Earth and Planetary Science Letters 436 (2016) 108–120

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Chemostratigraphic and U–Pb geochronologic constraints on carbon cycling across the Silurian–Devonian boundary

Jon M. Husson [a,b,*], Blair Schoene [b], Sarah Bluher [b], Adam C. Maloof [b]

[a] Department of Geoscience, University of Wisconsin–Madison, 1215 W. Dayton Street, Madison, WI 53706, USA
[b] Department of Geosciences, Princeton University, Guyot Hall, Washington Road, Princeton, NJ 08544, USA

ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 18 November 2015
Accepted 27 November 2015
Available online 23 December 2015
Editor: D. Vance

Keywords:
Helderberg Group
chemostratigraphy
Klonk Event
CA-ID-TIMS
U–Pb geochronology

ABSTRACT

The Devonian Period hosts extraordinary changes to Earth's biosphere. Land plants began their rise to prominence, with early vascular vegetation beginning its colonization of near-shore environments in the latest Silurian. Across the Silurian–Devonian (Pridoli–Lochkovian) transition, carbon isotope analyses of bulk marine carbonates ($\delta^{13}C_{carb}$) from Laurentian and Baltic successions reveal a positive $\delta^{13}C_{carb}$ shift. Known as the Klonk Event, values reach +5.8‰, making it one of the largest carbon isotope excursions in the Phanerozoic. Assigning rates and durations to these significant events requires a robust, precise Devonian time scale. Here we present 675 micritic matrix and 357 fossil-specific $\delta^{13}C_{carb}$ analyses from the lower Devonian Helderberg Group of New York and West Virginia that exhibit the very positive $\delta^{13}C_{carb}$ values observed in other Silurian–Devonian basins. This chemostratigraphic dataset is coupled with 66 ID-TIMS U–Pb dates on single zircons from six ash falls intercalated within Helderberg sediments, including dates on the stratigraphically lowest Devonian ashes yet developed. In this work, we (*a*) demonstrate that matrix and fossil-specific $\delta^{13}C_{carb}$ values track one another closely in the Helderberg Group, (*b*) estimate the Silurian–Devonian boundary age in New York to be 421.3 ± 1.2 Ma (2σ; including decay constant uncertainties), and (*c*) calculate the time required to evolve from baseline to peak $\delta^{13}C_{carb}$ values at the onset of the Klonk event to be 1.00 ± 0.25 Myr. Under these constraints, a steady-state perturbation to the global carbon cycle can explain the observed excursion with modern fluxes, as long as DIC concentration in the Devonian ocean remained below ∼2× the modern value. Therefore, potential drivers, such as enhanced burial of organic carbon, need not rely on anomalously high total fluxes of carbon to explain the Klonk Event.

1. Introduction

The Early and Middle Devonian (419.2–358.9 Ma; Becker et al., 2012) mark an acme in genus-level diversity of marine invertebrates (Alroy et al., 2008) and widespread tectonism associated with the initial closing of the Rheic ocean that separated the Laurussian and Gondwanan paleocontinents (Nance et al., 2010). The end-Silurian records the initial colonization of terrestrial ecosystems by vascular plants, and this process continued in the Early Devonian with the development of larger body sizes, seeds and leaves (Gensel, 2008). Macroscale root systems become prevalent in alluvial systems in the Lochkovian Stage (Raven and Edwards, 2001), broadly coeval with the initiation of a putative, 100-Myr decline in atmospheric CO_2 that some attribute to the rise of a terrestrial biosphere (Berner and Kothavala, 2001).

At the dawn of this major biotic innovation in the global carbon cycle, basins that span the Silurian–Devonian transition record a large, positive excursion in the $\delta^{13}C$ values of carbonate rock ($\delta^{13}C_{carb}$). Values rise from 0 to +5.8‰ in Laurentian (Nevada, Oklahoma and West Virginia; Saltzman, 2002) and Baltic (Czech Republic and Carnic Alps; Buggisch and Mann, 2004) sections (Fig. 1), making the Silurian–Devonian boundary excursion one of the largest in the Phanerozoic Eon (Saltzman and Young, 2005). Known as the 'Klonk Event' after the location of the GSSP for the Silurian–Devonian boundary in the Czech Republic, the similar shape and magnitude of the excursions recorded in globally disparate basins, constrained biostratigraphically to be Silurian–Devonian in age, has led many to argue that it represents a perturbation to the global carbon cycle, with rising values in $\delta^{13}C_{carb}$ representing the evolving isotopic composition of global dissolved inorganic carbon ($\delta^{13}C_{DIC}$). Workers have invoked global regression and the weathering of exposed, isotopically heavy Silurian

* Corresponding author at: Department of Geoscience, University of Wisconsin–Madison, 1215 W. Dayton Street, Madison, WI 53706, USA. Tel.: +1 608 262 8960; fax: +1 608 262 0693.
E-mail address: husson@wisc.edu (J.M. Husson).

http://dx.doi.org/10.1016/j.epsl.2015.11.044
0012-821X/

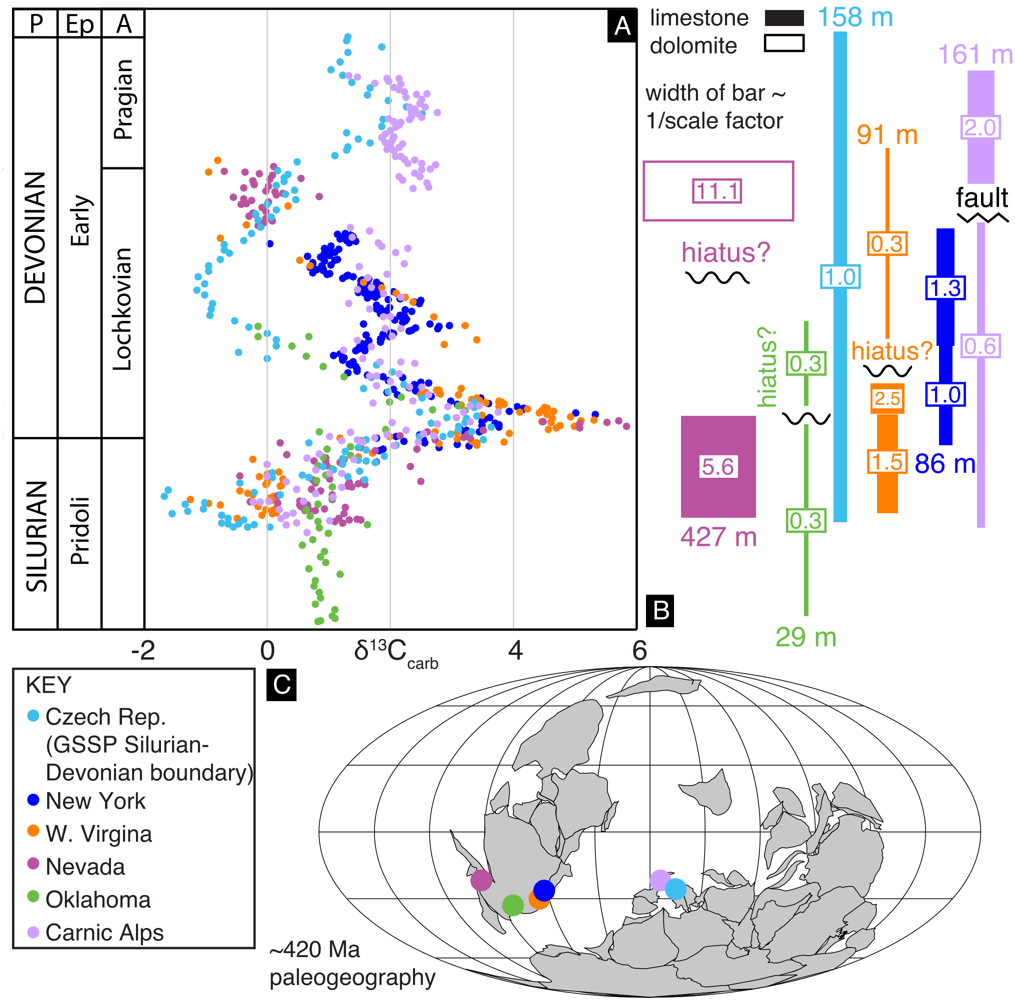

Fig. 1. (A) Silurian–Devonian $\delta^{13}C_{carb}$ data from the Czech Republic and the Carnic Alps (Buggisch and Mann, 2004), Oklahoma (Saltzman, 2002), Nevada (Saltzman, 2002), New York and West Virginia (sections H4 and H5 from this work). The similar shapes of the individual $\delta^{13}C_{carb}$ profiles have been used to create this composite, as well as biostratigraphic considerations for correlation at the epoch/age level. Despite divergences in $\delta^{13}C_{carb}$ values between localities, especially in the middle Lochkovian, all sections exhibit a positive $\delta^{13}C_{carb}$ excursion concordant with the Silurian–Devonian boundary. (B) The width of the bars, color-coded by section and lithology and labeled with true section thicknesses (in meters), correlates with $1/S$, where S is the stretch factor applied to the dataset; values of $1/S$ are labeled in the colored squares. If these stratigraphic $\delta^{13}C_{carb}$ profiles are a product of secular change in global DIC, then $1/S$ would also correlate with relative sedimentation rates of each section. (C) ∼420 Ma paleogeographic reconstruction from http://www.gplates.org (Wright et al., 2013), with section localities rotated to their approximate paleo-position. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

carbonate platforms (Saltzman, 2002) or enhanced organic carbon burial of newly evolved terrestrial biota (Malkowski and Racki, 2009) as drivers for the Klonk Event. The general paradigm that (*a*) $\delta^{13}C_{carb}$ reflects $\delta^{13}C_{DIC}$ and (*b*) secular isotopic change is forced by changes to the global carbon cycle has been widely applied by geologists and geochemists to interpret global $\delta^{13}C_{carb}$ excursions (*e.g.*, Kump et al., 1999). Such models, however, rarely are coupled with independently-derived age models (Maloof et al., 2010), which would allow for intra- and inter-basin chemostratigraphic correlation schemes to be tested, the global vs. local nature of the $\delta^{13}C_{carb}$ excursion to be established, the absolute duration of the excursion to be constrained and the carbon fluxes and reservoir sizes required to drive the perturbation to be quantified. Therefore, a coupled chemostratigraphic-geochronologic study of the Silurian–Devonian boundary in the Helderberg Group of North America, where carbonate strata are interbedded with ash falls amenable to U–Pb dating on volcanic zircon, represents a rare opportunity to constrain rates of change and assess potential drivers for a major perturbation to the ancient geologic carbon cycle.

2. Geologic background

The Helderberg Group (Gp.) is a 90–140 m thick succession of mixed carbonates and siliclastics (Clarke and Schuchert, 1899), deposited in a back-bulge Appalachian basin (*i.e.*, on the eastern margin of Laurentia, and west of the peripheral foreland bulge) in a period of relative tectonic quiescence between the Taconic and Acadian orogenies (Dorobek, 1987; Ver Straeten, 2004). It outcrops from central New York (measured sections H1–H4a,b on Fig. 2) to Virginia (H5 on Fig. 2), and is thickest near the axis of the Appalachian foreland basin in the Virginia–West Virginia region (Dorobek, 1987). Further north, the Heldeberg Gp. thins, and carbonate facies indicate a more restricted depositional environment, with basin isolation increasing from east to west in New York state (Rickard, 1962; Laporte, 1969). The Helderberg Gp. represents a transgressive system tract; in New York, deposition begins with the dolomite-cemented sandstones of the Rondout Formation (Fm.) which grades upward into the finely-bedded lagoonal carbonate mudstones with frequent microbialitic textures of the Manlius Fm. (Fig. 2). The more open-marine brachiopod–crinoid packstones and