



Reconstructing Late Ordovician carbon cycle variations

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Abstract

The role of carbon dioxide in regulating climate during the early Paleozoic, when severe glaciations occurred during a putative greenhouse world, remains unclear. Here, we present the first molecular carbon isotope proxy-based estimates for Late Ordovician (early Katian) $p\text{CO}_2$ levels, and explore the limitations of applying this approach to the reconstruction of Paleozoic $p\text{CO}_2$. Carbon isotope profiles from three sites in Laurentia (Iowa, Ontario and Pennsylvania) and one site in Baltica (Estonia) exhibit overall low isotope fractionation between organic and inorganic carbon during photosynthesis (ϵ_p) and these values declined during the early Katian carbonate carbon isotope excursion (or Guttenberg Carbon Isotope Excursion, GICE). Algal ϵ_p values are sensitive to changes in CO_2 concentrations, algae cell morphologies, and cell growth rates. To constrain these factors, we present molecular evidence that a decrease in the relative abundance of cyanobacteria and a change in the eukaryotic algae community co-occurred with the GICE. Regardless of local biotic or oceanographic influences, a decline in ϵ_p values indicates photosynthesis was sensitive to carbon concentrations, and via analogy with modern taxa, constrains $p\text{CO}_2$ to below $\sim 8\times$ pre-industrial levels (PIL), or about half of previous estimates. In addition, the global, positive carbon isotope excursions expressed in a wide variety of sedimentary materials (carbonate, bulk organic matter, *n*-alkanes, acyclic and cyclic isoprenoid hydrocarbons), provide compelling evidence for perturbation of the global carbon cycle, and this was likely associated with a decrease in $p\text{CO}_2$ approximately 10 million years prior to the Hirnantian glaciations. Isotopic records from deeper water settings suggest a complex interplay of carbon sources and sinks, with $p\text{CO}_2$ increasing prior to and during the early stages of the GICE and then decreasing when organic carbon burial outpaced increased volcanic inputs. © 2012 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The early Paleozoic is characterized as a time of high $p\text{CO}_2$ levels and warm temperatures. Geochemical models suggest $p\text{CO}_2$ levels over $14\times$ higher than modern PIL (e.g.

Berner and Kothavala, 2001 and references therein) and similarly high estimates have been derived from Hirnantian-age goethites (Yapp and Poths, 1992). However, the early Paleozoic is also punctuated by dramatic glacial events, most notably the end-Ordovician glaciation, that are hard to rationalize with $p\text{CO}_2$ levels over $8\times$ modern pre-industrial levels (PIL) (Herrmann et al., 2003). Similarly, Vandembroucke et al. (2010) required Sandbian atmospheric $p\text{CO}_2$ to be $8\times$ PIL for their model to yield temperatures that match those inferred from the paleobiogeographical distribution of chitinozoan marine zooplankton.

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An important paleo- $p\text{CO}_2$ proxy commonly applied to younger periods is the difference between the carbon isotopic compositions of marine organic and inorganic matter ($\Delta^{13}\text{C}$). The proxy is based on experimental and field observations of modern marine photoautotrophs and known relationships between growth conditions, carbon dioxide concentrations and carbon isotope fractionation (ε_p) during Rubisco (ribulose-1,5-bisphosphate carboxylase-oxygenase) mediated carbon fixation. Applications of this approach to past oceans extend through the Cenozoic (Pagani et al., 1999, 2005, 2011) and into the Cretaceous (Bice et al., 2006; Sinninghe Damsté et al., 2008). However, its application to Paleozoic climate has been less common, because it requires the physiological properties of algal carbon assimilation to have been similar to those in the modern ocean (Freeman and Pagani, 2005). However, changes in carbon isotope fractionation do require carbon dioxide concentrations to be low enough relative to physiological factors, such as cell geometry and growth rate, to limit cell carbon uptake, and this could represent a powerful tool in paleoclimate research. Based on modern algae, this amount is about 2200 ppmv, or $8\times$ PIL (Freeman and Pagani, 2005). Thus, observed $\Delta^{13}\text{C}$ changes in Phanerozoic strata suggest that the level of CO_2 was lower than this sensitivity threshold. For example, the Cenomanian–Turonian Boundary (CTB) has a positive carbon isotope excursion (CIE) that is associated with a decrease in $\Delta^{13}\text{C}$, suggesting a decrease in ε_p values and constraining $p\text{CO}_2$ below $8\times$ PIL (Arthur et al., 1988; Freeman and Hayes, 1992; Sinninghe Damsté et al., 2008). In contrast, no decrease in $\Delta^{13}\text{C}$ occurs across the Frasnian–Famennian Boundary (Joachimski et al., 2002), suggesting that carbon isotope fractionation was maximized because carbon dioxide concentrations were very high.

Previously, we applied that approach to a carbon isotope excursion in the early Katian (or Guttenberg Carbon Isotope Excursion, GICE), interpreting a decline in $\Delta^{13}\text{C}$ values in Pennsylvanian strata as evidence for a $p\text{CO}_2$ drawdown (Patzkowsky et al., 1997). More recently, Young et al. (2008) expanded those analyses to GICE records in West Virginia, China and Oklahoma, identifying marked differences among sections. Similar approaches are widely applied to other Paleozoic strata, such as the Hirnantian Carbon Isotope Excursion (HICE), but such work is typically based on bulk organic carbon, even though its $\delta^{13}\text{C}$ values can be affected by changes in the dominant primary producers (e.g. Pancost et al., 2001), differential preservation of isotopically distinct compound classes (e.g. van Kaam-Peters et al., 1998) or mixing of bacterial or zooplanktonic contributions with primary biomass. Although some marine compound-specific and bulk carbon isotopic records yield broadly similar conclusions, i.e. the Cretaceous Cenomanian–Turonian Boundary (CTB; Arthur et al., 1988; Freeman and Hayes, 1992; Sinninghe Damsté et al., 2008), that is not always the case, including some GICE sections (Pancost et al., 1999).

Another issue associated with the application of the $\Delta^{13}\text{C}$ proxy is its sensitivity to local ecologic and paleoceanographic processes. Both cell geometry and growth rates exert significant controls on algal ε_p values, and these can

be synergistic, such that low surface-to-area ratios tend to make fractionation more sensitive to growth rate variations (Popp et al., 1998). Many carbon isotope excursions, including the GICE, the Hirnantian Carbon Isotope Excursion (HICE), the F/F boundary and CTB CIEs, are associated with dramatic oceanographic and biological changes that likely impacted primary producers and bulk organic matter $\delta^{13}\text{C}$ values (Young et al., 2008). Specifically, the GICE is associated with sea level fall (marked by the M4–M5 sequence boundary, e.g. Patzkowsky and Holland, 1993) and early Katian biotic turnover (Sloan and Webers, 1987; Patzkowsky and Holland, 1993, 1996, 1997; Frey, 1995; Sloan, 1995; Ainsaar et al., 2004).

We present new and, in some cases, expanded $\delta^{13}\text{C}_{\text{org}}$ records for four sites (Iowa, Ontario, Pennsylvania and Estonia) across the GICE, an event that has been studied at exceptional geographic scales (e.g. Patzkowsky et al., 1997; Ainsaar et al., 2004; Ludvigson et al., 2004; Saltzman and Young, 2005; Young et al., 2008; Bergström et al., 2009, 2010a,b,c). Compound-specific isotopic analyses can restrict the taxonomic provenance of isotopic signals (e.g. Jasper and Hayes, 1990), and we have determined $\delta^{13}\text{C}$ values of phytoplankton biomarkers in the Iowa, Ontario and Estonia sections. We use these to calculate new $\Delta^{13}\text{C}$ and ε_p records for each site, and we use concentrations and distributions of algal and microbial biomarkers, steranes and hopanes, to constrain local biotic and environmental change from global influences on $\delta^{13}\text{C}_{\text{org}}$ records. We compare our isotopic records to recently published sea surface temperature estimates from conodont apatite (Buggisch et al., 2010, 2011; Herrmann et al., 2010, 2011; Rosenau et al., 2012) as well as lithological changes (Holland and Patzkowsky, 1996; Pope and Read, 1997). We conclude by integrating these records to advance our understanding of early Katian climate change. We also illustrate how the guidance from biomarkers can aid future efforts to reconstruct Paleozoic climates and ocean processes.

2. SAMPLES AND METHODS

2.1. Sample locations

North American rocks were collected in Pennsylvania, Southern Ontario, and Iowa: (1) from an outcrop located on the west bound exit ramp from Highway 322 at the intersection with Highway 655 in Reedsville, Pennsylvania; (2) from the Cominco SS-9 core (Millbrook Farms, Jackson County, Iowa; NE $\frac{1}{4}$ NE $\frac{1}{4}$, Sec. 29, T84N, R1E; archived at the Iowa Geological Survey); and (3) from the OGS-82-3 core (Southern Ontario; 81°9'45"W, 42°40'15"N; archived at the Ontario Geological Survey, Sudbury, ON). Estonian rock samples are from the Ristiküla (No. 174) core situated in south-western Estonia (24°48'30"E, 58°10'45"N; archived at the Estonian Geological Survey).

2.2. Paleogeographic setting and lithology

The Iowa and Ontario sections were deposited on a relatively stable carbonate platform in central Laurentia (Fig. 1), with circulation between the two locations

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