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Upper Kellwasser carbon isotope excursion pre-dates the F–F boundary in the Upper Devonian Lennard Shelf carbonate system, Canning Basin, Western Australia

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ABSTRACT

Here we report four high-resolution carbon isotope records in addition to trace element data for the Frasnian–Famennian (F–F) boundary interval in the Lennard Shelf carbonate system of the Canning Basin, Western Australia. This region lacks the characteristic black shale horizons associated with the global Late Devonian Kellwasser extinction events, yet still exhibits a trend in carbon isotope character similar to what has been reported from elsewhere in the world (two positive $\delta^{13}C$ excursions with ~3–4‰ amplitudes). Enrichments in select trace element ratios suggest that both excursions are related to periods of oxygen deprivation and perhaps increased biological productivity. Given the continuous and stratigraphically expanded nature of Lennard Shelf sections, together with high-density sampling constrained by both conodont biostratigraphy and magnetostratigraphy, we observe that the Upper Kellwasser isotope excursion (maximum $\delta^{13}C$ values) and associated trace element enrichments occur distinctly lower than the F–F boundary level. These results have implications for the paleoenvironmental conditions leading up to the Late Devonian Mass Extinction in terms of ocean chemistry and circulation patterns. This data set allows for a rare, detailed look at the temporal relationship between the Kellwasser events and the F–F boundary and constrains the pattern of carbon isotope perturbations at the intra-zonal scale.

1. Introduction

The Late Devonian Mass Extinction (LDME) is recognized as one the five greatest biotic crises of the Phanerozoic (Sepkoski, 1986). Decades of research on numerous European localities has led to the understanding that there are actually two separate extinction pulses known as the Upper and Lower Kellwasser events in the *linguiformis* (or Montagne Noire Zones 13b and 13c of Klapper, 1989) and *rhenana* (Montagne Noire Zones 12 and 13a) conodont zones, respectively, of the late Frasnian. These horizons are characterized by significant faunal turnover, positive carbon isotope excursions (average amplitude of about +3‰), and the deposition of black shales and bituminous limestones (e.g. McGhee, 1996), and are thought to reflect widespread anoxic conditions (Feist, 1985; Buggisch, 1991; Wendt and Belka, 1991; Hallam and Wignall, 1999) during pulses of sea level transgression (Johnson et al., 1985; Sandberg et al., 1988, 2002; Buggisch, 1991).

However, the timing of the carbon isotope excursion associated with the Upper Kellwasser deposits and extinctions in Europe (herein referred to as the Upper Kellwasser excursion) is not well constrained and the cause(s) poorly understood. The majority of Late Devonian geochemical studies document Upper Kellwasser excursion maxima at or slightly higher than the F–F boundary (e.g. Joachimski et al., 2002; Xu et al., 2003; Buggisch and Joachimski, 2006; George et al., 2014). As a result, they inadvertently lump the succession of related geo- and

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bio-events together and give the illusion that the Upper Kellwasser excursion and F–F boundary are time-equivalent. This can be particularly problematic when attempting to make chronostratigraphic correlations or to determine causal mechanisms.

Exacerbating these problems are the conflicting isotope records that have been reported for this time period, with some workers noting either the absence of isotopic excursions (Geldsetzer et al., 1987), or the occurrence of negative excursions (Goodfellow et al., 1988; Wang et al., 1991), or the absence of organic-rich deposits (e.g. Joachimski and Buggisch, 1993; Bond et al., 2004). These discrepancies have generated debate over the role of global anoxia as a potential kill mechanism. Paleo-redox data for this time interval are also contradictory: whereas the trace element analyses from most studies have given credence to oceanic anoxia (e.g. Riquier et al., 2006), others infer oxic conditions (e.g. George et al., 2014). Furthermore, in many localities around the world, F–F boundary sections are highly condensed (e.g. Joachimski et al., 2002), or incomplete due to unconformities and depositional hiatuses related to the sharp marine regression in the uppermost Frasnian (Johnson et al., 1985; Sandberg et al., 1988; Geldsetzer et al., 1993; Muchez et al., 1996; Stephens and Sumner, 2003), and/or limited in terms of sampling density or biostratigraphic control at the intra-biozonal scale (e.g. Bratton et al., 1999; Stephens and Sumner, 2003; van Geldern et al., 2006).

This contribution reports new data from the northern margin of Gondwana in order to constrain the timing of the Upper Kellwasser excursion and to better understand the causal mechanism(s) relating to the Kellwasser events. Here we present four detailed carbon isotope profiles, constrained at the intra-zonal level by high-resolution conodont biostratigraphy and magnetostratigraphy. We obtained our data from measured outcrop sections through organic-poor facies in variable slope environments of the Lennard Shelf mixed carbonate-siliciclastic system, Canning Basin, Western Australia (Fig. 1). In this region, middle-slope breccia-grainstone and upper-slope boundstone settings appear to be stratigraphically expanded relative to many other global localities. In Europe, for example, Conodont Zone 13 (Fig. 2) is generally <2 m thick (Buggisch and Joachimski, 2006), whereas in this study, the same interval of time is represented by >20 m of stratigraphy. As such, our sections provide a continuous, more expanded view of upper Frasnian to lower Famennian strata and allow for a more detailed examination of the Upper Kellwasser excursion as it relates to the timing of the F–F boundary. The stable isotope data, with some accompanying trace element analyses, also provide insight into changes in the global carbon pool and redox conditions of the ocean during this time.

2. Area descriptions, methods & materials studied

During the Middle Devonian, subsidence and rifting of the Canning Basin (e.g. Veevers and Wells, 1961; Kennard et al., 1994) led to the prolific growth of carbonate reefs along the shallow terraces of the Lennard Shelf. Today, over 350 km of Middle to Late Devonian carbonates are exposed in the northern part of the basin and have been subjected to decades of stratigraphic, paleontological, and geochemical research (Guppy et al., 1958b; Playford and Lowry, 1966; Druce, 1976; Playford, 1980; Becker and House, 1997; George et al., 1997; Stephens and Sumner, 2003; Nothdurft et al., 2004; Playford et al., 2009; and others). During the interval of time most relevant to this study, namely, the Late Frasnian and Early Famennian, the reefal platform and slope system exhibited progradational growth morphology and experienced episodic collapse events that transported large amounts of material down-slope (Playford, 1980; Sandberg et al., 2002; Playton, 2008; Playford et al., 2009). An abrupt fall in sea level coincident with the F–F boundary resulted in the sub-aerial exposure and erosion of platform-top facies while sedimentation continued uninterrupted on

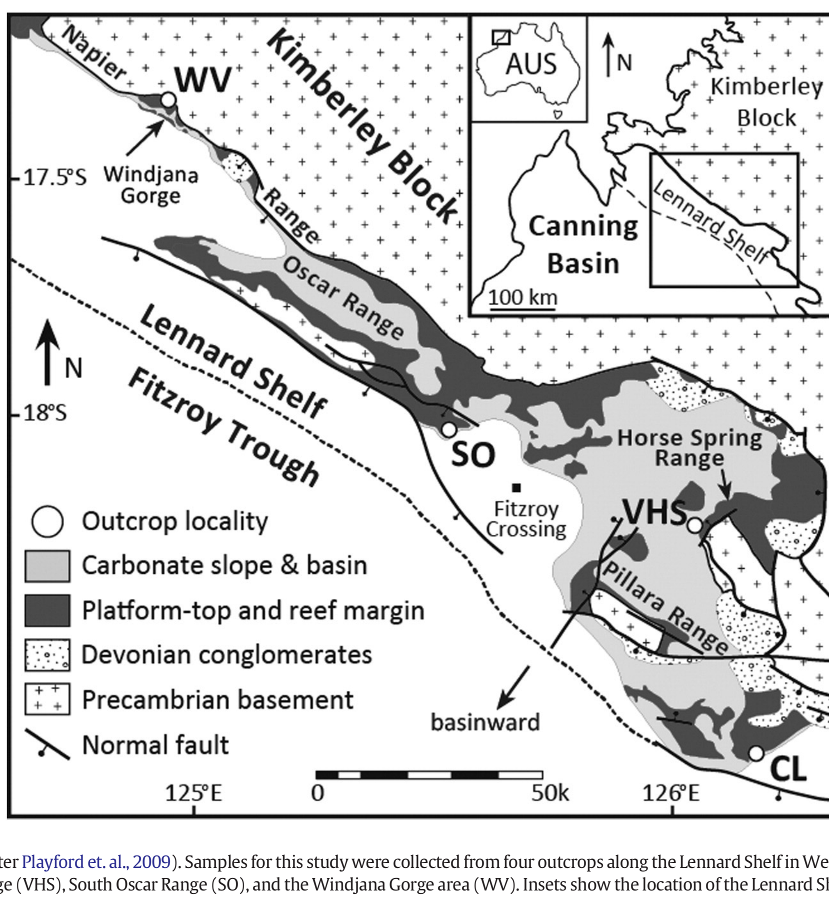

Fig. 1. Map of field area (modified after Playford et. al., 2009). Samples for this study were collected from four outcrops along the Lennard Shelf in Western Australia; Casey Falls (CL), Virgin Hills Formation at Horse Spring Range (VHS), South Oscar Range (SO), and the Windjana Gorge area (WV). Insets show the location of the Lennard Shelf carbonate system in relation to the Canning Basin and Australia.