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Nd isotope records of late Ordovician sea-level change—Implications for glaciation frequency and global stratigraphic correlation

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ABSTRACT

Detailed records of ice-sheet advances and retreats are reconstructed for the Hirnantian and Katian ages of the Late Ordovician using Nd isotopes (ε_{Nd}) as a sea-level proxy in three study sections from the western margin of Laurentia: two shallow water platform sections located south and north of the paleo-equator, and one deep water section located in a continental slope-rise setting. When sea-level was high and paleo-shorelines had migrated eastward, the ε_{Nd} value of seawater in the vicinity of each of the study sections shifted toward the ε_{Nd} value of the eastern Panthalassa Ocean (~−4.0). By contrast, when sea-level was low and paleo-shorelines had migrated westward, the ε_{Nd} value of seawater shifted toward the ε_{Nd} value of the continental weathering flux from Laurentia (-8.5 ± 0.2, $2\sigma_{mean}$). These stratigraphic patterns of changing ε_{Nd} values are interpreted to reflect the eustatic sea-level fluctuations that previous studies have documented in response to Gondwanan ice-sheet advances and retreats, thus linking the ε_{Nd} sea-level proxy to Late Ordovician global-scale climate changes. The ε_{Nd} profiles for the two platform sections yielded similar proxy sea-level curves with five cycles of oscillation recorded during the latest Katian and Hirnantian. Three additional cycles of late Katian sea-level change are recognized in the ε_{Nd} profile of the deep water continental slope-rise section.

The combination of ε_{Nd}, $\delta^{13}C$ and graptolite biostratigraphic data facilitates a precise interregional correlation of the Hirnantian Age and the paleoclimate changes that took place during this interval. The new correlations support previous findings that the Hirnantian ice age comprised two major glacial periods separated by a minor interglacial during the early part of the *Metabolograptus persculptus* Biozone. The younger glacial (confined to mid *M. persculptus* Biozone time) led to more extensive sea surface cooling than did the earlier one, and resulted in extensive eustatic sea-level drawdown and C-cycle changes. It records the strata most often recognized as HICE (the Hirnantian Carbon Isotope Excursion) in sedimentary successions worldwide, such as Anticosti Island, Scotland, Estonia, Siberia, and South China. The results of this study support and strengthen the view that glaciation predated the Hirnantian Age in the Late Ordovician, and that the records of small positive $\delta^{13}C$ excursions in Katian successions from Baltica and eastern North America are themselves proxy indicators of glaciation frequency and eustatic sea-level changes.

1. Introduction

Although glacial tillites record direct evidence for glaciation in the geological past, the tillite record is likely to be incomplete due to sediment reworking by successive ice sheet advances that erase evidence of smaller and earlier glaciations (Chamberlin, 1895). To investigate the fine details of climate change during periods of glaciation, sedimentary or geochemical proxies must be employed in depositional settings located far away from the site of glaciation. The best known example is the $\delta^{18}O$ proxy for temperature and continental ice-volume changes, pioneered during studies of Pleistocene glaciation using stratigraphic records of $\delta^{18}O$ variation in foraminifera from deep sea sediment cores (Emiliani, 1955; Shackleton, 1974). The $\delta^{18}O$ proxy has seen only limited application to the study of glaciation in the Paleozoic, such as during the period of Hirnantian glaciation in the Late Ordovician (Brenchley et al., 1995). The problem stems from the fact that Paleozoic records of $\delta^{18}O$ variation must be reconstructed from fossil carbonate or phosphate preserved in the deposits of epeiric seas, where the clarity of cause and effect relationships between ice-volume changes and seawater $\delta^{18}O$ values may be

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blurred by temperature and salinity variability in shallow seas, poor knowledge of vital effects among carbonate producing organisms (Grossman, 1987), and diagenetic alteration (Duplessy et al., 1970; Wadleigh and Veizer, 1992; Grossman et al., 1996; Sharp et al., 2000)—problems that also hamper seawater $\delta^{18}O$ estimation using clumped-isotope paleothermometry (e.g., Tripati et al., 2010; see also, Finnegan et al., 2011).

In this paper, a Nd isotope technique is presented that has the potential to reveal detailed records of ice sheet fluctuations in Paleozoic and older periods of earth history. It is based on the premise that stratigraphic variations in ε_{Nd} values preserved in the seawater fraction of whole-rock sedimentary carbonate and shale will behave as a sea-level proxy (Fanton et al., 2002). The subject of this study is the ice advances and retreats leading up to and including the approximately one million year-long Hirnantian Glaciation in Northern Gondwana (time-scale based on Cooper and Sadler, 2012; see also recent syntheses in Ghienne et al., 2007; Le Heron et al., 2010; and Moreau, 2011) and peri-Gondwanan Europe (Gutiérrez-Marco et al., 2010), which provides an exceptional opportunity to develop tools for the study of sea-level change in deep time (Ghienne et al., 2007; Le Heron et al., 2010; Delabroye et al., 2011; Desrochers et al., 2011; Finnegan et al., 2011). Contrasting the traditional use of $\delta^{18}O$ as a sea-level proxy, fossil material is not required to employ ε_{Nd} for the same purpose. Seawater ε_{Nd} values may be extracted from virtually any marine sedimentary rock, and the sedimentary Nd-isotope records are highly resistant to diagenetic alteration (Banner et al., 1988; Fanton et al., 2002; Gourlan et al., 2008; Martin et al., 2010; Theiling et al., 2012). Therefore, sampling resolution is not limited by the frequency of fossil occurrences in the sedimentary succession, or the degree of fossil preservation.

Three sections were chosen for study along the western margin of Laurentia (Fig. 1)—the Monitor Range and Vinini Creek sections, located south of the paleoequator, and the Blackstone River section, located north of the paleoequator. Positive $\delta^{13}C$ excursions occur in the Hirnantian glacial interval in all three sections (Finney et al., 1999; Kump et al., 1999; LaPorte et al., 2009). The Vinini Creek section has received further study using $\delta^{15}N$ as a paleoredox proxy (LaPorte et al., 2009), and the Monitor Range section has been the subject of a Ca cycling study that utilized $\delta^{44/40}Ca$ as a tracer (Holmden et al., 2012). Evidence was presented in these earlier studies that the circulation of seawater between the submerged portions of the western Laurentian continent and the adjacent Panthalassa Ocean was restricted during the glacio-eustatically controlled Hirnantian sea-level lowstand (LaPorte et al., 2009; Holmden et al., 2012).

The ε_{Nd} sea-level proxy is founded upon the discovery of shelf-gradients in seawater ε_{Nd} values in ancient epeiric seas (Grandjean et al., 1988; Holmden et al., 1998), and the idea that spatial patterns of ε_{Nd} variation are affected by sea-level changes (Fanton et al., 2002). A feasibility test was therefore undertaken using the Monitor Range section to determine whether a seawater ε_{Nd} gradient existed across the submerged margin of western Laurentia in the Late Ordovician, and whether further investigation of ε_{Nd} as a sea-level proxy would be warranted in this setting. Analyses of ε_{Nd} values in carbonate sediment deposited during the Hirnantian sea-level lowstand yielded -8, whereas carbonate sediment deposited during the post-glacial sea-level highstand yielded -5. From these preliminary analyses and the application of Walther's Law (cf. Middleton, 1973), a shore-to-basin gradient in seawater ε_{Nd} values is inferred for the western margin of Laurentia during the Hirnantian. The working hypothesis regarding the origin of the gradient is mixing between Panthalassa seawater with high ε_{Nd} values, and weathered Nd from the Laurentia craton with low ε_{Nd} values. This hypothesis is supported by studies documenting spatial variations in seawater ε_{Nd} variations in both modern (Andersson et al., 1992; Copland et al., 2011) and ancient (Grandjean et al., 1988; Holmden et al., 1998; Fanton et al., 2002) epeiric seas, where the seawater residence time for Nd is shorter than the time required to flush the epeiric seas with open ocean waters (Holmden et al., 1998).

2. Study sections

2.1. Monitor Range (Nevada, USA)

The Monitor Range section of the Hanson Creek Formation is a composite of two nearby Upper Ordovician outcrop sections located in central Nevada (Figs. 1–2) (Finney et al., 1999). The sediment exhibits characteristics of quiet water deposition in a sub-basin with low-oxygen bottom waters that Dunham (1977) designated the Martin Ridge Basin—a

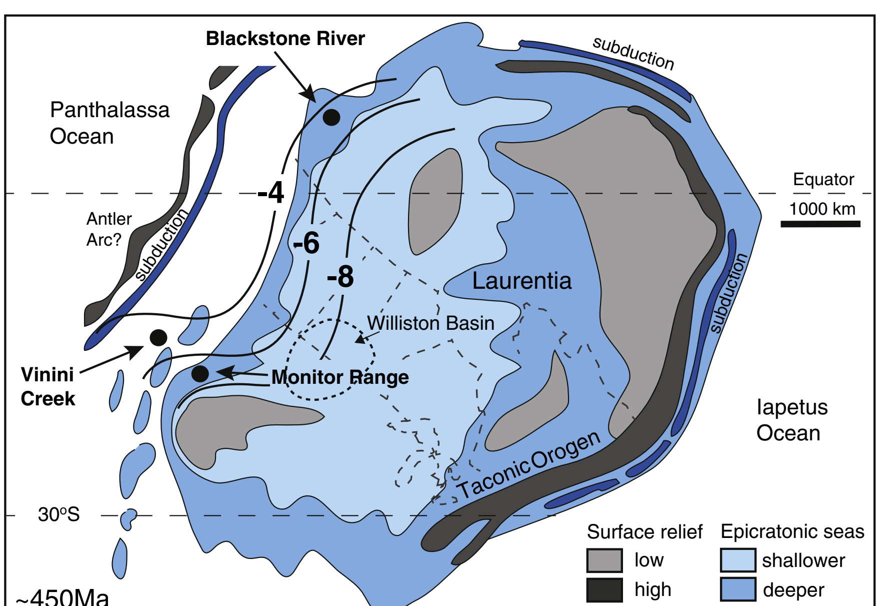

Fig. 1. Late Ordovician paleogeography modified after Ron Blakey (http://jan.ucc.nau.edu/~rcb7/globaltext.html) showing the locations of the three study sections. The ε_{Nd} contours are hand-drawn and for illustrative purposes only. The pattern shown is for high sea-level where the shoreline (the source of weathered Nd with ε_{Nd} of ~ −8.5) is shifted far to the east. During these times, the seas overlying the western edge of Laurentia approach the ε_{Nd} value of the Panthalassa Ocean of ~ −4. When sea-level subsequently falls, as would occur during glaciation, the ε_{Nd} contour lines migrate westward keeping their positions relative to the paleo-shoreline, and seawater ε_{Nd} values shift toward the continental weathering flux signature of −8.5. Therefore, study sections located along the path of the gradient would record negative ε_{Nd} excursions during glacial–interglacial cycles.