43 | 0.1 | 1.66 | 2.7 |

*heights are meters above base of cap carbonate

⁺uncertainty for B isotope data is $\pm 1\%$ 2σ mean

TABLE DR2. Boron and carbon isotope data, post-Sturtian Neoproterozoic carbonate sections, Namibia.

| unit | lithology | sample | height (m)* | $\delta^{13}\text{C}_{\text{CC}}$ (‰) | $\delta^{11}\text{B}_{\text{CC}}$ (‰) ⁺ |
|---|---------------------|---------|-------------|---------------------------------------|--|
| FRANSFONTEIN (20° 11' 49.90"S 15° 04' 14.07"E) | | | | | |
| Rasthof Fm | microbial dolostone | FF3 15 | 28.0 | 4.46 | 1.6 |
| | " | FF3 12 | 16.0 | 4.27 | 4.8 |
| | " | FF3 9 | 11.5 | 2.16 | 4.6 |
| | lam. dolostone | FF3 6 | 8.0 | 3.83 | 5.6 |
| | " | FF3 3 | 2.6 | 2.81 | 2.2 |
| | " | FF3 2 | 2.5 | 2.99 | 2.0 |
| | " | FF3 G | 2.4 | 2.8 | 6.5 |
| | " | FF3 1 | 2.0 | 1.43 | 5.0 |
| | " | FF3 E | 1.0 | 4.48 | 3.2 |
| | " | FF3 D | 0.5 | 4.25 | 2.5 |
| | " | FF3 C | 0.2 | 4.18 | 6.0 |
| | " | FF3 A | 0.0 | 1.94 | 4.7 |
| ENTRANCE (19° 10' 50.51"S 13° 58' 09.65"E) | | | | | |
| Rasthof Fm | microbial dolostone | ET 29 | 45.0 | 2.99 | 3.8 |
| | " | ET 27 | 35.0 | 3.88 | 8.0 |
| | " | ET 23 | 18.2 | 3.03 | 4.6 |
| | " | ET 22 | 16.2 | 2.61 | 7.1 |
| | lam. limestone | ET 21 | 14.2 | 0.47 | 2.1 |
| | " | ET 14 | 6.2 | -2.38 | 8.0 |
| | " | ET 12 | 4.2 | -1.87 | 7.8 |
| | " | ET 10 | 2.7 | -2.96 | 1.9 |
| | " | ET 9 | 2.2 | -2.49 | 3.8 |
| | " | ET 8 | 1.7 | -3.65 | 6.9 |
| | lam. dolostone | ET 5 | 0.9 | -2.86 | 1.8 |
| OMBAATJIE (19° 15' 18.23"S 13° 59' 59.86"E) | | | | | |
| Ombaatjie Fm | thin-bd dolostone | OBTJ 40 | -2.0 | 3.53 | 2.4 |
| | " | OBTJ 36 | -4.8 | 4.94 | 4.2 |
| | " | OBTJ 34 | -5.0 | 5.51 | 2.7 |
| | thin-bd limestone | OBTJ 30 | -28.0 | 5.41 | -1.8 |
| | thin-bd dolomicrite | OBTJ 29 | -36.0 | 5.92 | 4.4 |
| | thin-bd limestone | OBTJ 27 | -44.0 | 5.99 | 4.4 |
| | " | OBTJ 25 | -54.0 | 5.81 | 1.9 |
| | " | OBTJ 23 | -65.0 | 5.71 | 2.7 |
| | " | OBTJ 21 | -81.0 | 5.87 | 4.9 |

*heights are meters above base of cap carbonate; Ombaatjie samples are given as meters below the base of the Ghaub glacial

+uncertainty for B isotope data is $\pm 1\%$ 2 σ mean