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Disentangling the record of diagenesis, local redox conditions, and global seawater chemistry during the latest Ordovician glaciation

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ABSTRACT

The Late Ordovician stratigraphic record integrates glacio-eustatic processes, water-column redox conditions and carbon cycle dynamics. This complex stratigraphic record, however, is dominated by deposits from epeiric seas that are susceptible to local physical and chemical processes decoupled from the open ocean. This study contributes a unique deep water basinal perspective to the Late Ordovician (Hirnantian) glacial record and the perturbations in seawater chemistry that may have contributed to the Hirnantian mass extinction event. We analyze recently drilled cores and outcrop samples from the upper Vinini Formation in central Nevada and report combined trace- and major element geochemistry, Fe speciation ($\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ and $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$), and stable isotope chemostratigraphy ($\delta^{13}\text{C}_{\text{Org}}$ and $\delta^{34}\text{S}_{\text{Py}}$). Measurements of paired samples from outcrop and core reveal that reactive Fe is preserved mainly as pyrite in core samples, while outcrop samples have been significantly altered as pyrite has been oxidized and remobilized by modern weathering processes. Fe speciation in the more pristine core samples indicates persistent deep water anoxia, at least locally through the Late Ordovician, in contrast to the prevailing interpretation of increased Hirnantian water column oxygenation in shallower environments. Deep water redox conditions were likely decoupled from shallower environments by a basinal shift in organic matter export driven by decreasing rates of organic matter degradation and decreasing shelf areas. The variable magnitude in the record of the Hirnantian carbon isotope excursion may be explained by this increased storage of isotopically light carbon in the deep ocean which, in combination with increased glacio-eustatic restriction, would strengthen lateral- and vertical gradients in seawater chemistry. We adopt multivariate statistical methods to deconstruct the spatial and temporal re-organization of seawater chemistry during the Hirnantian glaciation and attempt to isolate the latent magnitude and global perturbation in the carbon cycle. We speculate, using a two component mixing model and residual estimates from principal component analysis, that the secular open ocean Hirnantian C isotope excursion possibly amounts to only $\sim +1.5\%$. Such an increase could be mechanistically driven by the combination of sea-level fall, persistent deep water anoxia, and cooler glacial temperatures that increased the organic carbon burial efficiency in the deeper basins.

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1. Introduction

The ice-house conditions of the Hirnantian (latest Ordovician ~ 444 Ma) coincide with the first of five major Phanerozoic mass extinctions (Berry and Boucot, 1973; Raup and Sepkoski, 1982). The concomitance of the mass extinction event and glaciation has been used to argue a causal relationship associated with a perturbation in the global carbon cycle recorded by a positive

excursion in stable C isotopes of both carbonates and organic matter ($\delta^{13}\text{C}_{\text{Carb}}$ and $\delta^{13}\text{C}_{\text{Org}}$, respectively, Brenchley et al., 1994; Melchin et al., 2013). However, the specific glacio-eustatic process that could cause a major Hirnantian carbon isotope excursion and mass extinction remain ambiguous. Previous studies propose a number of plausible drivers, such as increased thermohaline circulation and marine productivity during the glacial interval, increased limestone weathering from carbonate platforms exposed by the glacio-eustatic sea-level fall, and increased silicate and phosphorus weathering driven by the colonization of the first land plants (Brenchley et al., 1994; Kump et al., 1999; Lenton et al., 2012).

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The discrepancies surrounding the Hirnantian carbon cycle partly originate from intricate glacial ocean dynamics and re-organization of water column redox conditions such as those observed more recently during the Pleistocene glaciations. Cooler glacial temperatures during the Hirnantian would likely have increased oxygen saturation in surface seawater, in particular at high latitudes where deep- and intermediate water masses are presently sourced (e.g. Jaccard and Galbraith, 2012). However, water column oxygen is intimately tied to the carbon cycle and controlled by the export and degradation of organic matter (Southam and Hay, 1977). Glacio-eustatic processes are noted to transfer the export of organic carbon and oxygen demand towards the open ocean (Cartapanis et al., 2016; Jaccard et al., 2009). These processes involve changes in ocean circulation, decreasing metabolic rates of organic matter degradation associated with cooler temperatures, and decreasing shelf area (Bjerrum et al., 2006; Finnegan et al., 2012). In the Pleistocene, for example, these mechanisms are observed to result in diminishing Oxygen Minimum Zones (OMZs) on the outer shelf and decreasing oxygen concentrations in the deep ocean (Cartapanis et al., 2016; Jaccard et al., 2009). The Hirnantian stratigraphy potentially records similar changes of locally increased oxygenation in shallow water environments while widespread anoxia developed in deeper basins (Hammarlund et al., 2012). The Hirnantian stratigraphic record, however, is dominated by deposits from epeiric seas that are susceptible to local processes that are decoupled from the open ocean (e.g. Jones et al., 2011, in press). An understanding of spatial variability in seawater chemistry is thus essential to reconstruct the secular record of Hirnantian redox conditions and carbon-cycle dynamics.

Extensive Hirnantian sedimentary rocks in central Nevada offer a unique context to investigate the past environmental conditions across a transect from shelf to basin during the glaciation. Deep water facies are rarely preserved in the ancient geological record due to the continuous subduction of the ocean floor. In Nevada, however, Hirnantian deep water siliciclastic facies of the Roberts Mountain thrust plate have been juxtaposed with coeval shallow carbonate ramps following the late Devonian Antler orogeny (Merriam and Anderson, 1942; Finney et al., 2000). This study contributes analyses of outcrop samples and new shallow drill core samples from the deep basinal Vinini Formation (Fm.) of Roberts Mountain. We report combined major- and trace element geochemistry, Fe speciation, and stable isotope chemostratigraphy ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}_{\text{py}}$). A Monte Carlo approach is used to quantify the propagation of uncertainty in Fe speciation measurements and evaluate the effects of modern oxidative weathering on the speciation of Fe-rich phases. Multivariate statistical methods are adopted to deconstruct the spatial and temporal re-organization of sea water chemistry and redox conditions during the Hirnantian glaciation, and used to isolate the latent magnitude and global perturbation in the carbon cycle.

2. Geological setting

Late-Ordovician strata are exposed in the upper 30 m of the Vinini Formation in the Roberts Mountain (Fig. S1). In 1994, Finney et al. (1998) excavated the Vinini Creek section by bulldozer and exposed a unique deep-marine Late-Ordovician section recording the Hirnantian glacial interval. The excavated Vinini Creek section has since been thoroughly studied (e.g. Finney et al., 1998, 1999, 2007; LaPorte et al., 2009; Rohrssen et al., 2013).

The Vinini Creek section spans from the mid Katian to the lowest Silurian and has been correlated to other Ordovician sections based on graptolite biostratigraphy (Fig. 1) (Finney et al., 1999). The bottom of the section (0–9.8 m) covers the upper part of the Katian *D. ornatus* biozone (~447.87–446.20 Ma) and consists of interbedded siltstone and periplatform limestone mud deposited by

density currents in lower slope to basin-margin settings (Finney et al., 2007). The overlying 9.8–17.0 m strata cover the upper Katian *P. pacificus* biozone (~446.20–444.68 Ma) consisting of organic-rich interbedded black shale and siliceous ooze. Previously, this specific interval has been interpreted as reflecting a development of an OMZ in overlying waters on the outer shelf during sea-level highstand (Finney et al., 1999, 2007; LaPorte et al., 2009). The transition to the Hirnantian glacial stage is marked by a pronounced change from siliciclastic dominated sediments in the upper Katian to carbonate dominated sediment in the Hirnantian. However, the Hirnantian transition is complicated by a tectonic fault underlying the Hirnantian *M. extraordinarius* biozone (Fig. 1A). This structural feature potentially marks a smaller unconformity and may additionally be prone to post-depositional fluid flow along the fracture zone. Above this zone, the *M. extraordinarius* biozone (~444.68–444.13 Ma) contains both the first extinction pulse and the glacial maximum. This interval is characterized by tan-gray periplatform dolomites and transitions into micritic limestone in the *M. persculptus* biozone (~444.68–443.41 Ma). The lithological transition has been linked to ice house dynamics and a possible interglacial period in the mid Hirnantian (Melchin et al., 2013). The transition from the Hirnantian- to the Silurian is marked by a shift to distinct green shale across an unconformity, where the top of the *M. persculptus* biozone and much of the lower Llandovery (lower Silurian) is missing.

3. Methods

In the fall of 2012 and 2013, we collected outcrop and core samples throughout the Vinini Creek section. Outcrop samples were recovered every ~10 cm from the bulldozed trench using a hammer and chisel after removing the top layer of obviously weathered rock. In addition, we obtained multiple shallow drill-cores through specific intervals. The boreholes were drilled near vertically at an oblique angle to the dipping beds covering a total of ~12.7 m of the total 26 m of measured outcrop. The cores were obtained using a hand held portable rock drill with a 41 mm diamond core bit mounted on a 122 cm long threaded lead with a water circulation system (Tanka engine drill re-gearred from Shaw Tool's). Extension core barrels were used, permitting a total vertical drill depth of up to 10 m under ideal conditions (Bjerrum, unpublished). Core and outcrop samples were correlated to within decimeter scale precision by both drilling depth and sedimentology and further related to previous published data by litho- and organic carbon isotope stratigraphy (Fig. 1). All comparisons between core- and outcrop samples are restricted to the top 15 m of the section and exclude the lower Katian stratigraphy where no cores have been drilled.

All samples comprise ~1–2 cm³ of rock that were freeze dried before storage and subsequently split, crushed and homogenized to powder <125 μm . A tungsten-carbide shatterbox was used to crush core samples while outcrop samples were drilled using a coated Ti–Al hardened steel drill for selective sampling to avoid impurities such as veins and clearly weathered rock.

3.1. Geochemical analysis

The majority of carbon measurements were performed at the University of Copenhagen and a subset of samples were measured at Iso-Analytical Limited (UK) using similar methods. Carbonate content was approximated by mass loss following acid treatment in 10% HCl heated to 80 °C for 1 h. Total Organic Carbon (TOC) was measured on the basis of CO₂ (g) released from the decarbonized material during combustion using a Metalyt CS-500 and reported as a percentages of the total mass of the original sample. Long-term reproducibility of the instrument is better than $\pm 0.2\%$

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