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Sulfur isotope evidence for low and fluctuating sulfate levels in the Late Devonian ocean and the potential link with the mass extinction event

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ABSTRACT

High amplitude positive carbon isotope excursions in the Late Devonian, the *punctata* and Kellwasser events, reflect major perturbations in the global carbon cycle that have been attributed to increased continental weathering and subsequent ocean eutrophication. Despite the comparable carbon isotope anomalies, however, a major extinction has been reported only for the Kellwasser Events, while the *punctata* Event is marked by low extinction intensity. This study presents multiple sulfur isotope records of carbonate-associated sulfate (CAS) and pyrite from Late Devonian sections in the Great Basin, USA, in order to document changes in the coupled (or decoupled) geochemical cycles of carbon and sulfur during the *punctata* and Upper Kellwasser events. A positive sulfur isotope shift in both CAS and pyrite accompanies the onset of the *punctata* Event, but to a larger extent in the latter. As a result, the sulfur isotope offset between CAS and pyrite ($\Delta^{34}S_{\text{CAS-py}}$) dropped to less than 10‰. In the middle of the *punctata* Event, a sharp negative $\delta^{34}S_{\text{CAS}}$ excursion and negative $\Delta^{34}S_{\text{CAS-py}}$ values coincide with the Alamo impact. Unlike the rapid $\delta^{34}S_{\text{py}}$ and $\delta^{34}S_{\text{CAS}}$ oscillations associated with the *punctata* Event, the Upper Kellwasser was a period of relative stability, except for a brief $\delta^{34}S_{\text{CAS}}$ drop before the event. Paired sulfur isotope data, aided by a simple box model, suggest that the geochemical cycle of sulfur may have been partly responsible for the contrasting biological responses that define these events. High stratigraphic $\delta^{34}S_{\text{py}}$ and $\delta^{34}S_{\text{CAS}}$ variability, coupled with strong reservoir effect, demonstrates a relatively small oceanic sulfate pool existed during the *punctata* Event. Further, the Alamo impact likely triggered the rapid oxidation of microbially-produced sulfide within this event. The expansion of sulfidic bottom water thus may have been impeded during the *punctata* Event. In contrast, the lack of a positive shift in $\delta^{34}S_{\text{CAS}}$ and sizable $\Delta^{34}S_{\text{CAS-py}}$ values (>15‰) throughout the Upper Kellwasser Event imply higher relative sulfate levels. A larger seawater sulfate reservoir may have promoted the development of sulfidic bottom waters in the eutrophic epicontinental seas, increasing biological stress and potentially contributing to the mass extinction.

1. Introduction

The Late Devonian extinction at the Frasnian–Famennian (F–F) boundary is one of five major biological catastrophes that characterize the Phanerozoic fossil record. This crash in biodiversity has been related to intense biological and environmental change, including (but not limited to): terrestrial afforestation (Algeo et al., 1995), a series of asteroid impacts (McGhee, 2001), global cooling (Joachimski and Buggisch, 2002), and active orogeny due to the accretion of continental blocks (Averbuch et al., 2005). Among them, eutrophication and marine anoxia, triggered by increased continental weathering, nutrient delivery and organic carbon production, are widely thought to contribute to the Late Devonian mass extinction (Murphy et al., 2000; Bond et al., 2004). The evidence for eutrophication and marine anoxia at this time is found in the Lower and Upper Kellwasser Horizons that straddle the F–F boundary, which are each marked by positive carbon isotope excursions in marine carbonate and organic carbon (Fig. 1) (Murphy et al., 2000; Buggisch and Joachimski, 2006). However, the widespread deposition of organic-rich facies and the existence of comparable carbon isotope anomalies prior to the Kellwasser events suggest

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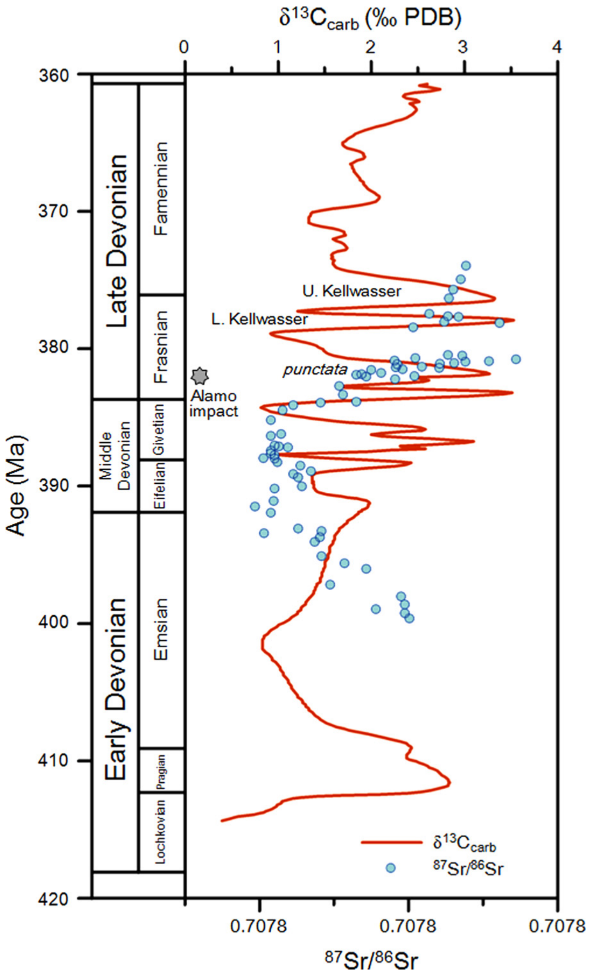

Fig. 1. Seawater $\delta^{13}C_{carb}$ and $^{87}Sr/^{86}Sr$ curves for the Devonian period, modified after Becker et al. (2012) and John et al. (2008). Time scale is after Kaufmann (2006), and the numerical age of Alamo impact is after Morrow et al. (2009).

that multiple episodes of oxygen depletion occurred during the Late Devonian (Buggisch and Joachimski, 2006; Yan et al., 2007). Seawater $^{87}Sr/^{86}Sr$ values indeed indicate that an increase in continental weathering flux predates the F–F transition (Fig. 1). The biological consequences of earlier anoxic events were, nevertheless, noticeably different from those of the Kellwasser events. The early to middle Frasnian transition, for example, records a marine hypoxic/anoxic event (Casier et al., 2006; Marynowski et al., 2008) and a large-scale carbon isotope perturbation through the earliest middle Frasnian *punctata* biozone (Fig. 1), but this so-called "*punctata* Event" is not correlated with extinction events (Morrow et al., 2009; Pisarzowska and Racki, 2012) except for the regional reef crisis in central Europe (Copper, 2002). While previous work has highlighted the contrasting biological response to the *punctata* and Kellwasser events (John et al., 2008; Pisarzowska and Racki, 2012), the underlying mechanism/s for these differences remain unknown.

Due to its wide range of oxidation states, sulfur is cycled through a variety of environmental and biological reservoirs. Organic carbon availability and marine anoxia influence the geochemical cycle of sulfur through microbial sulfate reduction (MSR), an anaerobic process that couples the oxidation of organic matter to the reduction of sulfate. MSR relies on the supply of organic matter to oxygen-depleted environments, and therefore increased deposition of organic matter can accelerate sulfate reduction in marine sediments (Berner and Raiswell, 1983). Importantly, the product of sulfate reduction, H_2S, is lethal to most aerobic organisms, and also the buildup of sulfidic bottom water can influence the cycles of other essential elements such as phosphorous and iron, exacerbating biological stress during an oceanic anoxic event (Murray, 1995; Kleeberg, 1997). Since significant isotopic discrimination accompanies MSR (Chambers et al., 1975; Sim et al., 2011a), global changes in H_2S production can be inferred by tracking the sulfur isotope composition of seawater sulfate through time.

Here we present the sulfur isotope composition of carbonate-associated sulfate ($\delta^{34}S_{CAS}$) and pyrite ($\delta^{34}S_{py}$) from Late Devonian carbonate successions in Nevada and western Utah in order to evaluate the nature of sulfur cycling during the *punctata* and Upper Kellwasser events. Distinct sulfur isotope patterns recorded in these events, along with their quantitative interpretation using a simple box model, highlight the importance of marine sulfate concentration as a potential determinant in environmental stress during ocean anoxic events. In addition to conventional $^{34}S/^{32}S$ ratios, analyses of minor sulfur isotopes (^{33}S and ^{36}S) help constrain Late Devonian sulfur cycle dynamics. Finally, proximity of the studied area to the site of the Alamo impact, which has been implicated as a cause of the Late Devonian extinction (McGhee, 2001), provides a unique opportunity to examine what influence, if any, a large asteroid impact had on the sulfur cycle.

2. Geologic setting

Devonian shelf deposits in Nevada and western Utah reflect progressive deepening from east to west, representing inner shelf, middle to outer shelf, ramp, slope and oceanic basin environments (Morrow and Sandberg, 2008) (Fig. 2). During the late Givetian to middle Frasnian, limestones of Devil's Gate and Guilmette formations were deposited in the Great Basin, overlying the middle Givetian Fox Mountain Formation (Sandberg et al., 1997). The Guilmette Formation in eastern Nevada and Utah consists of limestone and minor sandstone units deposited in the central part of a carbonate platform, while its deep-water equivalent, the Devil's Gate Limestone in central Nevada represents a platform to slope setting (Sandberg et al., 1989). Throughout the latter Devonian, however, the development of the proto-Antler forebulge in central Nevada altered the depositional regime and reduced the area of carbonate deposition (Morrow and Sandberg, 2008). The backbulge basin developed to the east of the proto-Antler forebulge. Basin facies of the Pilot Shale, including siltstones, thin micrites, and sandy turbidites, filled this intra-shelf basin, covering the former middle to outer shelf carbonate deposits (Sandberg et al., 1989).

The Alamo bolide impact interrupted the middle Frasnian sedimentary record of this area. A large body of evidence, including megabreccia, carbonate accretionary lapilli, displaced conodonts, shocked quartz grains, and an iridium anomaly, indicates that a km-scale meteorite impacted the offshore setting west of the carbonate-shelf margin (Warme and Sandberg, 1996; Warme and Kuehner, 1998; Fig. 2). Conodont biostratigraphy constrains the timing of the Alamo event to the earliest middle Frasnian *Palmatolepis punctata* zone at ~382 Ma (Morrow et al., 2009). Although this large impact to a subtropical carbonate shelf likely caused a mega-tsunami and released large amounts of climatically active and potentially lethal volatiles, bioherm mudmounds directly above the Alamo Breccia and taxonomic comparison of pre- and post-breccia stages suggest that the impact had no major affect on the carbonate platform fauna near the impact site (Warme and Kuehner, 1998; Casier et al., 2006).

In this study, data are presented from three stratigraphic sections, including Hancock Summit West (HSW), Devil's Gate (DG), and Granite Mountains (GM). We investigated the middle Frasnian interval at HSW and DG sections, while focusing on the F–F boundary at the GM section (Fig. 3). Sedimentology and conodont biostratigraphy of these sections are described