



Continental weathering following a Cryogenian glaciation: Evidence from calcium and magnesium isotopes



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ABSTRACT

A marked ocean acidification event and elevated atmospheric carbon dioxide concentrations following the extreme environmental conditions of the younger Cryogenian glaciation have been inferred from boron isotope measurements. Calcium and magnesium isotope analyses offer additional insights into the processes occurring during this time. Data from Neoproterozoic sections in Namibia indicate that following the end of glaciation the continental weathering flux transitioned from being of mixed carbonate and silicate character to a silicate-dominated one. Combined with the effects of primary dolomite formation in the cap dolostones, this caused the ocean to depart from a state of acidification and return to higher pH after climatic amelioration. Differences in the magnitude of stratigraphic isotopic changes across the continental margin of the southern Congo craton shelf point to local influences modifying and amplifying the global signal, which need to be considered in order to avoid overestimation of the worldwide chemical weathering flux.

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1. Introduction

The response of the Earth system to recent changes in forcing parameters has attracted much attention. The response to and recovery from a hypothesised ultra-greenhouse state following the global glaciations of the Neoproterozoic represent one of the most acute tests of feedbacks within the Earth system to maintain an equable environment. Such events are marked geologically by deposition worldwide of ‘cap carbonate’ (Hoffman and Schrag, 2002), a distinctive rock layer that directly overlies glacial deposits or glaciated surfaces (Hoffman and Schrag, 2002; James et al., 2001; Kennedy, 1996; Kennedy et al. 1998, 2001a, 2001b; Williams, 1979).

Although cap carbonates are recognised as a fingerprint of the icehouse-to-greenhouse transition (Hoffman et al., 1998), no con-

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sensus exists as to their causal mechanism or the atmospheric-oceanic conditions under which they formed. A widely held view is that elevated atmospheric CO₂ would have generated extreme greenhouse conditions, acidified the post-glacial ocean, increased surface temperatures and precipitation and, as a consequence, continental weathering and riverine transport. This in turn led to enhanced rock (silicate) weathering thereby augmenting CO₂ consumption, increasing ocean alkalinity and pH, and, ultimately, lowering temperatures.

Stratigraphic trends in the stable isotope compositions of the cap carbonates are distinctive and largely consistent with the model described above. Carbon isotopes initially display a sharp negative excursion followed by recovery to more positive values. Even though lively debate remains regarding the exact cause of this excursion, many studies have shown the overall isotopic trends to be stratigraphically systematic and of global significance (e.g. Halverson et al., 2005). Further, concomitant negative boron isotope excursions in post-glacial carbonates have been used in a recent approach to address ocean pH fluctuations during the transition from icehouse to greenhouse states (Kasemann et al., 2010).

Having reconstructed ocean pH conditions for the older and younger Cryogenian pan-glacial states and identified a temporary

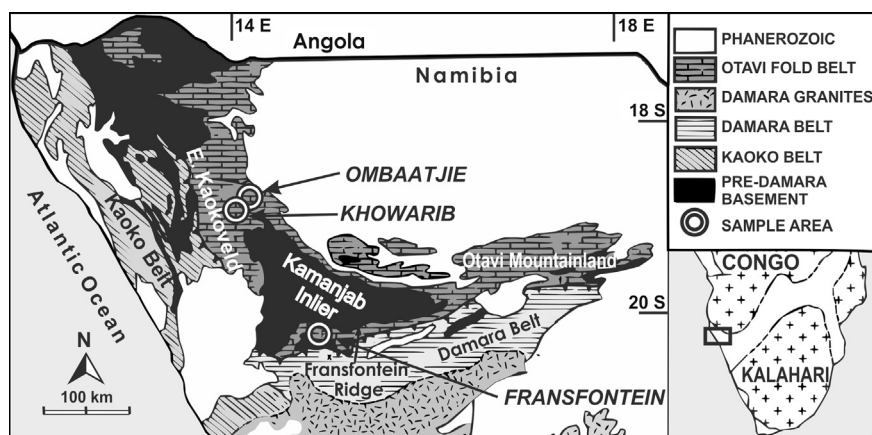


Fig. 1. Generalised geological map of northern Namibia showing location of three Neoproterozoic carbonate sections (modified after Kasemann et al., 2010). See text for discussion.

ocean acidification event for the younger interglacial (Kasemann et al., 2010), this study deals with the next critical step in deciphering Cryogenian environmental conditions: to resolve the discrepancy between having an acidic ocean whilst maintaining relatively high rates of carbonate sedimentation, and how the Earth system recovered from the extreme ocean pH conditions. The combined application of calcium and magnesium isotopes provides unique insight into the evolution of continental weathering, ocean alkalinity, and carbonate sedimentation under these unusual conditions.

1.1. Background

Chemical weathering of continental silicates consumes atmospheric CO_2 , and acts as a climate-moderating process (e.g. Kump et al., 2000). In addition, weathering delivers carbonate and metal ions to the oceans (Bernier et al., 1983, 1990; Kump et al., 2000; Walker et al., 1981) where they are removed via precipitation of calcium carbonate with implications for ocean alkalinity (Archer et al., 2000; Dessert et al., 2003; Gaillardet et al., 1999). Calcium and magnesium are key components in both chemical weathering reactions (e.g. Bernier et al., 1983, 1990; Kump et al., 2000; Walker et al., 1981) and carbonate precipitation. In seawater and carbonates, their isotope ratios can change in response to large flux imbalances, fluctuations in ocean temperature, variations in mineralogy and rates of precipitation (e.g. Blättler et al., 2011; De la Rocha and DePaolo, 2000; Li et al., 2012; Pogge von Strandmann, 2008; Shen et al., 2009; Tang et al., 2008; Tipper et al., 2006a, 2006b; Zhu and Macdougall, 1998). Importantly, calcium and magnesium isotope ratios in ancient carbonates are strongly rock-buffered, hence largely unaffected by diagenesis (Fantle and DePaolo, 2007).

Ca and Mg have long modern oceanic residence times of ca. 1 Myr and 10 Myr, respectively (e.g. Bernier and Bernier, 1996; Holland, 1978). Accordingly, Ca and Mg isotopes preserved in Neoproterozoic interglacial carbonates can be used to trace and potentially quantify changes in continental weathering and ocean alkalinity and, consequently, yield insights into Earth's ancient climatic states. However, the isotope composition of seawater may still change over shorter time intervals if the influence of the driving factor is large enough and/or seawater exchange within the depositional basin is restricted (Holmden et al., 2012).

To test this, we have measured Ca and Mg isotope ratios on samples from carbonate units of the Neoproterozoic Otavi Group in NW Namibia (Fig. 1; Kasemann et al., 2005, 2010). These sections were deposited on the low-latitude continental margin of the southern Congo craton, represent different depositional facies (foreslope and platform) and contain a record of the younger Cryogenian (ca. 635 Ma) pan-glacial to greenhouse transition. The

combined stable isotopic datasets for these sections enable us to construct and combine weathering/alkalinity, palaeo-pH and carbon chemistry profiles over a variety of water depths and settings for one depositional basin. Further, we can assess if Ca and Mg isotopes can be used: (i) as stratigraphic fingerprints recording characteristic trends specific to the younger Cryogenian (Marinoan) glaciation–deglaciation sequence; (ii) to identify their regional (local) and/or global significance; and (iii) to evaluate the nature and scale of chemical weathering and Earth system recovery during the Cryogenian climatic extremes.

2. Material and methods

2.1. Samples

Samples selected for this study were collected from the Neoproterozoic Otavi Group in NW Namibia (see Supplemental Online Material), and are the same samples on which Kasemann et al. (2005, 2010) previously obtained and reported C, O, and B isotope ratios (Supplementary Online Material). The sampled sections were from two well-exposed areas (Fig. 1), the eastern Kaokoveld carbonate platform (Ombaatjie and Khowarib sections) and the Fransfontein Ridge shelf-slope break (Fransfontein section), and define a transect from shallow- to deeper-marine settings across the palaeocontinental margin of the Congo craton (Kasemann et al., 2010). In addition, the sections capture the meltback phase of the younger Cryogenian (ca. 635 Ma) Ghaub Formation and the return to more moderate climatic conditions (Halverson et al., 2005; Hoffmann et al., 2004).

As noted in Kasemann et al. (2005, 2010), the sample localities have not experienced any degree of metamorphism and are only moderately deformed with broad and open folds. The rocks selected for isotope analyses preserve exquisite evidence of original depositional features and structures, are uniform and micritic in texture, and contain no observed evidence of secondary alteration or recrystallisation. Prior to isotope analyses, the quality of the samples was checked by scanning electron microscope (SEM) and trace element analyses using secondary ionisation mass spectrometry (SIMS), as detailed in Kasemann et al. (2005, 2010).

2.2. Analytical techniques

Calcium isotope ratios were determined in the laboratories of the Bristol Isotope Group (BIG) using the preparation technique, measurement routine and data collection method detailed in Kasemann et al. (2005, 2008) and Supplemental Online Material. Analyses were performed on a Thermo Finnigan Triton thermal

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