Earth and Planetary Science Letters 503 (2018) 68–77

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Global seawater redox trends during the Late Devonian mass extinction detected using U isotopes of marine limestones

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ARTICLE INFO

Article history:
Received 5 February 2018
Received in revised form 12 September 2018
Accepted 16 September 2018
Available online xxxx
Editor: D. Vance

Keywords:
Late Devonian seawater redox
anoxia
uranium isotopes
epeiric seas
extinction
redox-sensitive metals

ABSTRACT

The Late Devonian extinction ranks as one of the 'big five' Phanerozoic extinctions affecting up to 80% of marine species and is characterized by two major extinction events that are separated by <3 My. The leading hypotheses explaining both extinction events are global cooling and/or widespread marine anoxia. We test the marine anoxia hypothesis by analyzing uranium isotopes (δ^{238}U) across a ~7 My interval of well-dated Upper Devonian marine limestones from the Devil's Gate Formation in Nevada, USA. The measured δ^{238}U curve shows no co-variation with local sediment-derived redox trends, water-depth dependent facies changes, redox-sensitive metals, TOC, or diagnostic elemental ratios. From these relationships, we infer that the δ^{238}U curve represents global seawater redox conditions. Two negative δ^{238}U excursions (indicating more reducing seawater) are observed with durations of ~3.8 My (late Frasnian) and ~1.1 My (early Famennian), respectively. Steady-state modeling of the observed −0.2 to −0.3‰ shifts in δ^{238}U points to a ~5–15% increase in the total area of anoxic seafloor during these excursions. The late Frasnian negative excursion is broadly coincident with the first extinction event (late *rhenana* Zone or lower Kellwasser event), whereas the early Famennian negative excursion (lower-middle *triangularis* zones) occurs after the most intense Frasnian–Famennian boundary (F–F) extinction event (upper Kellwasser event). Compilations of local sediment redox conditions from Upper Devonian marine deposits with conodont zone-level age control indicates that the extinction events were coincident with widespread anoxic deposits accumulating in subtropical epeiric sea and some open ocean settings, supporting previous interpretations that widespread marine anoxia had an important influence on the Late Devonian extinctions. The temporal relationships between global-ocean redox trends represented by the δ^{238}U curve and the newly compiled subtropical marine redox sediment trends indicates that local epeiric seawaters carried a similar U-isotopic composition as the open ocean for the majority of the studied interval except for a brief interval (<500 ky) spanning the F–F boundary.

1. Introduction

The Late Devonian extinction ranks as one of the 'big five' Phanerozoic faunal crises, with over 80% of benthic, planktonic, and nektonic marine species affected and terrestrial plants and animals influenced as well (McGhee, 1996, 2001; Hallam and Wignall, 1997; Racki, 2005; Bambach, 2006; Bond and Grasby, 2016). The leading hypotheses explaining the extinction involve two brief, global cooling pulses occurring during an overall long-term warming trend (Copper, 1986; Joachimski and Buggisch, 2002) and/or widespread ocean anoxia generated by increased nutrient flux and resultant enhanced productivity, leading to increased oxygen demands related to organic matter decay (Algeo and Scheckler, 1998).

To test the influence of marine anoxia driving the Late Devonian extinction, we utilize U isotopes from marine limestones to evaluate globally integrated ocean redox trends. In contrast to typical marine redox proxies (i.e., laminated organic-rich facies, framboidal pyrite size and distribution, $\delta^{34}S_{pyrite}$ and redox sensitive trace metals or RSMs) which record local redox conditions, U isotopes of marine limestones can provide a globally-integrated estimate of ocean redox conditions (Montoya-Pino et al., 2010; Brennecka et al., 2011; Dahl et al., 2014; Lau et al., 2016, 2017; Hood et al., 2016; Elrick et al., 2017; Song et al., 2017; Dahl et al., 2017; Jost et al., 2017). U isotopes are sensitive to marine redox conditions because the reduction of soluble U(VI) to insoluble U(IV), which is sequestered into anoxic sediments, is associated with a large isotope fractionation (Weyer et al., 2008). This sig-

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https://doi.org/10.1016/j.epsl.2018.09.020
0012-821X/

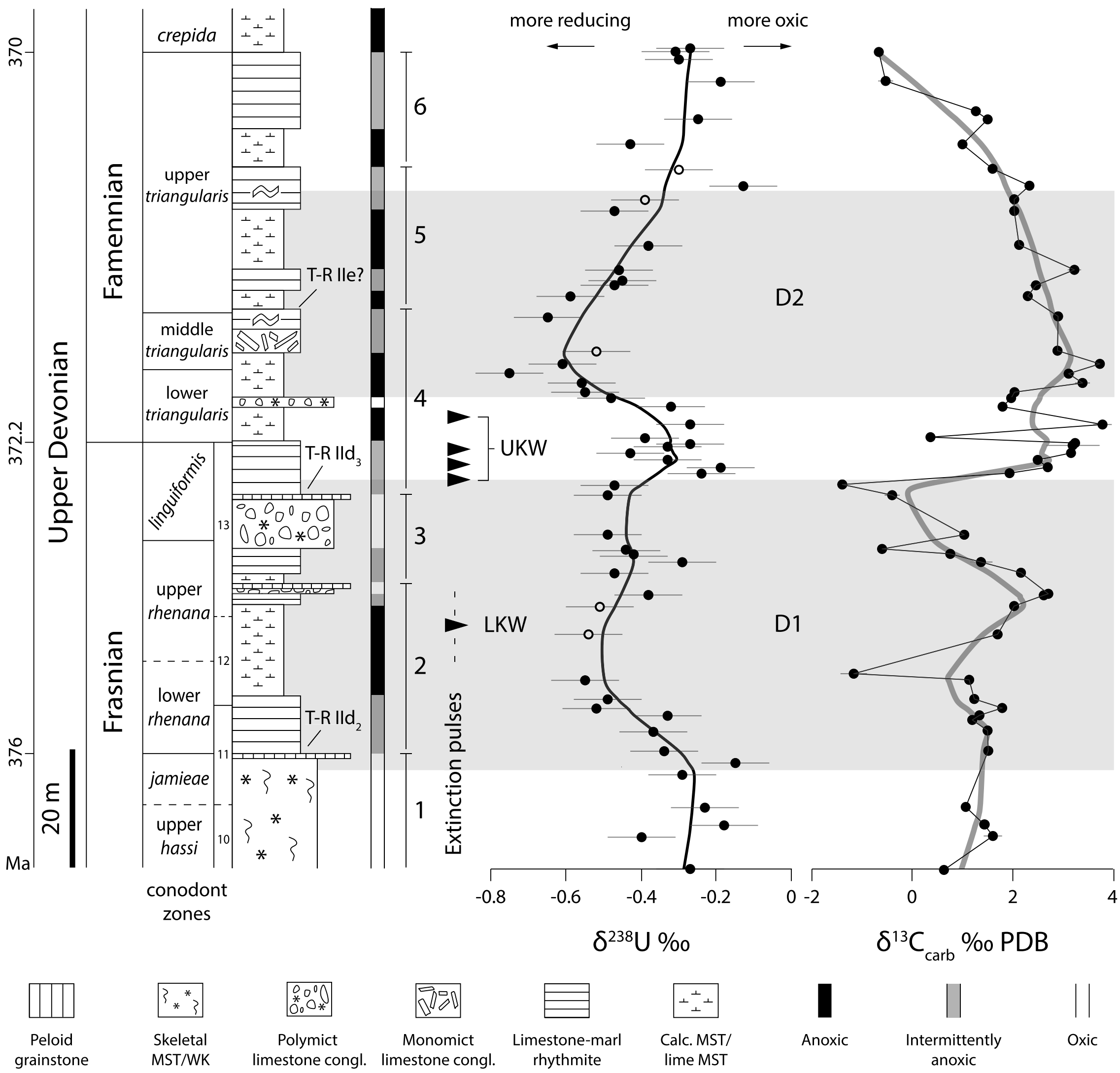

Fig. 1. Stratigraphic, depositional sequence, δ^{238}U, and $\delta^{13}C_{carb}$ records for the Upper Devonian upper Devil's Gate Limestone from central Nevada with the transgressive onset of global transgressive–regressive cycles (T–R cycles of Johnson et al., 1985), and five Late Devonian extinction pulses (black triangles; McGhee, 2001). UKW and LKW refer to the upper and lower Kellwasser extinction events. Conodont biostratigraphy from Sandberg et al. (1988, 2003). Light gray horizontal shaded bands refer to events D1 and D2 defined by negative δ^{238}U excursions described in text. Vertical lines with numbers 1–6 refer to My-scale depositional sequences identified in this study. Vertical bar immediately right of stratigraphic column with black, gray, white shading illustrates the interpreted local redox conditions derived from sedimentological characteristics detailed in Table S1. Isotopic curves are smoothed using LOWESS smoothing procedure. Open circle data points are samples with elevated Fe concentrations; see text for discussion. Congl. = conglomerate, MST = lime mudstone, WK = wackestone, calc. = calcareous.

nal propagates globally because the modern ocean residence time of U (∼400 ky; Ku et al., 1977) is significantly longer than ocean mixing times (<1.5 ky). Consequently, open-ocean seawater and limestones precipitating from that seawater, should record a homogeneous U-isotope value that is representative of globally-averaged ocean redox conditions.

The specific objectives of this study are to 1) describe and interpret Late Devonian U-isotopic and trace element trends, and 2) discuss relationships among U-isotope trends, extinction records, and global and epeiric sea redox records.

2. Background

2.1. Late Devonian extinction, paleogeography, and paleoclimate

The two Late Devonian extinctions occur in the late Frasnian (*rhenana* conodont Zone often termed the lower Kellwasser event; LKW) followed by extinctions clustered near the Frasnian–Famennian (F–F) boundary (upper Kellwasser event; UKW) (Fig. 1; Hallam and Wignall, 1997; McGhee, 1996, 2001; Bond and Grasby, 2016). In the marine realm, benthic, planktonic, and nektonic organisms were all affected, with tropical stromatoporid-coral reef ecosystems particularly devastated (Copper, 2002; Kiessling et al., 2000). Previous studies have suggested that this biocrisis was a function of reduced speciation rather than elevated extinction rates (Sepkoski, 1996; Bambach et al., 2004; Stigall, 2012). Nevertheless, biodiversity loss patterns indicate that 1) low-latitude regions experienced greater loss than higher-latitudes, 2) surviving organisms experienced post-extinction latitudinal compression, and 3) shallow-water marine benthic organisms experienced more severe losses than deep-water organisms (House, 1985; McGhee, 1996, 2001; Kiessling et al., 2000). Coincident with the extinction events is the occurrence of widespread organic-rich marine facies (including the German organic-rich Kellwasser deposits) which was first used to suggest that marine anoxia controlled extinction trends (e.g. Buggisch, 1991; Joachimski and Buggisch, 1993).

Late Devonian global paleogeography is characterized by Laurentia straddling the paleoequator and separated from Gondwana by the narrow and closing Rheic ocean (Fig. S1; Blakey, 2016).