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Climate instability and tipping points in the Late Devonian: Detection of the Hangenberg Event in an open oceanic island arc in the Central Asian Orogenic Belt

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ABSTRACT

Sedimentary petrology and trace element geochemistry indicate that the Late Devonian to Early Carboniferous Heishantou Formation near Boulongour Reservoir (NW Xinjiang, China) was deposited on a steep slope, mid-latitude accreting island arc complex in an open oceanic system. Bulk ⁸⁷Sr/⁸⁶Sr ratios show excursion patterns that are consistent with excursions at the Devonian–Carboniferous (D–C) boundary in epicontinental margin sediments. Sedimentation rates for the Boulongour Reservoir sediments show highly variable rates that range from 0.5 cm/ky to 10 cm/ky, consistent with other Late Devonian sections and modern arc environments. Multiple whole rock geochemical proxies for anoxia and the size and distribution of pyrite framboids suggest the presence of the Hangenberg Event in the sediments associated with the D–C boundary, despite the lack of visible black shale. The presence of anoxia in an open ocean, island arc environment cannot be explained by upwelling of anoxic bottom waters at this paleolatitude, but can be explained by the global infliction of oceanic shallow water eutrophication on to a climate system in distress.

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1. Introduction

The Late Devonian was a time of intense ecological crisis in both terrestrial and marine ecosystems. It is bracketed by two oceanic anoxia events that are associated with major mass extinctions. The Kellwasser Event at the Frasnian–Famennian (F–F) boundary decimated coral reef and other benthic marine communities (Copper, 1994) while slightly older extinctions decimated terrestrial ecosystems (Stigall, 2012; McGhee, 2013). In contrast, the Hangenberg Event at the Devonian–Carboniferous (D–C) boundary primarily affected pelagic marine communities including fish (Sallan and Coates, 2010) and cephalopods (Becker, 1993; Zong et al., 2014). In fact, a revised taxonomic severity ranking places the end Famennian (D–C boundary) and F–F extinction events as the fourth and fifth largest biodiversity crises in the Phanerozoic, respectively (McGhee et al., 2013, Table 3). These ocean anoxia events are also associated with a series of transgressions and regressions (Becker et al., 2012) and references therein, with the Hangenberg Event resulting from global cooling and the onset of glaciation at the end of the Famennian (Isaacson et al., 2008; Brezinski et al., 2009, 2010; Myrow et al., 2014; Cole et al., 2015). The trigger for these anoxia events

in the Late Devonian has long been debated (Racki, 2005), with proposed mechanisms ranging from the evolution of land plants (causing both a drawdown of atmospheric CO₂ and the influx of nutrients into the oceans) (Algeo and Scheckler, 1998) to tectonic influence (Copper, 1986) to orbital forcing (De Vleeschouwer et al., 2013), to the influence of large igneous provinces (Bond and Wignall, 2014).

Regardless of trigger mechanism, many studies have concluded that upwelling of anoxic bottom waters was responsible for the widespread ocean anoxia in the Late Devonian (Caplan et al., 1996; McGhee, 1996; Caplan and Bustin, 1999; Cramer et al., 2008; Formolo et al., 2014), while others have invoked sea level rise and resulting water column stagnation within epicontinental basins as a causal mechanism (Bond et al., 2004; Bond and Wignall, 2008). Until recently, all of the studies of the Late Devonian anoxia events have been conducted on continental margins or in epicontinental basins, primarily in North America (Geldsetzer et al., 1993; Caplan et al., 1996; Caplan and Bustin, 1998; Smith and Bustin, 1998; Murphy et al., 2000; Caplan and Bustin, 2001; Rimmer, 2004; Rimmer et al., 2004; Bond and Wignall, 2005; Algeo et al., 2007; Algeo and Maynard, 2008; Cramer et al., 2008; Perkins et al., 2008; Schieber, 2009; Myrow et al., 2011; Bond et al., 2013; Tuite and Macko, 2013; Myrow et al., 2014; Cole et al., 2015; Whalen et al., 2015) and Europe (Joachimski and Buggisch, 1993; Schindler, 1993; Racki et al., 2002; Bond et al., 2004; Brand et al., 2004; Gharraie et al., 2004; Kaiser et al., 2006; Pujol et al., 2006; Riquier et al., 2006;

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Marynowski and Filipiak, 2007; Azmy et al., 2009; Myrow et al., 2011; Kazmierczak et al., 2012; Chen et al., 2013; Kumpan et al., 2014a,b; Matyja et al., 2015). Many of these study sites have been strongly influenced by increased sedimentation from the rising Appalachian Mountains. Additional studies have been conducted in locations that would presumably not be affected by the Appalachian/Variscan Orogenic Events, but all are associated with sediments derived from the cratonic blocks of Indochina (Hara et al., 2010; Königshof et al., 2012), South China (Zheng et al., 1993; Chen et al., 2005; Gharaie et al., 2007; Du et al., 2008; Chen et al., 2013; Komatsu et al., 2014; Whalen et al., 2015), Australia (Stephens and Sumner, 2003; George et al., 2014), Russia/Siberia (Gutak et al., 2008; Izokh et al., 2009; Tagarieva, 2013) and northern Africa (Kaiser et al., 2011). In contrast, only one study has unequivocally shown the presence of a Late Devonian anoxia event in an open oceanic setting far from continental-derived sediments: Carmichael et al. (2014) have documented the Kellwasser Event using multiple geochemical proxies within the Central Asian Orogenic Belt (CAOB), which therefore required an overhaul of the established models for ocean anoxia. To explain anoxia in the open ocean, Carmichael et al. (2014) suggested that the Kellwasser Event had to be caused by surface eutrophication rather than upwelling or basinal stagnation during transgressions. Earlier studies by Kido et al. (2013) and Suttner et al. (2014) have also suggested the presence of either the Hangenberg or Kellwasser Events in the CAOB based on field data and/or carbon and oxygen isotope data.

Although the Kellwasser Event is generally characterized by two organic rich black shale units, there is considerable variability in the expression of Hangenberg Event sediments, and this variability complicates not only its recognition in some sections, but in turn obscures the root cause (or causes) of this major ocean anoxia event. Many studies have specifically used the presence of a black shale facies to identify the Hangenberg Event and from there infer the presence of the D–C boundary (Caplan and Bustin, 1999; Rimmer, 2004; Perkins et al., 2008; Kaiser et al., 2011; Formolo et al., 2014; Komatsu et al., 2014; Kumpan et al., 2014a,b; Myrow et al., 2014). However, some locations that span the D–C boundary do not contain black shale (Azmy et al., 2009; Kaiser et al., 2011; Myrow et al., 2011; Königshof et al., 2012; Kumpan et al., 2014a; Matyja et al., 2015; Cole et al., 2015) due to their depositional environment. In the absence of a straightforward, visible manifestation of the Hangenberg Event in the form of a black shale bed or unconformity, the D–C boundary has historically been determined via conodont biostratigraphy (Flajs and Feist, 1988). However, the reliability of conodonts at the GSSP (La Serre section, Montagne Noire, France) has recently been demonstrated to be deeply problematic (Kaiser, 2009; Corradini et al., 2011; Kaiser and Corradini, 2011). Becker et al. (2012) noted that the GSSP for the D–C boundary in the Montagne Noire must be reevaluated and Aretz (2013) has advocated the use of other fossils to define the D–C boundary. In the absence of appropriate fossil assemblages and visible black shales or unconformities, an alternative to biostratigraphy may be required in some sections to constrain both the Hangenberg Event and the D–C boundary.

Whole rock geochemistry and/or isotope chemostratigraphy have long been used in combination with biostratigraphy in many Late Devonian sections to develop global correlations across mass extinction intervals. Although positive $\delta^{13}\text{C}$ excursions in carbonate sediments have often been used to denote the Hangenberg Event interval (Brand, 2004; Kaiser et al., 2006; Cramer et al., 2008; Kaiser et al., 2008; Königshof et al., 2012; Day et al., 2013; Kumpan et al., 2014b; Whalen et al., 2015), these excursions are variable depending on the carbonate material used (Buggisch and Joachimski, 2006), and may be obscured by diagenetic processes during local lowstands and therefore may not represent global marine signatures (Myrow et al., 2013). As other locations that cross the D–C boundary do not show noticeable positive excursions (Caplan et al., 1996; Buggisch and Joachimski, 2006; Kaiser et al., 2006, 2008; Azmy et al., 2009; Kumpan et al., 2014a,b; Matyja et al., 2015), the use of $\delta^{13}\text{C}_{\text{carb}}$ as a correlative chemostratigraphic tool is limited at best. This is

compounded by the problem that paleogeographic locations in the open ocean may record different $\delta^{13}\text{C}$ signatures than those from within epicirc seas (Brand et al., 2009). The use of $\delta^{13}\text{C}_{\text{org}}$ excursions in total organic carbon (TOC) has been used successfully in several studies across the D–C boundary (Caplan et al., 1996; Joachimski et al., 2001; Kaiser et al., 2006) but its use (so far) has generally been limited to sections with visible organic-rich units, and therefore its use as a correlative tool across sediments without visible organic-rich units is not yet widespread.

In addition to carbon isotope stratigraphy, trends in $^{87}\text{Sr}/^{86}\text{Sr}$ have been used for chemostratigraphy as oceanic strontium isotope ratios have varied over time (McArthur et al., 2012). Brachiopods are the preferred material for obtaining $^{87}\text{Sr}/^{86}\text{Sr}$ in the Devonian (Becker et al., 2012), although there are very few measurements during the Famennian that have been fit to the accepted LOWESS curve (McArthur et al., 2012), and there are no accepted $^{87}\text{Sr}/^{86}\text{Sr}$ values for the latest Famennian above the *crepida* conodont zone (Van Geldern et al., 2006). Despite the apparent lack of data in the LOWESS database for this interval, three $^{87}\text{Sr}/^{86}\text{Sr}$ isotope studies specifically span the D–C boundary (Kürschner et al., 1993; Brand et al., 2004; Azmy et al., 2009). Of these three studies, two show sharp $^{87}\text{Sr}/^{86}\text{Sr}$ excursions in conodont apatite at the D–C boundary from European sections (Kürschner et al., 1993) and in brachiopod calcite from locations in Europe and basins within North America (Brand et al., 2004). The remaining study (also located in Europe) does not exhibit an $^{87}\text{Sr}/^{86}\text{Sr}$ isotope excursion (Azmy et al., 2009), although this can be explained by the presence of an unconformity within the section as well as biostratigraphic uncertainty about the exact location of the D–C boundary. The presence of a significant $^{87}\text{Sr}/^{86}\text{Sr}$ excursion in both brachiopods and conodonts across two continents suggests that these excursions are not local phenomena, and can be used for chemostratigraphic correlations in future studies.

Magnetic susceptibility (MS) measurements have long been used as a correlative tool in sedimentology (Hansen et al., 2000; Hladil et al., 2006; Da Silva et al., 2009; Riquier et al., 2010; Whalen and Day, 2010; Ellwood et al., 2011). It is an excellent method for detecting sea level oscillations due to astronomical forcing (Ellwood et al., 2011; De Vleeschouwer et al., 2012, 2013), and new research shows that the regression associated with the Hangenberg Event is easily detectable via MS (Day et al., 2013; De Vleeschouwer et al., 2013; Whalen et al., 2015), which is particularly useful in sections where there is an absence of a visible unconformity or black shale facies.

Whole rock geochemistry and the presence and distribution of pyrite framboids have been used by many to characterize changes in redox conditions in Late Devonian marine black shales (Beier and Hayes, 1989; Pujol et al., 2006; Algeo and Maynard, 2008; Marynowski et al., 2012). Even in the absence of visible black, organic-rich lithologies, the Kellwasser Event has been detected via whole rock geochemistry and/or pyrite framboid distribution in a variety of locations (Bond et al., 2004; Bond and Wignall, 2005; Bond et al., 2013; Carmichael et al., 2014; George et al., 2014).

Here we propose a combined methodology to detect an “invisible” Hangenberg Event and the D–C boundary that incorporates sedimentology and chemostratigraphy ($^{87}\text{Sr}/^{86}\text{Sr}$ isotopes, magnetic susceptibility, and whole rock geochemistry) in a fundamentally different tectonic and depositional setting from previous studies of the Hangenberg Event, in an open ocean island arc complex in the Central Asian Orogenic Belt (CAOB). The presence of the Hangenberg Event in an open ocean environment such as this would indicate that ocean anoxia was global in scope, and that the mechanisms of anoxia invoked for sediments along continental margins and within continental basins are impossible for anoxia development in isolated island arc settings. If the Hangenberg Event is detected here, it is necessary to develop an alternative mechanism for anoxia during the Late Devonian.

2. Regional geology of the CAOB in northwestern China

The CAOB (Fig. 1a), a complex amalgamation of intra-oceanic island arcs and continental fragments, was formed prior to the end of the

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