Palaeogeography, Palaeoclimatology, Palaeoecology 414 (2014) 146–154

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Geochemical evidence for euxinia during the Late Devonian extinction events in the Michigan Basin (U.S.A.)

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ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 23 August 2014
Accepted 26 August 2014
Available online 3 September 2014

Keywords:
Frasnian–Famennian event
Late Devonian
Euxinia
Iron limitation

ABSTRACT

Several mass extinction events occurred in the Late Devonian, but the trigger for these events remains elusive. In this study, geochemical evidence in the Late Devonian Antrim Shale, Michigan Basin, U.S.A., records episodic euxinia contemporaneous with these extinction events. Diagnostic changes in iron proxy data and elevated trace metal enrichments correspond to the Kellwasser Crisis. In this study, carbon, sulfur, iron and trace metal geochemistry preserved in the Antrim Formation validates the establishment and expansion of euxinic conditions associated with the Kellwasser Crisis and the Frasnian–Famennian boundary. The strength of the sequential extraction iron mineral data presented here, in concert with trace metal and sulfur isotope proxies, provides definitive signatures of euxinia when other data may be more ambiguous in regard to paleoredox conditions. During the time of the Frasnian–Famennian boundary extensive sulfide oxidation at the chemocline, the result of Fe-limiting conditions within the basin, provides an alternative explanation for the oceanic decline in $\delta^{34}S_{SO_4}$ during, and following, the Frasnian–Famennian event. Our geochemical evidence, indicating the presence of anoxia in the Michigan Basin, is consistent with data from other globally distributed locations. Euxinia should be considered a key driver for these global extinction events, and possibly others such as the Hangenberg Event in the Late Devonian.

1. Introduction

The Frasnian–Famennian (F–F) extinction event is one of the most severe extinction events in the Phanerozoic (Sepkoski, 1986; McGhee et al., 2013). Unlike other major Phanerozoic extinction events, the F–F event was protracted, lasting several millions of years (Buggisch, 1991; McGhee, 1996), and particularly impacted temperate and tropical shallow water faunas (McLaren, 1970; Copper, 1986; Stearn, 1987; McGhee et al., 2013). Globally, this event can be recognized as a couplet of horizons, the Lower Kellwasser Event (LKE) and the Upper Kellwasser Event (UKE), where the UKE is nearly contemporaneous with the F–F boundary. Multiple trigger mechanisms have been hypothesized for the F–F event, including changes in primary productivity, major carbon burial events, eutrophication (Buggisch, 1991; Joachimski and Buggisch, 1993; Joachimski, 1997; Murphy et al., 2000; Chen et al., 2002; Racki et al., 2002; Yudina et al., 2002; Tribovillard et al., 2004; Averbuch et al., 2005), climatic cooling (McGhee, 1989), igneous processes (Orth et al., 1988; Pujol et al., 2006), global warming (Thomspon and Newton, 1988; Joachimski et al., 2009), sea-level change (Johnson et al., 1985; Hallam and Wignall, 1999; House et al., 2000; Bond and Wignall, 2008) and bolide impacts (McLaren, 1970).

Regardless of the trigger, the development and spread of euxinia in the oceans have been hypothesized as key drivers of the F–F extinctions (Savoy, 1992; Joachimski and Buggisch, 1993; Joachimski et al., 2001; Yudina et al., 2002; Bond et al., 2004, 2013; Brown and Kenig, 2004; Tribovillard et al., 2004; Riquier et al., 2006; Carmichael et al., 2014). This mechanism has been invoked for other Phanerozoic extinction events, such as the end-Permian event (e.g., Newton et al., 2004; Grice et al., 2005; Riccardi et al., 2006). However, the role of oxygen deficiency, and euxinia, as a driver of the F–F extinctions has been questioned (Becker et al., 1991; John et al., 2010; Kazmierczak et al., 2012; George et al., 2014). To investigate the relationship between anoxia and the extinction events in the Late Devonian, we collected and analyzed shale samples from the Michigan Basin of the United States.

The Antrim Shale Formation of the Michigan Basin hosts a record of the paleoceanographic conditions and events during the Late Devonian. The unit was deposited during the Taghanic Onlap event in the Michigan Basin, one of a series of Devonian basins associated with the low-latitude epeiric seas that covered Laurentia at the time (Fig. 1). Published datasets of $\delta^{34}S$ from pyrite in other Devonian basins do not unequivocally support euxinia, and biomarker data in the Antrim Fm. appear to conflict with prior paleoredox interpretations (see Brown

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http://dx.doi.org/10.1016/j.palaeo.2014.08.024
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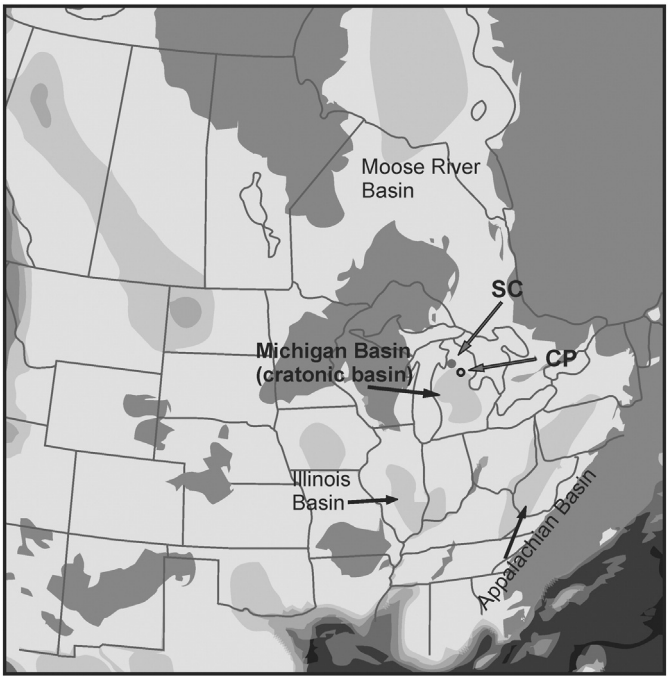

Fig. 1. Late Devonian paleogeographic map of North America showing the Michigan Basin. Sample locations for the Consumers Power #1–10 (CP) and the State Chester #18 (SC) cores.

and Kenig, 2004). In this study, we examine the carbon, sulfur, iron and trace metal signatures, preserved in the Antrim Formation, to investigate the establishment and expansion of euxinic conditions associated with the Kellwasser Crisis and F–F boundary.

1.1. Geologic history and Antrim stratigraphy

The Michigan Basin was part of the Late Devonian Eastern Interior seaway that changed in depositional environment from a carbonate platform to deep basin (the Taghanic Onlap) through the Frasnian (Fig. 1; Johnson, 1970; Gutschick and Sandberg, 1991a). During this transgression the Antrim Fm. was deposited and consists of four members that are laterally present throughout the Michigan Basin, though it grades into the Ellsworth Fm. along the western and northwestern basin margins. The onset of the Taghanic Onlap caused the transition from a shallow-water carbonate platform environment to a deeper basinal environment region in the Late Devonian Michigan Basin (Johnson, 1970; Gutschick and Sandberg, 1991a) and initiated the deposition of the Antrim. During this event the progressively rising sea-level and subsidence in the Eastern Interior seaway led to the formation of a stratified water column that was anoxic and culminated in the deepest water-depths during the deposition of the Antrim and Ellsworth shales (Gutschick and Sandberg, 1991a).

The Antrim Fm. consists of finely laminated, organic-rich, silty and pyritic black shales that are occasionally interbedded with gray and green shales and carbonate units (Gutschick and Sandberg, 1991a; Martini et al., 1998; Over, 2002). The Antrim Fm. members pertinent to this study include, in ascending order, the Norwood, Paxton, and Lachine (Gutschick and Sandberg, 1991a). The lower portion of the Norwood Member consists of black fissile pyritic shales with small-scale fossiliferous limestone beds, calcareous concretions, and bioturbated rhythmites represented by alternations of greenish gray and black fissile shales (Gutschick and Sandberg, 1991a). The lower Norwood transitions into the upper Norwood, which is a radioactive black shale. The Paxton Member is an interbedded light gray argillaceous limestone and greenish gray calcareous shale (Gutschick, 1987; Dellapena, 1991; Martini et al., 1998) that is generally lower in total organic carbon relative to other units. The Lachine Member is a black shale interbedded with greenish-gray shales and carbonate concretions (Gutschick and Sandberg, 1991a). The Early-Famennian Lachine Member conformably underlies the upper Antrim Member and overlies the Frasnian Paxton Member. The boundary between the Lachine and Paxton members corresponds to the Frasnian–Famennian extinction event, the UKE horizon and is correlated with the *Polygnathus linguiformis* and *Polygnathus triangularis* conodont zones (Gutschick and Sandberg, 1991a,b). The LKE is hosted in the Norwood Member in these cores, associated with the *Polygnathus triangularis* conodont zone (Gutschick and Sandberg, 1991b).

2. Materials and methods

Samples of the Antrim Fm. in the Michigan Basin were selected from two cores. The Consumers Power #1–10 (CP; Oscoda County, Michigan, U.S.A.; 44°34′17″N, 84°34′54″W) is located closer to the center of the basin, while the State Chester #18 (SC; Otsego County, Michigan, U.S.A.; 44°54′33″N, 84°29′59″W) is from the basin margin. Samples (<20 g) were taken every 1 to 4 m in both cores and homogenized and finely powdered for all analytical procedures. Stratigraphic boundaries within the formations were determined by gamma-logs and sedimentological evidence during sampling. The Michigan Geological Repository for Research and Education at Western Michigan University provided gamma-logs and cores. Because of the small sample amounts no additional conodont biostratigraphy could be carried out as part of this study. Instead, the locations of the Kellwasser events were defined by geochemical proxy evidence ($\delta^{13}C$) and the F–F boundary in the Antrim was defined by previous conodont biostratigraphic study of Gutschick and Sandberg (1991a,b).

2.1. Concentrations and stable carbon isotopes of organic carbon

Total carbon and total organic carbon (TOC) were measured using a Carlo Erba NC500 elemental analyzer. The TOC samples were pretreated with HCl to remove carbonate phases. The isotope composition of TOC ($\delta^{13}C_{TOC}$) was determined using a NC2500 elemental analyzer (Carlo Erba, Milan, Italy) interfaced to a Delta Plus isotope ratio mass spectrometer (IRMS; Thermo Finnigan, Bremen, Germany) at the University of Arkansas Stable Isotope Laboratory. Samples were combusted with oxygen in a stream of helium. Nitrogen species were further reduced to N_2 in a reduction column. The resulting CO_2–N_2 gas mixture was separated on a 3-meter C/N column and introduced through a Gas Bench II interfaced to a Delta Plus XP IRMS via an open split. Samples were referenced to a working pure gas, also introduced through the open split. Raw isotope values were normalized to respective scales by the use of certified and in-house standards. Data was corrected for instrumental drift using standards throughout the run. For each sample sequence (up to 49 samples) three different standards were used and standards and blanks represented ~40% of the sequence. $\delta^{13}C_{TOC}$ are reported as per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) isotopic standard. Replicate analyses and standard precision are within 0.1‰.

2.2. Trace metal concentrations

Total digestions for trace metal determinations were performed at Activation Laboratories Ltd (Ontario, Canada). Depending on sample availability 75–400 mg of powdered sample was digested using a four acid total digestion. The acids include HF, $HClO_4$, HNO_3, and HCl. The combination of these acids breaks down organics and resistant mineral phases such as silicates. Samples were diluted and measured using a Perkin Elmer SciexElan ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). Most samples were measured using two isotopes in the optimal mode for that element and replicate analyses had an error of less than 5%. Standard reference materials (USGS GXR-1, -4, -6, SDO-1, and SCo-1) were digested and analyzed with each set of extractions.