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## Paleogeography And Paleoenvironments Of The Late Devonian Kellwasser Event: A Review Of Its Sedimentological And Geochemical Expression

By: Sarah K. Carmichael, Johnny A. Waters, Peter Königsof, Thomas J. Suttner, & Erika Kido

#### Abstract

The Late Devonian (383-359 Ma) was a time of prolonged climate instability with catastrophic perturbation of global marine ecosystems at the Frasnian-Famennian (F-F) and the Devonian-Carboniferous (D-C) boundaries. The causes and mechanisms of anoxia and extinction at the F-F interval are not clearly delineated, and alternative explanations for virtually every aspect of this interval are still intensely debated. In many (but not all) locations, the F-F interval is characterized by two dark, organic-rich lithologies: the Lower and Upper Kellwasser beds (as originally described in Germany) that represent a stepwise ocean anoxia and extinction sequence. The Upper and Lower Kellwasser anoxia event beds are often collectively termed the Kellwasser Event, and the termination of this sequence is within the Upper Kellwasser Event at the F-F boundary. Current knowledge is limited by significant sampling bias, as most previous studies sampled epicontinental seaways or passive continental shelves, primarily from localities across Europe and North America. Together these formed a single equatorial continent with a rising mountain chain during the Late Devonian. Our understanding of the Kellwasser Event is thus based on data and observations from a restricted set of paleoenvironments that may not represent the complete range of Late Devonian environments and oceanic conditions. In the last decade, new methodologies and research in additional paleoenvironments around the world confirm that the Kellwasser Event was global in scope, but also that its expression varies with both paleoenvironment and paleogeography. Studying the many differing geochemical and lithological expressions of the Kellwasser Event using a) a wide variety of paleoenvironments, b) a multiproxy approach, and c) placement of results into the broader context of Late Devonian marine biodiversity patterns is vital for understanding the true scope of ocean anoxia, and determining the causes of the marine biodiversity crisis at the F-F boundary.

**Carmichael, Sarah K.**, Waters, Johnny. A., Königshof, Peter, Suttner, Thomas S., and Kido, Erika (2019). Paleogeography and paleoenvironments of the Late Devonian Kellwasser Event: a review of its sedimentological and geochemical expression, Global and Planetary Change (Special issue on Devonian global changes - recent advances and challenges in different domains, eds. G.Racki and P. Wignall), https://doi.org/10.1016/j.gloplacha.2019.102984. Publisher version of record available at: https://www.sciencedirect.com/science/article/pii/S0921818118306258

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Carmichael, Sarah K., Waters, Johnny. A., Königshof, Peter, Suttner, Thomas S., and Kido, Erika, accepted, *Paleogeography and paleoenvironments of the Late Devonian Kellwasser Event: a review of its sedimentological and geochemical expression*, submitted to Global and Planetary Change (Special issue on *Devonian global changes - recent advances and challenges in different domains*, eds. G. Racki and P. Wignall), https://doi.org/10.1016/j.gloplacha.2019.102984

The copy of record is available from Elsevier at <a href="https://www.sciencedirect.com/science/article/pii/S0921818118306258">https://www.sciencedirect.com/science/article/pii/S0921818118306258</a>

## Paleogeography and paleoenvironments of the Late Devonian Kellwasser Event: a review of its sedimentological and geochemical expression

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### **Graphical Abstract**



Article history: Received 16 November 2018 Received in revised form 27 June 2019 Accepted 28 June 2019 Handling Editor: G. Racki

#### Keywords:

Frasnian-Famennian Kellwasser Event Late Devonian mass extinction ocean anoxia

### Highlights

- There is considerable paleogeographic and paleoenvironmental bias in existing sample sets which precludes full understanding of the Frasnian-Famennian biodiversity crisis and the associated Kellwasser ocean anoxia event.
- The Kellwasser Event was global in scope but its geochemical and lithologic expression in the rock record is highly dependent on both paleoenvironment and paleogeography.
- Analysis of paleoenvironments in a global (rather than local) context suggests that the Kellwasser Event did not occur as a "bottom up" mechanism with upwelling of anoxic bottom waters into shallow water environments, but was likely due to "top-down" climate forcing and/or surface eutrophication.
- The Frasnian-Famennian biodiversity crisis was not a mass extinction resulting from a single catastrophic event, but rather was due to a lack of species origination in environments experiencing long-term environmental stresses, such as climate change coupled with changes in sediment and nutrient supply

### Abstract

The Late Devonian (383-359 Ma) was a time of prolonged climate instability with catastrophic perturbation of global marine ecosystems at the Frasnian-Famennian (F-F) and the Devonian-Carboniferous (D-C) boundaries. The causes and mechanisms of anoxia and extinction at the F-F interval are not clearly

delineated, and alternative explanations for virtually every aspect of this interval are still intensely debated. In many (but not all) locations, the F-F interval is characterized by two dark, organic-rich lithologies: the Lower and Upper Kellwasser beds (as originally described in Germany) that represent a stepwise ocean anoxia and extinction sequence. The Upper and Lower Kellwasser anoxia event beds are often collectively termed the Kellwasser Event, and the termination of this sequence is within the Upper Kellwasser Event at the F-F boundary. Current knowledge is limited by significant sampling bias, as most previous studies sampled epicontinental seaways or passive continental shelves, primarily from localities across Europe and North America. Together these formed a single equatorial continent with a rising mountain chain during the Late Devonian. Our understanding of the Kellwasser Event is thus based on data and observations from a restricted set of paleoenvironments that may not represent the complete range of Late Devonian environments and oceanic conditions. In the last decade, new methodologies and research in additional paleoenvironments around the world confirm that the Kellwasser Event was global in scope, but also that its expression varies with both paleoenvironment and paleogeography. Studying the many differing geochemical and lithological expressions of the Kellwasser Event using a) a wide variety of paleoenvironments, b) a multiproxy approach, and c) placement of results into the broader context of Late Devonian marine biodiversity patterns is vital for understanding the true scope of ocean anoxia, and determining the causes of the marine biodiversity crisis at the F-F boundary.

### 1. Introduction

Raup and Sepkoski (1982) identified four major mass extinctions whose magnitudes were statistically different from background extinction intensities. They also note that "a fifth extinction event in the Devonian stands out from the background but is not statistically significant in these data," (Raup and Sepkoski, 1982, p. 1501). Rather than one sharp and sudden mass extinction event, the Devonian mass extinction is actually a series of pulsed major extinctions at the Givetian-Frasnian (G-F) boundary 383 million years ago, the Frasnian/Famennian (F-F) boundary 372 million years ago, and the Devonian-Carboniferous (D-C) boundary 359 million years ago (see reviews by Becker et al., 2012; Becker et al., 2016). Unlike other mass extinction events that were cosmopolitan, these Devonian extinction events were more targeted in scope. The G-F event was a significant extinction event for benthic groups such as echinoderms and bryozoans (McGhee et al., 2013), the F-F event decimated coral reef ecosystems (Copper and Scotese, 2003), and the D-C boundary primarily affected pelagic organisms such as fish (Sallan and Coates, 2010) and cephalopods (Becker, 1993; Zong et al., 2014). There are already numerous reviews that focus on the specific fossil communities impacted by the Late Devonian extinctions (Becker et al., 2012; Becker et al., 2016: Kaiser et al., 2016: McGhee, 1996: McGhee, 2013; Racki, 2005; Sandberg et al., 2002; Sandberg et al., 1988; Walliser, 1996); this review instead will focus on the lithological and geochemical signatures associated with the F-F extinction, in order to provide important context for both the causes and mechanisms of the Late Devonian mass extinctions as a whole.

#### 1.1. Mass extinction or mass depletion?

Taxonomic severity rankings place the Late Devonian (a combination of the F-F and D-C extinctions) as the fifth to seventh most severe extinction event (Bambach et al., 2004; McGhee, 1996; Stanley, 2007; Stanley, 2016), but when the F-F and D-C extinction events are considered

separately, they are ranked sixth and eighth (Sepkoski, 1996) or sixth and ninth (Bambach et al., 2004), respectively. Concerns about sample bias were dismissed by Bambach et al. (2004), but have been raised with respect to ranking methodologies employed in these earlier studies by Alroy (2010). A later ecological (versus taxonomic) severity index places the F-F and D-C extinctions at fifth-most and fourth-most most severe, respectively (McGhee et al., 2013).

Bambach et al. (2004), Racki (2005), and Stanley (2016) have argued that the decreased diversity at the F-F boundary is the result of dramatic reduction in origination rather than increased extinction, preferring to call it a mass depletion. Stigall (2012) attributed the biodiversity drop to the effect of invasive species migrations rather than a typical mass extinction event. Although most paleontologists agree there was a biodiversity crisis at the F-F boundary, a consensus regarding the mechanism (extinction versus lack of origination) and severity of the crisis (compared to other times of biotic crisis) has remained elusive. One of the main challenges in attaining this consensus is a parallel lack of consensus about the cause of the extinction/depletion itself, due to its variable expression within the rock record.

#### 1.2. Devonian paleoclimate

Understanding the paleoclimates in the Devonian is critical to evaluating its atypical extinction pattern compared with other extinction events. The Devonian was a time of prolonged climate instability triggered by rapid changes in  $CO_2$ , which was likely due in part to the rapid diversification of land plants during the Middle Devonian (Algeo et al., 1995; Algeo and Scheckler, 1998; Algeo and Scheckler, 2010; Algeo et al., 2001). The first multi-storied forests and the first development of thick and widespread topsoil occurred during the Devonian, leading to changes in silicate weathering profiles as well as carbon sequestration in coal beds (Algeo and Scheckler, 1998). This process

also resulted in a massive drawdown of atmospheric CO<sub>2</sub>, resulting in gradual global cooling (Algeo et al., 2001).

Although the Algeo et al. (2001) model for long-term Devonian climate change remains well-established, it has been criticized by Racki (2005) and Sageman et al. (2003), who noted that river-borne nutrients would only stimulate oceanic eutrophication within near-shore or estuarine domains, and that other mechanisms of eutrophication must be invoked for off-shore anoxia.

In contrast to the Algeo et al. (2001) model, Retallack and Huang (2011) presented an alternative scenario for the interval between the emergence of trees and the climatically-driven Famennian glaciation. In their view, the Middle to Late Devonian was characterized by transient extrinsic perturbations, such as volcanoes and meteorite impacts, that affected both atmospheric CO<sub>2</sub> levels and precipitation. Thus, plants muted the impact of these transient climatic spikes through growth and subsequent carbon sequestration. In contrast to the model of Algeo et al. (2001), the model of Retallack and Huang (2011) suggests that woodland expansion repaired the climatic damage caused by extrinsic perturbations rather than caused the CO<sub>2</sub> drawdown. Based on their analysis of paleosols from New York, Retallack and Huang (2011; figure 9) correlated Middle and Late Devonian ocean anoxia events (section 1.3) with intervals of higher temperature and higher than average annual precipitation. This correlation between temperature/precipitation and anoxic facies is consistent with recent models for deposition within the organic-rich Bakken Formation (Petty, 2019). In the Petty (2019) model, high rainfall perhumid conditions resulted in elevated organic and fine sediment deposition in shallow waters within the Lower and Upper Bakken Formation, while arid to semi-arid climates resulted in carbonate and coarser siliciclastic deposition in the Middle Bakken Formation. Other models that use a variety of inputs and proxies likewise support increases in continental runoff with the development of anoxic facies at the F-F boundary (Averbuch et al., 2005; De Vleeschouwer et al., 2017; Percival et al., 2019; Tribovillard et al., 2004, among others).

In addition to the long term changes to Devonian climate that were caused by (or mitigated by) land plants and precipitation, tectonic activity also had a considerable effect on climate. Throughout the Devonian, the equatorial Appalachian/Variscan Mountains were emerging and the Rheic Ocean was closing as Pangaea accreted, resulting in major changes in global climate, increased weathering. and altered ocean circulation (Averbuch et al., 2005; Joachimski and Buggisch, 2002; Racki, 1998). These unprecedented changes in global carbon and nutrient cvcles were associated with several complete reorganizations of both marine and terrestrial ecosystems (McGhee, 1996), and are closely associated with geochemical signals of ocean oxygen loss (anoxia).

#### 1.3 Ocean anoxia in the Devonian

The association of Devonian oceanic anoxia events with extinction events has long been considered ubiquitous, where ocean anoxia has been the accepted mechanism" for these marine mass extinctions for nearly four decades (Becker and House, 1994; Bond and Wignall, 2005; Caplan and Bustin, 1999; House, 1985; Murphy et al., 2000; Walliser, 1980; Walliser, 1983). However, debate still surrounds the cause/effect relationship between anoxia and extinction in the Devonian (Bratton et al., 1999; Copper, 2002; George et al., 2014; Joachimski and Buggisch, 2002; Racki et al., in press; Song et al., 2017a), as the epeiric seas and tectonic basins of eastern North America and Europe generally show a close association between the two (Bond and Wignall, 2008 and references therein), but sites elsewhere (particularly in Australia) do not (Becker et al., 1991; Bratton et al., 1999; George et al., 2014). Some have posited that climate cooling, rather than anoxia, caused the Late Devonian mass extinctions (Copper, 1986; Huang et al., 2018a; Joachimski and Buggisch, 2002; Song et al., 2017a), and that other anoxia events in the Devonian do not appear to be related to widespread extinction events at all (Becker et al., 2012; Brett and Baird, 1995).

The most severe of the Late Devonian ocean anoxia events are the Kellwasser Event, a coupled anoxic interval associated with the dramatic decrease in diversity at the F-F boundary (Walliser, 1996; Becker et al., 2012; Gereke and Schindler, 2012), and the Hangenberg Event, a complex combination of anoxia and sea-level change associated with similar diversity decreases and the D-C boundary (see reviews by Kaiser et al. (2016) and Becker et al. (2016)). In some studies, the Kellwasser Event is divided into the Lower Kellwasser Event (LKE) and Upper Kellwasser Event (UKE); this differentiation is based on its appearance in Germany, where it forms two distinct beds (referred to as the Lower and Upper Kellwasser Horizons) (Buggisch, 1991; Riquier et al., 2006; Schindler, 1990a; Schindler, 1990b). The LKE is found within the Lower gigas/Palmatolepis rhenana Zone, and the UKE is found at the top of the Palmatolepis linguiformis Zone, which forms the F-F boundary (Becker et al., 2012; Klapper et al., 1994). In studies where there is no differentiation, the term "Kellwasser Event" typically refers to the UKE at the F-F boundary, per Walliser (1986).

Comprehensive reviews of the Hangenberg Event and D-C extinction already exist (Becker et al., 2016; Kaiser et al., 2016), but aside from numerous reviews of the F-F extinction and its expression in the fossil record (see Becker et al., 2012 for references), there are no recent reviews that concentrate on the geochemistry and sedimentology of the F-F boundary and the lithological manifestations of the Kellwasser Event.

# *1.4 Paleogeography and paleoenvironments of Late Devonian studied sections*

Early research by Goodfellow et al. (1988), Buggisch (1991), and Sandberg et al. (2002) on were based only on Variscan sites in Europe and Morocco, with additional

reviews also restricted to single regions, such as South China (Ma et al., 2016) and eastern North America (Over, 2002). Bond and Wignall (2008) do discuss the Kellwasser Event and F-F boundary on a global scale, but only in the context of sea-level changes. Although there are several reviews that focus on links between Devonian anoxia events and extinctions in general (McGhee, 1996; McGhee, 2013; Racki, 2005; Walliser, 1996), many of these are also based primarily on data from Laurussia (Europe and North America) and northern Gondwana (North Africa), and a handful of sites in South China and Australia.

Racki (2005) noted the strong paleogeographic bias in low latitude versus high latitude localities. In this review, we aim to expand significantly the discussion of sampling bias and the role it has played in our understanding of both the Kellwasser Event and F-F extinction. In the last decade, a number of new localities across the F-F boundary have been described in southeast Asia, central Asia, Siberia, and South America, and there are a number of new studies from additional sites in Australia and South China. These newer studies complicate many previous explanations offered for the Kellwasser Event that were developed on the basis of data from the epeiric seas and continental margins of the equatorial Laurussian and northern Gondwana continental blocks.

In light of the ongoing contradictions that occur through the comparison of old data from established field sites, new data from new field sites, and new analytical methods applied to both established field sites and new field sites, we find it necessary to step back and review how to recognize the Kellwasser Event in the rock record, as its expression appears to be highly dependent on paleoenvironment. A narrow lithological definition of how the Kellwasser Event "should" look, despite multiple examples of evidence to the contrary, hinders our understanding of the oceanic conditions that resulted in this event. Our goal is to construct a global (rather than regional) context for looking at the lithologic and geochemical expression of the Kellwasser Event, and use that information to provide constraints on its potential causes.

# 2. The Kellwasser Event: how is it recognized and defined?

The Kellwasser Event is named for the "Kellwasser Kalke" beds in the Harz Mountains in Germany (Römer, 1850). At the top of the Frasnian in the Kellwasser Kalke section, two black shales separated by limestone are defined as the Upper and Lower Kellwasser Horizons (Buggisch, 1991; Riquier et al., 2006; Schindler, 1990a; Schindler, 1990b). In later studies these are typically referred to as the Upper Kellwasser Event (UKE) and the Lower Kellwasser Event (LKE), or are coupled for simplicity and referred to as "the Kellwasser Event." In studies where the UKE and LKE are not specifically distinguished, the Kellwasser Event typically (but not always) refers to the UKE (Supplemental Table 1). Although Buggisch (1991) originally noted that the UKE and LKE can be variable in lithology, distribution, and appearance in the field, many authors continue define the Kellwasser Event in relation to its type section: as a black shale or black bituminous limestone with a positive  $\delta^{13}$ C excursion, even if the studied section does not exhibit these lithologies or isotopic signatures (Supplemental Table 1). In basinal and epicontinental sediments from Europe, eastern North America, North Africa, and South China, the Kellwasser Event is typically (but not always) preserved as a distinct UKE and LKE couplet of black shales or bituminous black limestones with positive  $\delta^{13}$ C excursions (Fig. 1, Supplemental Table 1). In shallow marine or intermediate depth sediments from parts of western North America, South America, northwestern China, Australia, Siberia, or southeast Asia, however, the expression of the Kellwasser Event is far more variable (Fig. 1, Supplemental Table 1) which has led some to argue that the UKE and LKE were localized rather than global in scope (Bond and Wignall, 2005; John et al., 2010; Whalen et al., 2015; White et al., 2018, among others). Others have argued that the UKE and LKE represent somewhat different events rather than a coupled event that represents identical environmental stresses (Boyer et al., 2014; Kelly et al., 2019; Riquier et al., 2006; Riquier et al., 2005). For these reasons, it is vital to recognize on a global scale which Late Devonian paleoenvironments were conducive to black shale development and positive  $\delta^{13}$ C excursions and which were not.

# 2.1. Paleogeographic and paleoenvironmental distribution

There are over 310 studies of 155 Kellwasser and F-F boundary localities where biostratigraphicallyor chemostratigraphically-constrained lithologic data are available (Fig. 1, Supplemental Table 1). Of these, Laurussia/Euramerica accounts for 66% of all studies of this interval, with 204 published studies on a total of 102 sites. In contrast, there are 33 studies across 21 sites in Gondwana (Australia, Africa, India, the Middle East, and South America combined), six studies across five sites in Iran, two studies based on two sites in Siberia, 49 studies on 18 sites in South China, seven studies from three sites in the Sibumasu/Inthanon region (Thailand and southern China), one study from one site on the Tarim Craton, and seven studies from two sites in the Central Asian Orogenic Belt, or CAOB (Mongolia, Kazakhstan, and northwest China). Most of the sites that exhibit a "typical" Kellwasser black shale or bituminous limestone sequence are within the Variscan/Appalachian epicontinental basins, epeiric seas, and other restricted tectonic basins from areas surrounding the closing Rheic Ocean, particularly in eastern North America, northern Africa, and Europe (Fig. 1).

Although Laurussia and northern Gondwana have generally been considered separate regions, there has been a long and lively debate within the tectonics literature



Fig. 1. Top: Approximate palaeogeographic locations of all 154 known study sites of the Late Devonian Kellwasser Anoxia Event and F-F extinction horizons that contain detailed stratigraphic logs constrained by biostratigraphy or chemostratigraphy (Table 1, supplemental data). Base map from Blakey (2016), with some continent positions and shapes modified from the tectonic data of Hara et al. (2010), Metcalfe (2011), and Xiao et al. (2010). Bottom: paleogeographic distribution of studied sections and the number and percentage of studies associated with each paleogeographic region.

about how close these regions actually were to each other (see reviews by Edel et al., 2018; Franke et al., 2017). Paleomagnetic data of the region originally suggested a wide ocean separating Laurussia and Gondwana during the Late Devonian (Tait et al., 2000), while biogeographic data suggested a narrow ocean (McKerrow et al., 2000). Newer paleogeographic studies of the Variscan region still present some uncertainties. Using paleomagnetism, petrology, structural geology, and biogeography surveys, Franke et al. (2017) suggest that the Variscan orogenic basins were closing from north to south (or had closed already) by the Late Devonian, while internal narrow basins were opening due to strike-slipe extension. Kinematic modeling likewise suggests that northwest Gondwana and southern Laurussa were sutured by 370 Ma (Young et al., 2018). In contrast, trace element geochemistry and zircon provenance analysis by Eckelmann et al. (2014) suggests that the northern part of the Rheic Ocean remained open through the beginning of the Carboniferous, and contained numerous island arcs and small islands. Regardless of tectonic interpretations, all sites with black shale facies most likely were located quite close together during the Late Devonian, at least within the southwestern part of

Laurussia and Gondwana, despite being located on three different continents today.

In addition to their proximity, these equatorial/tropical basins epeiric seaways and tectonic of the Euramerica/Laurussia paleocontinent were affected by the shedding of massive quantities of sediment from the rising Appalachian/Variscan mountain chain (Averbuch et al., 2005). It is therefore possible that much of what have been considered to be "typical" Kellwasser Event sequences actually represent deposition affected by a specific active mountain building regime instead of representative oceanic conditions. Racki (1998). Joachimski and Buggisch (2002) and Tribovillard et al. (2004) likewise argue that tectonic forces may have exerted a strong influence on the dynamics of the F-F transition, even in quiescent paleoenvironments.

Paleoenvironmental distributions of sites (Fig. 2) tell an even more skewed story than paleogeographic distributions, where 71 sections (46%) are from deep water, basinal or deep shelf paleoenvironments, 18 sections (13%) are from shallow water reefs or lagoonal/peritidal environments, 63 sections (43%) are from shallow continental shelf environments, and three sections (2%) are from shallow water island arc environments with steep slopes. Schematic diagrams of these environments are shown in Fig. 3.

The black shale facies are associated mainly with deep water, basinal environments and a few shallow shelf environments (Fig. 2, Supplemental Table 1), which are topographically capable of trapping and sequestering organic carbon within fine clastic sediments (Fig. 3), although pelagic facies settings are not necessarily always associated with black shales and/or bituminous dark limestone facies (Königshof et al., 2012; Racki et al., in press). In general, the reef-related paleoenvironments do not exhibit black shale or bituminous black limestone facies (Fig. 2, Fig. 3, Supplemental Table 1). These shallower environments tend to be understudied in comparison to basinal environments because there is not a visual representation of the Kellwasser Event in the field to help mark the area of interest (Fig. 3), and conodont biostratigraphy can be somewhat less precise in shallow water environments (Sandberg and Dreesen, 1984; Wang et al., 2016).

Nevertheless, shallow water anoxia interpreted as the Kellwasser Event has been recently documented using a variety of methodologies in locations around the globe, including Europe (Mottequin and Poty, 2016; Weiner et al., 2017), western North America (Bond et al., 2013; Petty, 2019), the eastern United States (Bush et al., 2015), and the Central Asian Orogenic Belt (Carmichael et al., 2014). Taken together, these new studies show that it is indeed possible to find the Kellwasser Event in shallow water



Paleoenvironment

Fig. 2. Distribution of black shale facies for each category of paleoenvironment for sites in Table 1 (supplementary data). There are essentially no black shales associated with island arcs or shallow water reef sites, and very few associated with shallow shelf environments.

paleoenvironments. These studies also underscore the obvious paleoenvironmental sample bias within Late Devonian sections (Fig. 2), which when taken with the paleogeographic sample bias (Fig. 1), has caused previous researchers to undercount the number of locations that exhibit the Kellwasser Event and, in turn, skewed the understanding of this event's onset mechanism and root causes.

#### 2.2. Stable isotope expression

If the lithological expression of the Kellwasser Event varies across different paleoenvironments and paleogeographic settings, it is certainly possible that the isotopic expressions of the Kellwasser Event could likewise be variable. Evidence for this variability is provided in numerous studies of carbon, oxygen, sulfur and other isotopes across the F-F boundary (Supplemental Table 1).

#### 2.2.1. Stable isotopes: carbon

A positive excursion in  $\overline{\delta}^{13}$ C in both carbonates and organic carbon has typically been one of the chemostratigraphic markers for the Kellwasser Event (Supplemental Table 1). These positive excursions at the UKE and LKE are noted throughout many European basinal sections in Laurussia, including Germany (Bond et al., 2004; Buggisch, 1991; Buggisch and Joachimski, 2006; Joachimski et al., 2002; Joachimski and Buggisch, 1993; Joachimski et al., 2002; Joachimski and Buggisch, 1993; Joachimski et al., 2006; Schindler, 1993), Belgium (Casier, 2017; Kaiho et al., 2013), Austria (Bond et al., 2004; Buggisch and Joachimski, 2006; Joachimski and Buggisch, 1993), France (Bond et al., 2004; Dopieralska et al., 2016; Joachimski and Buggisch, 1993; Tribovillard et al., 2004), Poland (Bond et al., 2004; De Vleeschouwer et al., 2013; Joachimski et al., 2002; Joachimski et al., 2001; Racki et al., 2002), and the Urals of eastern Russia (Gharaie et al., 2007; Izokh, 2009; Yudina et al., 2002). Interestingly, an island arc carbonate platform section in the Urals exhibits a weak positive excursion immediately above the F-F boundary, but not in the expected location of the UKE, which has no excursion (Mizens et al., 2015).

The North American Laurussian sections are somewhat less uniform than those in Europe. While some of the Appalachian foreland basin sections in the United States show positive  $\delta^{13}$ C excursions through the UKE and LKE (Murphy et al., 2000; Sageman et al., 2003), others show negative  $\delta^{13}$ C excursions or show excursions that are somewhat offset from the UKE and LKE intervals expected from biostratigraphy (Lash, 2017; Uveges et al., 2018) or do not show significant excursions at all (Tuite and Macko, 2013; Uveges et al., 2018). In the cratonic basins in the midcontinent, a mix of positive excursions are associated with the UKE (Bond and Wignall, 2005; Day and Witzke, 2017) as well as sections where there is no appreciable change in  $\delta^{13}$ C across the UKE or LKE (Uveges et al., 2018). Sections in the western part of North America are even more variable, with positive excursions (Wang et al., 1996; Whalen et al., 2015), no excursions (Goodfellow et al., 1988), negative excursions (Wang et al., 1996), or coupled positive excursions in carbonate with negative excursions in organic carbon (Levman and Bitter, 2002).

In Gondwana, generally positive excursions across the UKE and LKE are found in Morocco (Dopieralska et al.,



epeiric seas/tectonic basins



2006; Joachimski et al., 2002), with a tentative positive excursion in Libya (Elkelani et al., 2014). Although  $\delta^{13}$ C was measured in organic carbon from a core in Bolivia, there are some sampling gaps coupled with biostratigraphic uncertainty that make determining the presence (or absence) of an excursion conjectural (Haddad et al., 2016). In the Lennard Shelf and Canning Basin of Australia,  $\delta^{13}$ C excursions are present but provide somewhat contradictory information. Positive excursions are correlated with the biostratigraphic locations of the UKE and LKE at the Casey Falls section (Hillbun et al., 2015; Joachimski et al., 2002), and the Dingo Gap section (Stephens and Sumner, 2003), and for the UKE but not the LKE at the McWhae Ridge section (Goodfellow et al., 1988; Joachimski et al., 2002; Playford et al., 1984).

Positive  $\delta^{13}$ C excursions pre-date the expected location of the UKE and LKE in the Horse Spring Range (both section and core samples) (George et al., 2014; Hillbun et al., 2015), the South Oscar Range (Hillbun et al., 2015; Stephens and Sumner, 2003), and the Windjana Valley section (Hillbun et al., 2015; Stephens and Sumner, 2003).

Carbon isotope signatures from deep-water basins in the South China continent are highly variable. There are negative excursions in  $\delta^{13}$ C in many sections (Gharaie et al., 2007; Ma and Bai, 2002; Wang et al., 1991; Zheng et al., 1993), but positive excursions in others (Chen et al., 2005; Huang and Gong, 2016; Königshof et al., 2012; Song et al., 2017a; Xu et al., 2008; Xu et al., 2003), sites where the UKE has a positive excursion and the LKE has a negative excursion (Huang et al., 2018b) and still others where there is no pronounced excursion at all (Whalen et al., 2015). Locations from the Sibumasu microcontinent and the Inthanon Zone do show positive  $\delta^{13}$ C excursions, but do not contain a black shale lithofacies (Königshof et al., 2012; Racki et al., in press; Savage, 2013; Savage et al., 2006). The Thong Pha Phum section from the exhibits UKE  $\delta^{13}C$ Sibumasu terrane signatures comparable with the peculiar Western Australian signature of the Kellwasser Event (Racki et al., in press). In contrast, shallow water sections in the Central Asian Orogenic Belt area in northern China and in Siberia appear to show negative excursions at the UKE (Carmichael et al., 2014; Izokh et al., 2009; Wang et al., 2016), while basins from the Iranian microcontinent also show negative excursions at the UKE (Gharaie et al., 2007). These negative excursions are coupled with negative excursions in  $\delta^{18}O$ and have generally been interpreted as diagenetic alteration, although negative  $\delta^{13}$ C excursions in the CAOB could also be due mixing of freshwater and seawater, a concept that is supported by the presence of nearshore euryhaline fossil assemblages at the F-F boundary (Song et al., 2017b; Suttner et al., 2014; Wang et al., 2016).

Even the earliest studies of  $\delta^{13}$ C across the Kellwasser Event noted that positive excursions are not always present (Schindler, 1993). As it is not uncommon to have highly variable  $\delta^{13}$ C patterns outside of Laurussia, the absence of positive  $\delta^{13}$ C excursions across the UKE and LKE intervals should not preclude further investigations into the presence or absence of ocean anoxia using other proxies (ichnology, trace element geochemistry, pyrite framboid analysis, organic geochemistry, etc.).

#### 2.2.2. Stable isotopes: oxygen

Oxygen isotope signatures (which act as a proxy for sea surface temperatures) across the F-F boundary and Kellwasser Event interval remain puzzling. Calcite can easily exchange <sup>16</sup>O and <sup>18</sup>O with water via dissolution/reprecipitation reactions during diagenesis (see Carmichael and Ferry, 2008 for references and relevant mass transfer and rate calculations); therefore most published  $\delta^{18}$ O values in carbonates across the UKE and LKE are used as tests for the degree of diagenesis or alteration of  $\delta^{13}$ C values rather than actual estimates of Late Devonian seawater signatures.

Compilation studies on well preserved brachiopods show that their  $\delta^{18}$ O values vary widely, by as much as 10‰ (Van Geldern et al., 2006; Veizer et al., 1999). Overall, average brachiopod  $\delta^{18}O$  values of -5‰ and -6‰ PDB (Veizer et al., 1999) indicate extremely warm temperatures of Late Devonian seawater from 31-41°C, which is above the lethal temperature for many modern marine organisms (Thompson and Newton, 1988; Van Geldern et al., 2006). Some have argued for a different  $\delta^{18}$ O value of Devonian seawater to explain this phenomenon (Carpenter et al., 1991), but conodont apatite  $\delta^{18}$ O values do not support significant changes of the oxygen isotope signature of Devonian seawater compared to other time periods (Joachimski et al., 2004). The reasons for this discrepancy between calcite and apatite  $\delta^{18}O$  signatures remain unresolved, but conodonts do provide more realistic sea surface temperature values and do not require changes in the  $\delta^{18}$ O of the entire ocean (Joachimski et al., 2004).

Conodont apatite values of  $\delta^{18}$ O have been used in a variety of studies as a proxy for ocean paleotemperatures, and have been measured in studies of the F-F boundary from South China (Huang et al., 2018a), Germany (Girard et al., 2018; Joachimski et al., 2009; Joachimski and Buggisch, 2002), France (Girard et al., 2018; Le Houedec et al., 2013), the Czech Republic (Joachimski et al., 2009), Poland (Joachimski et al., 2009), Morocco (Le Houedec et al., 2013), and Australia (Joachimski et al., 2009). Variations in  $\delta^{18}$ O between conodont taxa are explained by habitat variations (i.e. water depth), and there are variations between sections as well, corresponding to the local temperature of each paleoenvironment (Girard et al., 2018). Conodont paleotemperature estimates suggest overall warming temperatures (to 35°C) leading up to the F-F boundary and into the Famennian (Joachimski et al., 2009), but with pulses of cooling at the onset of the Kellwasser Event, with the most severe at the UKE (Balter et al., 2008; Huang et al., 2018a; Joachimski et al., 2009; Joachimski and Buggisch, 2002).

Calcite and apatite are not the only sedimentary minerals used for  $\delta^{18}$ O analysis; John et al. (2010) analyzed the  $\delta^{18}$ O of carbonate-associated sulfate (CAS) and found no change in oxygen isotope values in sulfate across the F-F boundary or across the UKE and LKE in European sections, suggesting that any changes in the sulfur cycle were local, rather than global.

#### 2.2.3. Stable isotopes: strontium

<sup>87</sup>Sr/<sup>86</sup>Sr is typically used in the sedimentary record to show the relative inputs of continental weathering material vs. hydrothermal activity to the global ocean Sr budget. Across the F-F boundary, most <sup>87</sup>Sr/<sup>86</sup>Sr measurements do not show any particular trends, either across a single section (Chen et al., 2005) or using well-preserved brachiopod shells from representative sections around the world (Van Geldern et al., 2006). Other studies that lack an obvious excursion may be due to a low sampling density across the measured interval and/or diagenetic alteration (Gharaie et al., 2007), or may simply be due to a high degree of scatter when comparing rocks from differing locations (Denison et al., 1997). Only one study to date (from one site) shows any sort of trend in <sup>87</sup>Sr/<sup>86</sup>Sr values across the Kellwasser Event, where coupled positive  $^{87}$ Sr/ $^{86}$ Sr and  $\delta^{66}$ Zn isotope excursions are hypothesized to represent a global cooling and regression at both the UKE and LKE, via extreme continental weathering (Wang et al., 2018). Continental weathering may not be the only way to explain increases in radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr in the rock record: emerging work by Emsbo et al. (2018) links ocean eutrophication with the rapid release of biolimiting metals sedimentary-exhalative (SEDEX) hydrothermal from systems into sedimentary basins. These brine discharges are recorded locally in the rock record by elevated <sup>87</sup>Sr/<sup>86</sup>Sr signatures that exceed modern riverine input into oceans (Emsbo et al., 2018), and are correlated with ocean anoxic events throughout the Phanerozoic.

#### 2.2.4. Stable isotopes: nitrogen

Stable isotopes of nitrogen ( $\delta^{15}N_{org}$ ) are used in the rock record to track biologically available nitrogen, nitrogen cycling, and redox processes. Positive excursions in  $\delta^{15}N_{org}$  are expected within mass extinction horizons associated with plankton blooms (Liu et al., 2016 and references therein). The  $\delta^{15}N_{org}$  signature of the Kellwasser Event, however, is contradictory and appears to be highly dependent on local terrestrial-marine interactions.

Haddad et al. (2016) detected no change in  $\delta^{15}N_{org}$  across the F-F boundary, either in the low-latitude Appalachian Basin (in New York) or in the high latitude Madre de Dios Basin of southern Gondwana (Bolivia). Likewise, Tuite and Macko (2013) detected no changes in nitrogen isotopes across the F-F boundary or UKE and LKE in three sites in the Appalachian Basin (also in New York), In order to account for this apparent discrepancy, these authors suggested that terrestrial runoff may have overprinted the possible signatures of marine nitrogen fixation.

In contrast, Uveges et al. (2018) found a negative excursion at the UKE and LKE in the Appalachian Basin, but no obvious changes in the Iowa basin sections. Other sections from the Iowa Basin do show a negative trend at the F-F boundary (de la Rue et al., 2007), but low sampling density and an unconformity near the F-F boundary complicate interpretations of this pattern. An ambiguous pattern is also present in the Moose River Basin of Ontario, Canada (Levman and Bitter, 2002), where there is a negative trend in  $\delta^{15}N_{org}$  at the F-F boundary instead of a positive trend. Despite considerable scatter in the data, sections in the Jasper Basin in Alberta, Canada do show a coupling between  $\delta^{15}N_{org}$  and  $\delta^{13}C_{org}$ , but in South China this signal seems reversed (or at least not correlated), which has been attributed to a lack of detrital input in the Fuhe/Yangdi section (Whalen et al., 2015). Clearly, the existing nitrogen data across the F-F boundary and UKE and LKE are highly variable and this variability may be caused by any number of external factors. Accordingly,  $\delta^{15}N_{ord}$  is perhaps not the best proxy for determining global perturbations in the nitrogen cycle at this time.

#### 2.2.5. Stable isotopes: sulfur

Sulfur isotopes ( $\delta^{34}$ S) and sulfur fractionation ( $\Delta^{34}$ S =  $\delta^{34}$ S<sub>CAS</sub> –  $\delta^{34}$ S<sub>py</sub>, where CAS = calcite-associated sulfate and py = pyrite) are a useful way to track bacterial sulfate reduction and sulfur cycling in marine ecosystems.

In South China, Chen et al. (2013) note a positive excursion in both  $\delta^{34}S_{CAS}$  and  $\delta^{34}S_{py}$  at upper Palmatolepis triangularis zone in the Famennian but no appreciable change in sulfur signatures through UKE or LKE. The Moose River Basin in Ontario, Canada has variable  $\delta^{34}$ S values (CAS and py are not differentiated) does not show any clear trend associated with F-F boundary or UKE and LKE, and may only show changes in lithology (Levman and Bitter, 2002). In contrast, Wang et al. (1996) found positive excursions in  $\delta^{34}S_{ov}$  across the F-F boundary in sites in the Jasper Basin in Alberta, Canada. Bingham-Koslowski et al. (2016) record an overall negative  $\delta^{34}$ S signature throughout the Kettle Point section in Ontario, indicating long-term anoxic conditions in the Chatham Sag. Their data also contain two negative excursions at the expected location of the UKE and LKE (represented by single points) that they interpreted as intervals of more severe anoxia, but the biostratigraphy of the section is not well constrained and the sample interval is quite large (1 m or more). John et al. (2010) found no changes in  $\delta^{34}S_{CAS}$  across F-F boundary in sections in Belgium and Poland, and Sageman et al. (2003) show a single  $\delta^{34}S_{py}$  data point (in a very small data set) that creates a positive enrichment immediately above the F-F boundary. Like nitrogen isotopes, sulfur isotopes do not appear to be particularly useful in chemostratigraphic correlations or in determining sulfur cycling at this time.

#### 2.2.6. Stable isotopes: neodymium, uranium, and osmium

Neodymium isotope  $(\epsilon_{\text{Nd}})$  data has long been recognized as a proxy for distinguishing ocean water masses and

weathering inputs (Piepgras and Wasserburg, 1980), and has been used in paleoceanographic studies to track transgressions and regressions. Neodymium isotopic values extracted from conodonts across basinal sections in Morocco, Poland, France, and Germany (Dopieralska et al., 2006; Dopieralska et al., 2016) are somewhat variable, but their overall negative pattern in relation to Kellwasser facies rocks suggests that short-term regressions were occurring at the onset of both the UKE and LKE. This interpretation appears to be in good agreement with studies of oxygen isotopes in conodont apatite (section 2.2.2) that suggest the UKE and LKE were coeval with cooling pulses. However, it conflicts with interpretations from studies using sequence stratigraphy (section 2.6), which suggest the UKE and LKE were associated with sealevel rise. New measurements of osmium isotope ratios (<sup>187</sup>Os/<sup>188</sup>Os) suggest that extreme continental weathering may have caused the onset of the UKE. LKE, and possibly even the less severe Annulata Event in the Famennian (Percival et al., 2019). Although the trigger mechanism for these weathering pulses remains conjectural, these authors do suggest that the weathering products were an important contributor to marine anoxia throughout the Late Devonian.

New uranium isotope ( $\delta^{238}$ U) data from the carbonates of the Devil's Gate Formation in Nevada (White et al., 2018) and the Baisha section of South China (Song et al., 2017a) are now being used to model global oceanic redox conditions, due to the long residence time of  $\delta^{238}$ U signatures compared to oceanic mixing timescales. Both studies show positive excursions in  $\delta^{238}$ U at the onset of either the UKE alone (White et al., 2018) or both the UKE and LKE (Song et al., 2017a). The interpretation of these excursions offered by these authors differs considerably and the signatures are not particularly similar when plotted across conodont zones. White et al. (2018) suggest that  $\delta^{238}$ U signatures provide evidence for mixing of epeiric seawater with the open ocean seawater except during the Kellwasser Events (particularly the Upper Kellwasser Event), and that anoxia was restricted to epeiric seas. In contrast, Song et al. (2017a) suggest that  $\delta^{238}$ U signatures suggest not only a decoupling between redox conditions and productivity, but a complex scenario of ocean stratification and anoxic conditions at the onset of the Upper and Lower Kellwasser Event horizons due to longterm global warming, resulting in significant organic carbon accumulation and a drawdown of atmospheric CO<sub>2</sub>, leading glaciation and a mass extinction horizon at the F-F boundary due to climate cooling. Obviously, these interpretations are contradictory.

# 2.2.7. Stable isotopes: caveats, considerations and very different interpretations

Outside of Laurussia and parts of Gondwana, the  $\delta^{13}$ C patterns across the UKE and LKE appear to be variable, and at times contradictory. Local factors (in addition to diagenetic alteration) have been invoked to explain the decoupling of  $\delta^{13}$ C<sub>org</sub> from the global  $\delta^{13}$ C<sub>carb</sub> signature (Uveges et al., 2018), and some have suggested that 10

isotopic signatures from epeiric seas and restricted tectonic basins may not even represent global ocean isotope signatures (Brand et al., 2009; Dopieralska et al., 2006 and references therein; Holmden et al., 1998; Joachimski et al., 2009). There are further conflicting interpretations concerning the communication between water masses in the Late Devonian using a single isotope in the case of  $\delta^{238}$ U (Song et al., 2017a; White et al., 2018), although conodont  $\delta^{18}$ O and  $\epsilon_{Nd}$  appear to be in agreement in regards to interpretation (climate cooling and regressive events with the UKE and LKE), but not with sequence stratigraphy patterns (Johnson et al., 1985; McClung et al., 2013). It appears that conflicting signals are the norm rather than the exception; this is true when comparing the same isotope pattern across different paleogeographic regions, when interpreting different isotope signatures against each other, and when comparing different isotope signals against lithology, ichnofacies, or stratigraphy. Therefore, local isotopic investigations are likely suspect until considered in the context of all the available paleogeographic, trace element, and mineralogical data.

#### 2.3 Geochemical and mineralogical expression

#### 2.3.1. Trace elements

Trace elements have been used in numerous studies to determine the severity of anoxia during the Kellwasser Event in locations throughout Europe and eastern Russia (Bond et al., 2004; Girard and Lécuyer, 2002; Moreno et al., 2018; Pujol et al., 2006; Racki et al., 2002; Rakociński et al., 2016; Riguier et al., 2007; Riguier et al., 2006; Riquier et al., 2005; Tribovillard et al., 2004; Weiner et al., 2017; Yudina et al., 2002), North America (Algeo and Tribovillard, 2009; Bond et al., 2013; Geldsetzer et al., 1993; Goodfellow et al., 1988; Lash, 2017; Over et al., 1997; Sageman et al., 2003; Ver Straeten et al., 2011; Whalen et al., 2015), South China (Gharaie et al., 2007; Huang et al., 2018b; Wang et al., 1991; Xu et al., 2008; Zeng et al., 2011), North Africa (Riboulleau et al., 2018), Australia (George et al., 2014; Hillbun et al., 2015), and the CAOB (Carmichael et al., 2014). Trace elements can be particularly useful in determining the presence or absence of the Kellwasser Event in locations where the "characteristic" basinal black shales are not present (Bond et al., 2004; Bond et al., 2013; Carmichael et al., 2014; George et al., 2014; Gharaie et al., 2007; Hillbun et al., 2015; Mizens et al., 2014; Racki et al., 2002; Weiner et al., 2017), but their utility is highly dependent on local mineralogy, availability of organic carbon, and degree of diagenetic alteration (Algeo, 2004; Banner and Hanson, 1990; Tribovillard et al., 2006). Furthermore, in locations where both the UKE and LKE are present, their trace element signatures often differ (Riguier et al., 2006; Riguier et al., 2005). This is consistent with work by Boyer et al. (2014) and Kelly et al. (2019), who noted the same difference between UKE and LKE expressions in ichnofacies and microfossils (section 2.4), and numerous studies in South China that noted different carbon isotope signatures between the UKE and LKE (described in detail in section 2.2.1).

#### 2.3.2. Organic Chemistry

Organic compounds within the organic matter (OM) fraction of rocks act as biomarkers for different organic inputs, such as terrestrial biomass or marine plankton biomass. They can also provide information about redox conditions of a column. particularly photic-zone water anoxia. Prasinophyte blooms (a "disaster taxa" green algae) are thought to mainly occur in cold-water environments, in brackish surface layers of salinity-stratified basins and may represent dysoxic to anoxic conditions and have been reported from various Palaeozoic black shales (Riegel, 2008; Tyson, 1995) including the Kellwasser black shales in the Eifel area, Germany (Hartkopf-Fröder et al., 2007). At the Kowala Quarry in Poland, organic biomarker analysis shows evidence for a prasinophyte bloom in the form of elevated C28/C29 ratios at the F-F boundary (Joachimski et al., 2001; Schwark and Empt, 2006), as well as increased green sulfur bacteria and photic zone anoxia (in the form of elevated isorenieratane) in the aftermath of the F-F event (Marynowski et al., 2011). Gong et al. (2002) suggest the possibility red tide events at the F-F boundary in shallow water sections in South China based on pristane/phytane ratios, although dinoflagellates (the organisms that cause red tides today) are not found in the rock record until the Triassic (Stover et al., 1996). Attributing ratios of organic compounds to specific organisms can also be problematic if the thermal maturity of organic matter is not taken into account (Joachimski and Buggisch, 2003).

Organic geochemistry can also provide useful information about the source of OM preserved in the rock record. Organic geochemistry combined with other proxies in the Ghadames Basin in in northern Gondwana (Libya) indicate that most of the organic matter preserved in the basin was terrestrial in origin, except at the F-F boundary where it was marine in origin (Riboulleau et al., 2018). In the Canning Basin of Australia, Spaak et al. (2018) suggest that there were different sources of organic carbon depending on the section's location within the basin; i.e. some regions of the basin have OM associated with terrestrial runoff, and other regions indicate OM from a microbial source, possibly due to ocean stratification. A comparison of high and low latitude sections in the Appalachian Basin (New York) and Madre de Dios Basin (Bolivia) show differences in organic geochemical signatures (Haddad et al., 2016), further underscoring the localized nature of each biomarker signature. This point is well made in light of work by Kaiho et al. (2013), which suggested wildfires with runoff and soil erosion contributed to the UKE and resulting F-F extinction, at least within the Namur-Dinant Basin in Belgium. We note, however, that Marynowski and Racki (2015) disputed the results of Kaiho et al. (2013), interpreting the geochemical signatures to be the result of diagenesis.

While very useful for understanding individual basin dynamics, organic geochemistry is probably not the best tool for trying to extrapolate global signatures of organic 11

carbon (at least for the F-F extinction and the UKE and LKE), as it is very unlikely that the entire world simultaneously caught on fire, that the same exact microorganisms bloomed at the same time globally, all parts of all basins had equivalent patterns of terrestrial vs. marine organic inputs at the same time, or every section underwent simultaneous, identical diagenetic alteration.

#### 2.3.3. Mineralogical expression: pyrite framboids

Pyrite framboids have long been used as general indicators of anoxia (Love, 1966). Size distributions of framboids can determine not only the presence but also relative severity of anoxia in both modern and ancient environments (Paschall et al., 2019; Wignall and Newton, 1998; Wilkin and Barnes, 1997; Wilkin et al., 1996; Wilkin et al., 1997), and provide information about local sedimentation rates (Gallego-Torres et al., 2015). Pyrite framboid size distributions are a particularly useful tool for determining the severity of anoxia in mixed lithologies where trace element excursions can be masked or superimposed (Bond and Wignall, 2005; Carmichael et al., 2016; Carmichael et al., 2014). Care must be taken to screen for morphologies that indicate framboid formation in burrows or algal cysts, which represent localized anoxic conditions below the sediment-water interface (Carmichael et al., 2016; Schieber and Baird, 2001; Wang et al., 2013), or other post-depositional indicators (Cavalazzi et al., 2012; Lin et al., 2016; Love, 1971; Scott et al., 2009; Wacey et al., 2015). Framboidal pyrite size distributions have been used to determine the relative severity of anoxia both in basinal paleoenvironments during and immediately after the Kellwasser Event (Bond and Wignall, 2005; Bond et al., 2004; Marynowski et al., 2011; Riquier et al., 2006), as well as in shallow water locations (Bond et al., 2013; Carmichael et al., 2014).

#### 2.4. Trace fossil and microfossil expressions of anoxia

Ichnofacies and microfossil studies in the Appalachian Basin in New York indicate that the basin experienced persistent oxygen stress, but not persistent anoxia or euxinia (Boyer et al., 2014; Haddad et al., 2018; Kelly et al., 2019). Detailed trace fossil analysis does not support rapid-onset anoxia or euxinia as a cause of the F-F extinction event in the Appalachian Basin, and bottom water conditions fluctuated in oxygen levels leading up to the crisis, where smaller organisms were able to survive these oxygen stresses but larger organisms could not (Boyer et al., 2014). Trace fossil and microfossil observations also suggest that the UKE and LKE in the Appalachian Basin were different both in scope and severity, despite their similarities in lithology and geochemistry (Boyer et al., 2014; Kelly et al., 2019). This interpetation is consistent with observations of benthic microbial mats and burrowing behaviors in sites in Poland, where fluctuating anoxic to dysoxic conditions are inferred (Kazmierczak et al., 2012; Stachacz et al., 2017).

#### 2.5 Sedimentary record of anoxia

The earliest observations of the UKE and LKE noted the presence of laminations and lack of bioturbation in basinal sediments (see review by Schindler, 1993); similar observations have been made in numerous studies of deep water systems since that time (see the deep shelf/basinal studies in Supplemental Table 1). In addition to laminated sediments, storm/tsunami deposits have also been noted in many sections around the globe (Bond and Wignall, 2008; Du et al., 2008; Motteguin and Poty, 2016; Racki et al., 2002; Sandberg et al., 1988, among others).

Sedimentary microtextures in shallow water environments also show evidence of oxygen stress during the UKE and LKE. Laminated sediments and lack of bioturbation are present in shallow water deposits in the Moravian Karst region of the Czech Republic (Weiner et al., 2018), the platform carbonates of the Roche Miette in Canada (Bond et al., 2013), the shallow forearc basin sediments of the Appalachian Basin in New York (Lash, 2017), as well as in the shallow water facies of carbonate buildups along island arcs of the CAOB in northwestern China (Carmichael et al., 2014; Fan and Gong, 2016; Suttner et al., 2014). These regions also show shallow water storm deposits in the form of flat pebble conglomerates (Bond et al., 2013; Lash, 2017; Weiner et al., 2017) and winnowed "shell hash" lag deposits (Carmichael et al., 2014), indicating episodic environmental stress not only on the epicontinental seas of Laurussia and the Rheic Ocean, but also on the island arcs in the open Paleotethys Ocean.

#### 2.6. Stratigraphic expression: glaciation or tectonics?

The causes of sea-level change in the Late Devonian have long been debated, with no historical consensus between interpretations of glaciogenic sea-level change vs. tectonic sea-level change, particularly in Europe and North America (see review by Hallam and Wignall, 1999). Since that time, a number of studies have continued this argument but expanded the argument to a global stage.

In Europe and North America, debates about sea-level are ongoing. European sections may be overprinted by local tectonic changes in sea-level rather than reflecting a global signature (Hladil, 2002; Rodríguez-Cañero and Martín-Algarra, 2014). In North America, Brett et al. (in press) and Ver Straeten et al. (2011) use sequence stratigraphy in Appalachian Basin sediments to suggest a combination of sea-level rise and warming during the UKE and LKE, with sea-level changes attributed to glacioeustacy. As the Appalachian Basin is a foreland basin, however, it is possible that these sea-level changes may reflect local tectonic signals rather than global transgressive/regressive signals; Bush et al. (2015) and Beard et al. (2017) have revised some of the stratigraphic relationships between sections but both studies note that detailed, integrated correlations are still needed. Lash (2017) notes eustatic signals in the Appalachian Basin but contends they are likely tectonic. Other sequence stratigraphy work in the Appalachian Basin by McClung et al. (2013) suggests gradual global cooling in Late Devonian from hothouse Middle Devonian, although this work stands in contrast to conodont oxygen isotope data (section 2.2.2) suggesting 12

that the Middle Devonian was cooler but the Late Devonian was warmer.

Studies in the western part of North America have yielded detailed records of sea-level change based on magnetic susceptibility (Whalen et al., 2017; Whalen and Day, 2008; Whalen and Day, 2010), with sea-level rise at the UKE and LKE; the authors conclude these changes may be global (climate-related) or may be local (tectonic), but are probably a combination of both. Like the stratigraphic studies in the Appalachian Basin, these are at odds with the conodont oxygen isotope data that suggests global cooling rather than global warming at the onset of the UKE and LKE.

In other locations, different proxies for sea-level changes result in a number of different interpretations. In Australia, long term sea-level rise with a short-term drop at the F-F boundary is inferred based on  $\delta^{13}$ C chemostratigraphy in combination with sequence stratigraphy and correlations with sections in Europe (Stephens and Sumner, 2003). In South China, however, sea-level fall and global cooling at the UKE and F-F boundary are interpreted from <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>66</sup>Zn isotopes which are used as a proxy for continental weathering (Wang et al., 2018), conodont  $\delta^{18}$ O thermometry as a proxy for sea surface temperatures (Huang et al., 2018a),  $\delta^{238}$ U as a proxy for ocean mixing stimulated by cooling (Song et al., 2017a), and  $\delta^{13}$ C values as a proxy for cooling due to a drawdown of atmospheric CO<sub>2</sub> (Xu et al., 2012). Microfacies analysis, however, reveals transgressive events for both the UKE and LKE in South China (Zhang et al., 2019a). In northern Gondwana,  $\varepsilon_{Nd}$  isotope signatures from sections in Morocco suggest changes in seawater circulation at F-F boundary (Dopieralska, 2009), while in Libya sea-level rise is inferred from trace element signatures (Riboulleau et al., 2018). In contrast, a major regression is present at the F-F boundary Iran due to the presence of unconformities in (Gholamalian, 2007).

It is thus increasingly clear that different geochemical proxies for sea-level changes have resulted in varying interpretations, and are often at odds with the sedimentological record. Whether sea-level changes at the UKE and LKE are attributed to glacioeustacy or local tectonics remain matters of discussion (Wendt and Belka, 1991). At least in some sections, the sedimentological record mirrors transgressive-regressive cycles around the UKE and LKE, exhibiting breccias and/or hiatuses which are hard to interpret by local tectonics alone, because they occur in different paleogeographic settings all at the same time (e.g. Königshof et al., 2017; Pas et al., 2013; Schindler, 1993; Ver Straeten et al., 2011).

One of the challenges of assigning a glaciogenic origin vs. tectonic origin to the inferred sea-level drops at the UKE and LKE and the F-F boundary is the complete absence of obvious glacial sediments from late Frasnian sections. McGhee (2014) argues that "absence of evidence is not evidence of absence" with regard to the absence of glacial sediments in the late Frasnian rock record, and suggests

that instead of looking for diamictites in equatorial Laurussian sediments it is necessary to look for ice-rafted debris in late Frasnian (particularly Kellwasser Event) sediments derived from the Gondwana craton.

## 3. Mechanisms, Causes, and Triggers for the Kellwasser Event

Historically, one of the challenges of determining the mechanisms and triggers for Late Devonian ocean anoxia has been the timing and duration of the anoxia events. Schindler (1990b) initially posited that the Kellwasser Event was a stepwise series of crises that lasted for more than 1 million years. Subsequent astrochronology and geochronology studies have shortened this time period significantly (Brett et al., in press and references therein), although there are ongoing uncertainties particularly in regards to the revision of the time scale for many of the Late Devonian type sections (Schindler et al., 2018). Combining astrochronology models from De Vleeschouwer et al. (2017) with the detailed U-Pb ziron geochronology data of Percival et al. (2018), a more precise geochronology of the F-F boundary and Kellwasser Event has been obtained (Fig. 4 of Percival et al., 2018). In light these revised the of ages, earlier atmospheric/oceanographic models of the F-F boundary and Kellwasser Event (e.g. Goddéris and Joachimski, 2004) have become more conjectural, as some tectonic inputs and climate feedbacks in the models may be inconsistent with the newer, revised time scales. Other well-established ideas about the causes of and mechanisms for anoxia may also need to be reevaluated in light of the revised timing and duration of the UKE and LKE.

#### 3.1. Mechanisms of anoxia: top down or bottom up?

Applying the mass extinction patterns of Raup and Sepkoski (1982) to the temporal distribution of Paleozoic black shales (Berry and Wilde, 1978), Wilde and Berry (1984) suggested that upwelling of anoxic bottom waters into shallower ecosystems was a mechanism for at least some mass extinctions in the Phanerozoic. Their correlation between upwelling and extinction in the Devonian (primarily based on black shales in North America, and full of caveats and careful, somewhat noncommittal language) became the accepted mechanism for Devonian mass extinctions and anoxia for nearly two decades.

In the subsequent studies that invoke upwelling as a "bottom up" causal mechanism for anoxia, upwelling takes one of two forms: 1) expansion/migration of the oxygen minimum zone into shallow water environments via upwelling or transgression (e.g., Becker and House, 1994; Bond and Wignall, 2005; Goodfellow et al., 1988), or 2) upwelling of oxic, nutrient-rich bottom waters that then cause eutrophication (e.g., Crasquin and Horne, 2018; Uveges et al., 2018; Wang et al., 2018). These two upwelling scenarios are not always differentiated from each other, and many studies use an "either/or" explanation

coupled with changes in sea-level (e.g., Levman and Bitter, 2002; Schindler, 1990b; Schindler, 1993). These sea level changes are described as either transgressions or regressions, depending on the local stratigraphic or isotopic record. Others have suggested that a simple transgression or regression of oxic, well-mixed waters with consequent water-column stagnation could be a causal mechanisms for anoxia in basins and epeiric seas (e.g., Fig. 14 of Bond et al., 2004). Still others have suggested that influx of hydrothermal water masses caused anoxia (Emsbo et al., 2018; Xu et al., 2012; Zeng et al., 2011).

Neither the upwelling, stagnation, nor hydrothermal scenarios can explain the presence of ocean anoxia in isolated island arc settings (Fig. 4), however. Upwelling would indicate that the entire ocean was overturning at the same time, and stagnation is not possible due to topography (Carmichael et al., 2014), and synchronous hydrothermal inputs around the globe that are so severe as to affect open ocean waters are extremely unlikely. Paleoclimate models suggest that upwelling was minimal in most of the world during the Late Devonian (Ormiston and Oglesby, 1995), and that sequestration of organic carbon had more to do with seasonal, episodic, and/or climatedriven plankton blooms in shallow epeiric seas rather than widespread, synchronized upwelling into deep basins (Ormiston and Oglesby, 1995; Pedersen and Calvert, 1990; Petty, 2019). In fact, episodic anoxia, as first highlighted by Murphy et al. (2000) and Racki et al. (2002. and references therein), is supported by nearly all of the studies that have used a combination of detailed (cmscale) sampling in combination with petrography, regardless of the type of analysis. For example, in studies of thick black shale units in the Appalachian foreland basins there are a number of studies that have documented these rapid fluctuations of oxic/dysoxic/anoxic/euxinic conditions (Beard et al., 2017; Haddad et al., 2018; Lash, 2017; Schieber, 2009; Schieber and Baird, 2001). Episodic anoxia is also noted in palynological/microfossil studies (Kelly et al., 2019; Streel et al., 2000), and by distributions of ostracods (Song et al., 2019).

Rather than relying on complex basinal geometries and sea-level curves that may be controlled either wholly or in part by local tectonics to explain anoxia (episodic or otherwise), an alternative explanation must be found. This mechanism must not require numerous caveats about specific basin geometry or invoke complex (and often contradictory) sea-level data, must be consistent with deposition from episodic anoxia, and must work in any type of paleooceanographic environment, not just basins. An alternative explanation that fits these criteria is as follows: oxygen loss was "top down" rather than "bottom up" and was due to photic zone eutrophication (Fig. 4). This eutrophication may be caused by a number of factors. It may be a product of terrestrial nutrient input as shown in bright green in Fig. 4 (e.g., Algeo and Scheckler, 1998; Carmichael et al., 2014; George et al., 2014; Kaiho et al., 2013; Murphy et al., 2000; Percival et al., 2019; Riboulleau et al., 2018; Riguier et al., 2006; Riguier et al., 2005;

Tribovillard et al., 2004; Tuite and Macko, 2013; Whalen et al., 2017). Conversely, it could be due to changes in plankton communities (shown in gray in Fig. 4), which are responding to climate change (e.g., Paris et al., 1996; Schwark and Empt, 2006; Streel et al., 2000) or the addition of biolimiting nutrients from volcanic material (Over, 2002; Racki et al., 2018; Winter, 2015). or It may

also be due to a combination of effects, depending on the paleoenvironment (Spaak et al., 2018). Regardless of nutrient source, this "top down" mechanism is the *only* way anoxia can realistically occur in isolated island arc settings, which do not have large shallow epicontinental shelf topographies (Fig. 4).



Fig. 4. Schematic representation of "top down" eutrophication models vs. "bottom up" upwelling models. Upwelling (shown in dark green) is not feasible in island arc environments. In the top down model, eutrophication via continental or land-based runoff (shown in bright green) is differentiated from widespread eutrophication via changes in phytoplankton productivity (shown in gray).

This "top down" explanation ideally can be extrapolated to other Late Devonian anoxia events. For example, Petty (2019) recently presented an alternative explanation for the origin of the black shale in the Bakken Formation of the Williston Basin. Historically, the organic-rich shales of the Bakken Formation have been interpreted as deep water sediments, but in the shallow water silled basin model 15

proposed for the sediment deposition within the Bakken Formation, Petty (2019) concluded that the "top down" eutrophication models proposed by Algeo and Scheckler (1998), Carmichael et al. (2014) and Carmichael et al. (2016) were consistent with the development of anoxic conditions in the upper and lower Bakken Formation. Climate-driven "top down" eutrophication has likewise been

observed in modern shallow water systems, where harmful cyanobacterial blooms respond to changes in precipitation and N:P ratios (Davis and Koop, 2006).

Differentiating between a "top down" eutrophication mechanism and a "bottom up" upwelling/stagnation mechanism (Fig. 4) has profound implications in the search for trigger mechanisms of Late Devonian anoxia. If the ocean anoxia mechanism is a "top down" global eutrophication event rather than a "bottom up" basinal event, it implies that the onset of anoxia could be rapid and wholly climate driven, rather than dependent on longer-term changes in ocean circulation, basin topography, or changes in sea-level.

#### 3.2. Triggers for Anoxia and Extinction

Some of the most severe extinctions, such as the end-Cretaceous (K/Pg) and the end-Permian events are associated with the eruptions of large igneous provinces, severe glaciations, and/or meteorite impacts. A number of studies suggested that asteroids or comet impacts were responsible for Late Devonian extinction events, either based on textural evidence (Claeys et al., 1992; Du et al., 2008; Sandberg et al., 2002) or geochemical evidence (Hurley and Van Der Voo, 1990; Over et al., 1997; Playford et al., 1984; Wang et al., 1996; Wang et al., 1991). However, the influence of extraterrestrial impacts on the end-Devonian extinctions has firmly been discounted by others (see reviews by McGhee, 2005; Racki, 2012) and there are no recent studies that discuss bolide impacts as a potential trigger mechanism. Others have invoked the onset of glaciation to explain the F-F extinction event (Narkiewicz and Hoffman, 1989; Song et al., 2017a; Streel et al., 2000), despite the lack of evidence for major glaciations in the rock record (McGhee, 2014). Glaciation also does not necessarily explain anoxia events, as there have been many instances of glaciation in earth's history without associated anoxia.

Large igneous provinces (LIPs) have long been associated with extinctions (see reviews by Bond and Wignall, 2014; Ernst, 2014), but the role of LIPs on Late Devonian extinction events remains conjectural at this time. The F-F boundary was thought by some to be associated with some LIPs such as the Viluy Traps in Siberia (Courtillot et al., 2010; Kravchinsky, 2012; Ricci et al., 2013; with dates later confirmed by Tomshin et al., 2018), the Kola/Kontogero province (Kravchinsky, 2012) or the Pripyat-Dniepr-Donets rift system (Kravchinsky, 2012). These LIP locations are mapped in Fig. 1.6 of Ernst (2014). Newer and more precise age dates of the F-F boundary via U/Pb geochronology in zircons (Percival et al., 2018) are most closely associated with the Viluy Traps (Tomshin et al., 2018), but cyclostratigraphy studies and geochemical proxies for volcanism suggest that this association remains somewhat conjectural (Pas et al., 2018; Percival et al., 2018; Racki et al., in press). Furthermore, other Late Devonian pulses of extinction are not associated with any known LIPs (Bond and Wignall, 2014; Ernst, 2014), even if they show trace element evidence that suggests massive volcanism (Kalvoda et al., 2019; Paschall et al., 2019). It is of course possible that any LIPs in the Panthallasic Ocean have been completely subducted (Kaiser et al., 2016), or that LIPs associated with the F-F boundary simply have not vet been discovered.

New research by Racki et al. (2018), however, suggests that multiple arc volcanic events in quick succession rather than a single LIP might also be an effective volcanic trigger for extinction, at least at the F-F boundary. As volcanism on its own is rarely associated with ocean anoxia and mass extinctions, a "press-pulse" relationship that combines



Fig. 5. Location of subduction zones during the Late Devonian. Base map from Blakey (2016), with some continent positions and shapes modified from the tectonic data of Hara et al. (2010), Metcalfe (2011), and Xiao et al. (2010), and updated subduction zone locations from Huebner and Hatcher Jr (2017), Nie et al. (2016); Zhang et al. (2019b), Udchachon et al. (2017), and Yang et al. (in press).

increased volcanism with another short-term environmental stressor can better explain the correlation between volcanism and mass extinction within the Phanerozoic (Arens and West, 2008). As there were numerous arc volcano systems throughout the Late Devonian (particularly the Variscan/Appalachian Orogeny, the Antler Orogeny, and the numerous arc systems within the Central Asian Orogenic Belt, shown in Fig. 5), this multiple event hypothesis seems reasonable. Winter (2015) and Over (2002) note that there are increasing volcanic ash beds from various silicic volcanic sources throughout the Frasnian leading up to the F-F boundary. Although the potential matching reservoirs for these arc volcano systems have not been conclusively identified, massive and catastrophic explosive volcanism from a single silicic source (such as an arc volcano) is not generally preserved in the rock record (Frazer et al., 2014; Lundstrom and Glazner, 2016). Accordingly, lack of correlating plutonic source rock does not necessarily preclude massive, explosive arc volcanism as a potential causal mechanism for climate change that results in extinctions and anoxia.

#### 4. Concluding remarks

The original definition of the Kellwasser Event in Germany reflects the anoxia manifestations within a) regional conditions, and b) a specific paleogeography. However, the Kellwasser Event is expressed with considerable variability, depending on the paleoenvironment of the studied section. It is therefore necessary to expand significantly the scope of studies in these varied settings to fully understand the causes and impacts of climate-driven anoxia.

Due to the pulsed nature of Late Devonian anoxia events, it is increasingly likely that the Late Devonian extinctions and associated anoxia were caused by the effects of ongoing climate changes on marine ecosystems that were already distressed (Carmichael et al., 2016; De Vleeschouwer et al., 2014; De Vleeschouwer et al., 2017; Joachimski and Buggisch, 2002; Lash, 2017). It is also likely that an emerging Himalayan sized mountain chain in the tropics negatively impacted these ecosystems (Averbuch et al., 2005; Macdonald et al., 2019; Racki et al., 2018). This multicausal hypothesis is not new; Schindler (1993, p. 124) wrote that "development of stepwise deteriorations over a longer period of time makes Earthborn [sic] causes more plausible than extraterrestrial phenomena. It seems that complex multicausal factors succeeding one after the other and/or interacting with each other (and therefore amplifying each other) are responsible for the severe effects on a global scale." A quarter-century later, with more than 300 studies of the Kellwasser Event published, representing a variety of paleoenvironments from more than 150 sites around the globe, complex multicausal factors still remain the most reasonable explanation for the marine anoxia and the F-F mass extinction event.

Bambach et al. (2004) concluded that the F-F biotic crisis resulted from significant loss of origination rather than 17

elevated extinction, and (in quite an understatement) notes that "The Frasnian event is complicated" (p. 538). Intervals of exceptional diversity loss can result either from significantly elevated rates of extinction or from anomalously low rates of origination. Elevated extinction generally requires mechanisms that are capable of rapid, negative impacts on ecosystems, while low rates of origination can result from a mosaic of causes.

There were drastic changes in dominant organisms with the demise of reef builders in the Givetian and Frasnian. This loss of complex reef habitats could have resulted in reduced origination through the elimination of a normally diverse ecosystem. The devastating loss of diversity at the F-F boundary was likely a result of decreased origination at a time of elevated (but not abnormally high) rates of extinction. The scenario posited by Bambach et al. (2004) for the F-F biotic crisis is much more consistent with a topdown, climate driven series of events that caused oceanic anoxia and environmental degradation, instead of a more indiscriminate mass extinction scenario. A top-down mechanism would vary widely in severity and duration, would not necessarily be globally synchronous at a fine time scale, and also leads to predictions of where anoxia will be most severe. Sites that are restricted in some way (epicontinental basins, tectonic basins, etc.) and are in the tropics will be more prone to severe anoxia (as recorded by black shales and bituminous limestones) than cooler waters with better circulation (as recorded by fluctuating dysoxia in non-bituminous sediments) (Fig. 1). These latter sites cannot be discounted when trying to determine the distribution (and mechanism) of global oceanic anoxia. It appears that oxygen stresses plagued *all* of the locations in Supplemental Table 1, just not with the same severity. The analytical tools used to determine the presence or severity of anoxia in a basinal system therefore may not be appropriate to use in a shallower, steeper, or more isolated paleoenvironment.

We must recognize that all hypotheses about the Kellwasser Event involve a complex series of interactions, at both the local scale (e.g., tectonic environment, local volcanism, sediment type and supply, paleotopography, local paleoclimate) and the global scale (e.g., eustatic sealevel changes, global climate changes). Therefore, both a detailed biostratigraphic and sedimentological/facies record are required to understand these interactions across different paleogeographic settings, particularly those which are underrepresented in the geological record at present. Once these regional differences are acknowledged, the multicausal factors for the onset of the Kellwasser Event and F-F biotic crisis can begin to be decoupled, and we can more confidently answer some of the questions about this complicated, fascinating mass extinction event.

#### Acknowledgements:

The authors are grateful to C. Edwards for helpful discussions on sulfur, uranium, and nitrogen isotopes, and to several anonymous reviewers who greatly improved this

manuscript. R. Thomas assisted with paleogeographic map modifications. S. Carmichael and J. Waters received support from Appalachian State University's University Research Council. This paper is a contribution to *IGCP 652* - *Reading geologic time in Paleozoic rocks: the need of an integrated stratigraphy*.

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Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Central Asian Orogenic Belt: northwest China	West Junggar Basin (Boulongour Reservoir), Xinjiang, China	oceanic island arc; narrow shallow belt- mixed carbonate and volcanogenic siliciclastic	limestone & silt (UKE); LKE in terrestrial part of section	negative $\delta^{13}$ C excursion (coupled with negative $\delta^{18}$ O excursion); trace element and pyrite framboid evidence for dysoxia	Carmichael et al. (2014); Fan and Gong (2016); Song et al. (2017b); Suttner et al. (2014)
Central Asian Orogenic Belt: northwest China	West Junggar Basin (Wulankeshun), Xinjiang, China	oceanic island arc; narrow shallow belt - mixed carbonate and volcanogenic siliciclastic	limestone & silt (UKE); LKE in terrestrial part of section	negative $\delta^{13}$ C excursion; degree of anoxia not discussed	Fan and Gong (2016); Wang et al. (2016); Song et al. (2017b)
Tarim Craton: northwest China	Bachu Section, Tarim Craton, Xinjiang, China	rift basin?	* limestone & silt (UKE); LKE not exposed	N/A; degree of anoxia not discussed, biostratigraphy somewhat uncertain, F-F boundary determined by chemostratigraphy but may have hydrothermal overprinting	Hao et al. (2003)
Gondwana: Africa - Algeria	Ben Zireg section, Bechar Basin, Algeria	deep shelf / basin clastic/carbonate deposition	black shale (UKE); mixed limestone and silt (LKE)	N/A	Mahboubi et al. (2018); Mahboubi et al. (2015)

\* stratigraphic column extends across the expected biostratigraphic intervals of the UKE or LKE, but neither event is specifically mentioned in the literature

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Gondwana: Africa - Algeria	Marhouma section, Ougarta Basin, Algeria	deep shelf / basin clastic/carbonate deposition	mixed nodular limestone and black shale (UKE); gray shales and nodular limestones (LKE, difficult to recognize in field)	N/A	Mahboubi and Gatovsky (2015)
Gondwana: Africa - Libya	Borehole D1-26, Ghadames Basin, Libya	shallow shelf; clastics	black shale and nodular limestone (UKE); LKE not discussed	N/A; trace element evidence for anoxia	Riboulleau et al. (2018)
Gondwana: Africa - Libya	Murzuq Basin, Libya	basin; clastic deposition	* black shale; Kellwasser Events not differentiated	positive $\delta^{13}C_{org}$ excursion? (low sampling density)	Elkelani et al. (2014)
Gondwana: Africa - Morocco	Ait ou Nebgui	shallow shelf clastic/carbonate	black shale (UKE and LKE)	N/A; positive $\epsilon_{Nd}$ excursion at LKE only	Dopieralska et al. (2006)
Gondwana: Africa - Morocco	Anajdam, M'rirt, Azrou–Kenifra Basin, Morocco	deep shelf / basin clastic/carbonate deposition	bituminous black limestone (UKE and LKE)	N/A; trace element evidence for anoxia	Riquier et al. (2007)
Gondwana: Africa - Morocco	Bou-Ounebdou/Gara de M'rirt, Azrou–Kenifra Basin, Morocco	deep shelf / basin clastic/carbonate deposition	black shale interbedded with limestone (UKE); black limestone (LKE)	positive $\delta^{13}$ C excursion	Dopieralska et al. (2006); Joachimski et al. (2002); Riquier et al. (2007)
Gondwana: Africa - Morocco	Lahmida Section, Rheris Basin, Morocco	shallow shelf; clastics	black shale (UKE); black limestone (LKE)	N/A	Racki et al. (2018)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Gondwana: Australia	Barker River, Lennard Shelf/Canning Basin, Australia	shallow shelf clastic/carbonate	limestone (UKE and LKE lithologies not noted)	N/A	George and Chow (2002)
Gondwana: Australia	Carpenter Gap, Lennard Shelf/Canning Basin, Australia	shallow shelf clastic/carbonate	limestone (UKE and LKE lithologies not noted)	N/A	George and Chow (2002)
Gondwana: Australia	Casey Falls, Lennard Shelf/Canning Basin, Australia	reef; shallow shelf	silty limestone (UKE); LKE not exposed in section	positive $\delta^{13}$ C excursion just prior to UKE	Hillbun et al. (2015); Joachimski et al. (2002)
Gondwana: Australia	Dingo Gap, Lennard Shelf/Canning Basin, Australia	reef; shallow shelf	limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursions	George et al. (1997); George and Chow (2002); Stephens and Sumner (2003)
Gondwana: Australia	Horse Spring Range (core), Canning Basin, Australia	lower-middle fore- reef slope to toe-of- slope continental shelf	limestone/siltstone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion (does not line up with UKE or LKE)	George et al. (2014)
Gondwana: Australia	Horse Spring Range (section), Lennard Shelf/Canning Basin, Australia	reef; shallow shelf	limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion (pre-dates Kellwasser Events)	Hillbun et al. (2015)
Gondwana: Australia	McSherry Gap, Lennard Shelf/Canning Basin, Australia	reef slope; shallow shelf	limestone (UKE and LKE lithologies not noted)	N/A (upper Frasnian heavily dolomitized )	George et al. (1997); George and Chow (2002)
Gondwana: Australia	McWhae Ridge, Lennard Shelf/Canning Basin, Australia	reef slope; shallow shelf	limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion (UKE only)	Goodfellow et al. (1988); Joachimski et al. (2002); Playford et al. (1984)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Gondwana: Australia	NRD-3 core, Lennard Shelf/Canning Basin, Australia	reef slope; shallow shelf	limestone (UKE and LKE lithologies not noted)	N/A	George and Chow (2002)
Gondwana: Australia	NRD-6 core, Lennard Shelf/Canning Basin, Australia	reef slope; shallow shelf	limestone (UKE and LKE lithologies not noted)	N/A	George and Chow (2002)
Gondwana: Australia	South Oscar Range, Lennard Shelf, Australia	reef slope; shallow shelf	silty limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion (pre-dates Kellwasser Events)	Hillbun et al. (2015); Stephens and Sumner (2003)
Gondwana: Australia	Windjana Valley, Lennard Shelf/Canning Basin, Australia	reef; shallow shelf	limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion (pre-dates Kellwasser Events)	George and Chow (2002); Hillbun et al. (2015); Stephens and Sumner (2003)
Gondwana: South America - Bolivia	Pando X-1 Core, Madre de Dios, Bolivia	shallow shelf; clastics	sandstone lenses in shale (UKE and LKE)	positive (?) $\delta^{13}$ C excursion ( $\delta^{13}$ C measured organic carbon, with sandstone in F-F interval, pattern may be due to sample gaps through sandstone)	Haddad et al. (2016)
Iran: Iran	Chahriseh section, west- central Iran	shallow shelf; carbonates	* marly limestone, dolomite (UKE and LKE lithologies not noted)	N/A	Gholamalian (2007)
Iran: Iran	Ghale-Kalaghu section, central Iran	reef slope; shallow shelf	unconformity at UKE, laminated sandstone (LKE)	N/A	Gholamalian (2007)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Iran: Iran	Howz-e-Dorah section, central Iran	peritidal carbonates	unconformity at UKE, black laminated sandstone (LKE)	N/A	Gharaie et al. (2004); Gholamalian (2007)
Iran: Iran	Hutk section, Kerman, Iran	shallow shelf; clastics	thin black shale in limestone; Kellwasser Events not differentiated	negative $\delta^{13}$ C excursion (coupled with negative $\delta^{18}$ O excursion)	Gharaie et al. (2007)
Iran: Iran	Kal-e-Sardar section, central Iran	shallow shelf clastic/carbonate	sandstone (UKE and LKE lithologies not noted)	N/A	Gholamalian (2007)
Laurussia - Europe: Austria	Wolayer Glacier, Carnic Alps, Austria	shallow shelf carbonates	limestone (UKE); black shale (LKE)	positive $\delta^{13}$ C excursion; no evidence for anoxia at UKE	Bond et al. (2004); Buggisch and Joachimski (2006); Joachimski and Buggisch (1993)
Laurussia - Europe: Belgium	Hony section, Namur- Dinant Basin, Belgium	shallow shelf clastic/carbonate	dark gray mudstone capped with white claystone (UKE)	positive $\delta^{13}$ C excursion (limited sampling)	Casier (2017); Kaiho et al. (2013); Streel et al. (2000)
Laurussia - Europe: Belgium	Neuville section, Namur-Dinant Basin, Belgium	shallow shelf clastic/carbonate	limestone interbedded with black shale (UKE, LKE)	N/A	Mottequin and Poty (2016)
Laurussia - Europe: Belgium	Sinsin section, Belgium	shallow shelf clastic/carbonate	dark gray mudstone (UKE)	positive $\delta^{13}C$ excursion	Kaiho et al. (2013); Streel et al. (2000)
Laurussia - Europe: Czech Republic	Hády section, Morevo- Silesian Zone, Czech Rep	shallow shelf; carbonate	limestone (UKE and LKE inferred through MS)	N/A	Weiner et al. (2017)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Czech Republic	Lesní Iom section, Morevo-Silesian Zone, Czech Rep	shallow shelf; carbonate	limestone (UKE and LKE)	UKE and LKE inferred through U/Th ratios	Weiner et al. (2017)
Laurussia - Europe: Czech Republic	Šumbera section, Morevo-Silesian Zone, Czech Rep	shallow shelf; carbonate	limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Racki et al. (2002); Weiner et al. (2017); Weiner et al. (2018)
Laurussia - Europe: France	Col des Tribes section, Montagne Noire, France	mid to outer carbonate ramp; at F-F = deep shelf	black shale (UKE); LKE not exposed	N/A	Girard et al. (2014); Girard et al. (2018)
Laurussia - Europe: France	Coumiac section, Montagne Noire, France	shallow shelf; carbonates	limestone and dark gray shales (UKE and LKE)	positive $\delta^{13}$ C excursion; limited trace element and framboidal pyrite evidence for anoxia	Balter et al. (2008); Bond et al. (2004); Buggisch and Joachimski (2006); Dopieralska et al. (2016); Joachimski and Buggisch (1993); Klapper et al. (1994)
Laurussia - Europe: France	La Serre section, Montagne Noire, France	shallow shelf; carbonates	dark gray limestones and shales (UKE and LKE)	trace element and limited framboidal pyrite evidence for anoxia	Bond et al. (2004); Joachimski et al. (2009); Paris et al. (1996); Tribovillard et al. (2004)
Laurussia - Europe: Germany	Aeketal section, Harz mountains, Germany	carbonate swell, continental shelf/back arc basin?	black marlstones and limestones (UKE and LKE)	positive $\delta^{13}$ C excursion; framboidal pyrite and trace element evidence for anoxia	Gereke and Schindler (2012); Joachimski et al. (1994); Riquier et al. (2006); Schindler (1993)
Laurussia - Europe: Germany	Arfeld, Wittgenstein Syncline, Rheinisches Schiefergebirge, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE); LKE not exposed	N/A	Gereke (2007); Gereke and Schindler (2012)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Germany	Benner Quarry, Rheinisches Schiefergebirge, Germany	carbonate swell, continental shelf/back arc basin?	black limestones/shales (UKE and LKE)	positive $\delta^{13}$ C excursion; framboidal pyrite and fabric evidence for anoxia	Bond et al. (2004); Buggisch (1991); Buggisch and Joachimski (2006); Gereke (2007); Gereke and Schindler (2012); Joachimski and Buggisch (1993)
Laurussia - Europe: Germany	Beringhausen, Rheinisches Schiefergebirge, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE and LKE)	positive $\delta^{13}C$ excursion	Buggisch and Joachimski (2006); Joachimski et al. (2009); Joachimski and Buggisch (2002)
Laurussia - Europe: Germany	Bohlen, Schwarzburg Anticline, Thuringia, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE and LKE)	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Germany	Bubenkirchbach Valley, Wittgenstein Syncline, Rheinisches Schiefergebirge, Germany	restricted back-arc basin (clastic and carbonate)	black shale (LKE); UKE not exposed	N/A	Gereke (2007); Gereke and Schindler (2012)
Laurussia - Europe: Germany	Budesheimer Bach, Eifel Mountains, Germany	restricted back-arc basin (clastic and carbonate)	calcareous shale (UKE) and limestone (LKE)	positive $\delta^{13}C_{\text{org}}$ excursion	Joachimski et al. (2002)
Laurussia - Europe: Germany	Buschteich Section, Thuringia, Germany	restricted back-arc basin (clastic and carbonate)	limestone (UKE); LKE not exposed	UKE tentatively identified via positive $\delta^{13}$ C excursion	Girard et al. (2017); Girard et al. (2018)
Laurussia - Europe: Germany	Burgberg Quarry, Rhenisches Schiefergebirge, Germany	reef slope	argillaceous limestones and breccias (UKE and LKE)	positive $\delta^{13}C$ excursions	Buggisch and Joachimski (2006); Pas et al. (2013)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Germany	Drillhole Laasphe 1005, Wittgenstein Syncline, Rheinisches Schiefergebirge, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE); LKE not exposed	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Germany	Grube Christiane, Waldeck Syncline, Germany	restricted back-arc basin (clastic and carbonate)	interbedded limestone and black shale (LKE); UKE not exposed	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Germany	Hirtenrangen, Schwarzburg Anticline, Thuringia, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE and LKE)	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Germany	Hühnertal, Harz mountains, Germany	carbonate swell, continental shelf/back arc basin?	black marlstones and limestones (UKE and LKE)	positive $\delta^{13}$ C excursion; framboidal pyrite and trace element evidence for anoxia	Joachimski et al. (1994); Riquier et al. (2006)
Laurussia - Europe: Germany	Junge Grimme, Wittgenstein Syncline, Rheinisches Schiefergebirge, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE and LKE)	N/A	Gereke (2007); Gereke and Schindler (2012)
Laurussia - Europe: Germany	Kahlleite, Thuringia, Germany	restricted back-arc basin (clastic and carbonate)	gray/black shale (UKE and LKE)	N/A	Gereke (2004); Gereke (2007); Gereke and Schindler (2012); Joachimski et al. (2009); Racki et al. (2018)
Laurussia - Europe: Germany	Kellwassertal, Harz mountains, Germany	carbonate swell, continental shelf/back arc basin?	black marlstones and limestones (UKE and LKE)	positive $\delta^{13}$ C excursion; framboidal pyrite and trace element evidence for anoxia	Balter et al. (2008); Buggisch (1991); Gereke (2007); Gereke et al. (2014); Gereke and Schindler (2012); Joachimski et al. (1994); Riquier et al. (2006)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Germany	Liese Valley, Wittgenstein Syncline, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE); LKE not exposed	N/A	Gereke (2007); Gereke and Schindler (2012)
Laurussia - Europe: Germany	Schmidt Quarry, Rheinisches Schiefergebirge, Germany	swell within a carbonate basin, continental shelf	black limestones/shales (UKE and LKE)	positive $\delta^{13}$ C excursion	Dopieralska et al. (2016); Gereke (2007); Gereke and Schindler (2012); Goddéris and Joachimski (2004); Joachimski and Buggisch (1993); Joachimski et al. (2004); McGhee et al. (1986); Schindler (1993); Weiner et al. (2017)
Laurussia - Europe: Germany	Sessacker Trench VI, Dill Syncline, Rheinisches Schiefergebirge, Germany	carbonate swell, carbonate basin, continental shelf	greyish green limestone breccia (UKE); LKE either not exposed or combined with UKE	N/A	Schindler et al. (1998)
Laurussia - Europe: Germany	Usseln-Henkböhl, Waldek Syncline, Germany	restricted back-arc basin (clastic and carbonate)	laminated gray shales (LKE); UKE not exposed	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Germany	Vogelsburg Quarry, Thuringia, Germany	restricted back-arc basin (clastic and carbonate)	gray/black shale (UKE and LKE)	positive $\delta^{13}$ C excursion	Buggisch and Joachimski (2006); Gereke and Schindler (2012); Joachimski et al. (2009); Joachimski and Buggisch (1993); Joachimski and Buggisch (2002)
Laurussia - Europe: Germany	Weilburg-Ahausen, Lahn Syncline, Germany	restricted back-arc basin (clastic and carbonate)	black shale (UKE and LKE)	N/A	Gereke and Schindler (2012)
Laurussia - Europe: Italy	Stilo Unit, Calabria, Italy	back-arc basin; deep clastics and carbonates	black shale (UKE); LKE not discussed	N/A	Navas-Parejo et al. (2009)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Poland	Debnik Z7 borehole, Holy Cross Mountains, Poland	shallow shelf; carbonates	* limestone (UKE and LKE lithologies not noted)	N/A	Narkiewicz and Hoffman (1989)
Laurussia - Europe: Poland	Debnik Z17 trench, Holy Cross Mountains, Poland	shallow shelf; carbonates	marly limestone (UKE and LKE lithologies not noted)	N/A	Racki et al. (2002)
Laurussia - Europe: Poland	Janczyce 1 borehole, Holy Cross Mountains, Poland	shallow shelf; carbonates	* limestone (UKE and LKE lithologies not noted)	N/A	Matyja and Narkiewicz (1992)
Laurussia - Europe: Poland	Klucze BK-70 borehole, Holy Cross Mountains, Poland	shallow shelf; carbonates	* laminated marly mudstones (UKE and LKE lithologies not noted)	N/A	Narkiewicz and Hoffman (1989); Matyja and Narkiewicz (1992)
Laurussia - Europe: Poland	Kostomloty section, Holy Cross Mountains, Poland	shallow shelf; carbonates	* limestone (UKE and LKE lithologies not noted)	N/A	Casier et al. (2000)
Laurussia - Europe: Poland	Kowala Quarry, Holy Cross Mountains, Poland	carbonate; deep shelf / basin	laminated limestone and chert (UKE); limestone (LKE)	weakly positive $\delta^{13}$ C excursions; trace element and framboidal pyrite evidence for anoxia	Bond et al. (2004); Chen et al. (2013); Joachimski et al. (2002); Joachimski et al. (2001); Kazmierczak et al. (2012); Narkiewicz and Hoffman (1989); Percival et al. (2019); Racki et al. (2002); Schwark and Empt (2006); Stachacz et al. (2017)
Laurussia - Europe: Poland	Płucki section, Łysorg'ory Basin, Holy Cross Mountains, Poland	carbonate; deep shelf / basin	marly shale (UKE and LKE)	framboidal pyrite evidence for anoxia	Bond et al. (2004); Olempska (2002); Racki et al. (2002); Rakociński et al. (2016); Stachacz et al. (2017);

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Europe: Poland	Psie G´orki, Holy Cross Mountains, Poland	forereef; shallow shelf	limestone (UKE and LKE lithologies not noted)	positive $\delta^{13}$ C excursion, trace element and framboidal pyrite evidence for anoxia	Bond et al. (2004); Casier et al. (2002); Racki (1990)
Laurussia - Europe: Poland	Unislaw 2 borehole, western Pomerania, Poland	shallow shelf; carbonate	* laminated marly mudstones (UKE and LKE lithologies not noted)	N/A	Matyja and Narkiewicz (1992)
Laurussia - Europe: Poland	Wietrzrnia II quarry, Holy Cross Mountains, Poland	shallow shelf; carbonate	* laminated marly mudstones (UKE and LKE lithologies not noted)	N/A	Narkiewicz and Hoffman (1989)
Laurussia - Europe: Spain	FF Les Vilelles section, Catalan Coastal Ranges, Spain	lagoonal facies - shallow water	black shale (UKE); LKE not noted	N/A	Moreno et al. (2018)
Laurussia - North America: Canada	Abitibi River, Moose River Basin, Ontario, Canada	foreland basin; deep slope	green mudstone and black shale (UKE); LKE not noted	positive excursion in $\delta^{13}C_{carb}$ , negative excursion in $\delta^{13}C_{org}$ , correlated with positive $\delta^{18}O$ spike	Levman and Bitter (2002)
Laurussia - North America: Canada	Ancient Wall Section C (edge of Jasper Basin), Alberta, Canada	continental shelf margin; shallow carbonates	shale and mudstone (UKE and LKE)	positive $\delta^{13}C_{org}$ excursion; trace element evidence for anoxia	Whalen et al. (2017); Whalen et al. (2015)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Canada	Cinquefoil Mountain, Jasper Basin, Alberta, Canada	continental shelf margin; shallow carbonates	limestone, calcareous siltstone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	negative $\delta^{13}$ C excursion (localized negative excursion at F-F boundary in broadly positive excursion in Cinquefoil Mountain section; referred to frequently in literature as a negative excursion); anoxia inferred by higher TOC values	Wang et al. (1996)
Laurussia - North America: Canada	Kettle Point, Ontario, Canada	deep continental basin; clastics	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	negative $\delta^{34}$ S excursions at estimated location of UKE and LKE, but low sampling density	Bingham-Koslowski et al. (2016)
Laurussia - North America: Canada	Medicine Lake, Jasper Basin, Alberta, Canada	deep continental basin; carbonates	calcareous siltstone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	no change/positive $\delta^{13}$ C excursion; anoxia determined by higher TOC values	Goodfellow et al. (1988); Wang et al. (1996)
Laurussia - North America: Canada	Miette Platform (edge of Jasper Basin), Alberta, Canada	shallow continental shelf; carbonates	limestone (UKE); LKE not exposed	trace element and framboidal pyrite evidence for anoxia	Bond et al. (2013)
Laurussia - North America: Canada	Miette Section W4 (edge of Jasper Basin), Alberta, Canada	continental slope; carbonates; deep slope	silt/mudstone or unconformity (UKE), mudstone (LKE)	no obvious change in $\delta^{13}C_{org or} \delta^{15}N_{org}$ ; no geochemical evidence for anoxia	Whalen et al. (2017); Whalen et al. (2015)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Canada	Trout River, Northwest Territories, Canada	shallow continental shelf; carbonates	limestone/ unconformity (UKE); LKE not exposed	negative/positive δ <sup>13</sup> C excursion (potential unconformity and karstification at F-F boundary in broadly positive trend corresponding to UKE)	Geldsetzer et al. (1993); Goodfellow et al. (1988)
Laurussia - North America: Iowa, USA	Beaver Creek Quarry, Illinois Basin, IA, USA	shallow shelf/basin (carbonate/clastic)	limestone (LKE); UKE not exposed	N/A	Day and Witzke (2017)
Laurussia - North America: Iowa, USA	Bruns Quarry, Illinois Basin, IA, USA	shallow shelf/basin (carbonate/clastic)	limestone (LKE); UKE not exposed	positive $\delta^{13}C_{carb}$ excursion	Day and Witzke (2017)
Laurussia - North America: Iowa, USA	Buseman Quarry, Illinois Basin, IA, USA	shallow shelf/basin (carbonate/clastic))	limestone (LKE); UKE not exposed	N/A	Day and Witzke (2017)
Laurussia - North America: Iowa, USA	IGS Sullivan Slough Core, Illinois Basin, IA	deep shelf / basin (clastic)	black shale (UKE); mudstone (LKE)	no change in $\delta^{13}C_{\text{org}}$	Day and Witzke (2017); Uveges et al. (2018)
Laurussia - North America: Iowa, USA	Sweetland Creek section, Illinois Basin, IA, USA	deep shelf / basin (clastic)	black shale (UKE); brown shale (LKE)	N/A	Day and Witzke (2017); Over (2002); Uveges et al. (2018)
Laurussia - North America: Indiana, USA	Daviess 873 core, Illinois Basin, IN, USA	deep shelf / basin (clastic)	black shale (UKE); LKE not noted	positive (?) $\delta^{13}C_{org}$ excursion, but unconformity between samples near F-F boundary)	de la Rue et al. (2007)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Kentucky, USA	Bullitt County Core, Illinois Basin, KY, USA	deep shelf / basin (clastic)	black shale (UKE); LKE not noted	N/A	Over et al. (2019)
Laurussia - North America: Michigan, USA	Paxton Quarry, Michigan Basin, MI, USA	deep shelf / basin (clastic)	black shale (UKE); LKE not noted	N/A	Over (2002)
Laurussia - North America: Nevada, USA	Devil's Gate, Great Basin (Woodruff and Pilot), Nevada and Utah, USA	deep basin/slope (clastic)	siltstone and shale (UKE); LKE not noted	positive $\delta^{13}$ C excursion; framboidal pyrite evidence for anoxia at UKE only	Bond and Wignall (2005); Sandberg et al. (1988)
Laurussia - North America: Nevada, USA	North Antelope Range, Nevada, USA	deep basin/slope (clastic)	black shale (UKE); LKE not noted	trace element, pyrite framboid evidence for anoxia at UKE only	Bond and Wignall (2005)
Laurussia - North America: Nevada, USA	Northern Pancake, Nevada, USA	shallow continental shelf; carbonates	laminated siltstone (UKE), dark gray limestone (LKE); Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Giles et al. (2002)
Laurussia - North America: Nevada, USA	Tempiute Mountain, Nevada, USA	deep basin/slope (clastic)	black shale and limestone (UKE); LKE not noted	trace element, pyrite framboid evidence for anoxia at UKE only	Bond and Wignall (2005)
Laurussia - North America: Nevada, USA	Ward Mountain, Nevada, USA	shallow continental shelf; carbonates	laminated siltstone (UKE), dark gray limestone (LKE); Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Giles et al. (2002)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Nevada, USA	Warm Springs, Nevada, USA	deep continental basin (clastic)	black shale (UKE); LKE not noted	trace element, pyrite framboid evidence for anoxia at UKE only	Bond and Wignall (2005)
Laurussia - North America: Nevada, USA	WCK/Coyote Knolls section, Whiterock Canyon, Utah, USA	deep continental basin; clastic / carbonate	black shale and limestone (UKE); LKE not noted	trace element, pyrite framboid evidence for anoxia at UKE only	Bond and Wignall (2005); Bratton et al. (1999)
Laurussia - North America: New York, USA	Beaver Meadow Creek section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); dark shale (LKE)	N/A	Haddad et al. (2018); Haddad et al. (2016); Over (2002); Over et al. (1997)
Laurussia - North America: New York, USA	Cameron section (CAM), Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (LKE only)	N/A	Bush et al. (2015)
Laurussia - North America: New York, USA	Eighteen Mile Creek section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); LKE not exposed	anoxia measured by geochemistry and ichnofacies	Boyer et al. (2014); Haddad et al. (2018); Haddad et al. (2016)
Laurussia - North America: New York, USA	Hornell section (BCP), Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (LKE only)	N/A	Bush et al. (2015); Kelly et al. (2019)
Laurussia - North America: New York, USA	Irish Gulf section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); LKE not exposed	positive $\delta^{13}C_{org}$ excursion; anoxia measured by geochemistry and ichnofacies	Boyer et al. (2014); Haddad et al. (2018); Haddad et al. (2016); Over et al. (1997); Tuite and Macko (2013)
Laurussia - North America: New York, USA	Perry Farm section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); LKE not exposed	positive (?) $\delta^{13}C_{org}$ excursion, limited geochemical evidence for anoxia	Over et al. (1997); Tuite and Macko (2013)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: New York, USA	Pt. Gratiot section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); LKE not exposed	N/A	Over (2002); Over et al. (1997)
Laurussia - North America: New York, USA	Walnut Creek section, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE); LKE not exposed	negative then positive $\delta^{13}C_{org}$ excursion, anoxia measured by geochemistry and ichnofacies	Boyer et al. (2014); Haddad et al. (2018); Haddad et al. (2016); Kelly et al. (2019); Lash (2017); Tuite and Macko (2013); Uveges et al. (2018)
Laurussia - North America: New York, USA	West Valley NX-1 core, Appalachian Basin, NY, USA	foreland basin; deep; clastic	black shale (UKE and LKE)	positive $\delta^{13}$ C excursion trace element evidence for anoxia	Murphy et al. (2000); Sageman et al. (2003); Ver Straeten et al. (2011)
Laurussia - North America: Oklahoma, USA	Bass-Pritchard core #1, Lincoln Co. Arkoma Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	F-F boundary constrained via chemostratigraphy	Turner et al. (2016)
Laurussia - North America: Oklahoma, USA	Burning Mountain, Anadarko Basin, OK, USA	deep continental basin (clastic)	black shale and/or unconformity (UKE); Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Over (2002)
Laurussia - North America: Oklahoma, USA	Classen Lake (Hass B) section, Anadarko Basin, OK, USA	deep continental basin (clastic)	black shale (UKE) but FF boundary location uncertain; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Hass and Huddle (1965); Over (2002)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Oklahoma, USA	Henry House Creek (Hass A) section, Anadarko Basin, OK, USA	deep continental basin (clastic)	black shale (UKE); LKE not exposed	N/A	Over (2002)
Laurussia - North America: Oklahoma, USA	Huntington Anticline Quarry section A, Arkoma Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	F-F boundary constrained via chemostratigraphy	Turner et al. (2016)
Laurussia - North America: Oklahoma, USA	Huntington Anticline Quarry section B, Arkoma Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	F-F boundary constrained via chemostratigraphy	Turner et al. (2016)
Laurussia - North America: Oklahoma, USA	Jack Fork Creek (Hass E) section, Anadarko Basin, OK, USA	deep continental basin (clastic)	black shale (UKE); LKE not exposed	N/A	Over (2002)
Laurussia - North America: Oklahoma, USA	McAlister Cemetery Pit, Anadarko Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Over (2002)
Laurussia - North America: Oklahoma, USA	Pottawatomie Co. Core Ray 1-13, Arkoma Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	F-F boundary constrained via chemostratigraphy	Turner et al. (2016)

Paleocontinental RegionSection Name and LocationPaleoenvironmentKellwasser Event ithologyisotopic and geochemical signaturesReferencesLaurussia - North America: Oklahoma, USAWyche Farm Quarry core, Arkoma Basin, OK, USAdeep continental basin (clastic)black shale; Kellwasser Events ithologies not notedF-F boundary constrained via chemostratigraphyTurner et al. (2016)Laurussia - North America: USATioga section (TCB), Appalachian Basin, PA, USAdeep continental basin (clastic)black shale (LKE); UKE not exposedN/ABeard et al. (2017); Bush et al. (2015)Laurussia - North America: Utah, USABuckhorn Canyon sectionshallow continental shelf / slope; carbonates; clasticsmarly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABullion Canyon section shallow continental shelf / slope; carbonates; clasticsmarly sandstone; kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABurbank Hills section, ulah, USAshallow continental shelf; carbonates shelf; carbonates clasticelaminated siltstone (UKE), dark gray lithologies not notedN/ALaurussia - North America: Utah, USAResection, Confusion basin (clastic)deep continental shelf; carbonates shelf (carbonates)laminated siltstone tort differentiated, UKE and LKE lithologies not notedN/ALaurus						
Laurussia - North America: Oklahoma, USAWyche Farm Quarry core, Arkoma Basin, OK, USAdeep continental basin (clastic)black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not notedF-F boundary constrained via chemostratigraphyTurner et al. (2016)Laurussia - North America: Utah, USATioga section (TCB), Appalachian Basin, PA, USAdeep continental basin (clastic)black shale (LKE); UKE not EXPOSEdN/ABeard et al. (2017); Bush et al. (2015)Laurussia - North America: Utah, USABuckhorn Canyon sectionshallow continental shelf / slope; carbonates; clasticsmariy sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABullion Canyon section shallow continental shelf / slope; carbonates; clasticsshallow continental shelf / slope; carbonates; clasticsmarly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABurbank Hills section, utah, USAshallow continental shelf; carbonatesmarly sandstone; kellwasser Events not differentiated, UKE and LKE lithologies not notedN/A(Giles et al., 2002)Laurussia - North America: Utah, USABurbank Hills section, carbonatesshallow continental shelf; carbonatesmariae silts on toifferentiated, UKE and LKE lithologies not notedN/A(Giles et al., 2002)Laurussia - North America: Utah, USACR4 section, Conf	Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Pennsylvania, USATioga section (TCB), Appalachian Basin, PA, USAdeep continental basin (clastic)black shale (LKE); UKE not exposedN/ABeard et al. (2017); Bush et al. (2015)Laurussia - North America: Utah, USABuckhorn Canyon sectionshallow continental shelf/ slope; 	Laurussia - North America: Oklahoma, USA	Wyche Farm Quarry core, Arkoma Basin, OK, USA	deep continental basin (clastic)	black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	F-F boundary constrained via chemostratigraphy	Turner et al. (2016)
Laurussia - North America: Utah, USABuckhorn Canyon sectionshallow continental shelf / slope; carbonates; clasticsmarly sandstone; NUKE and LKE UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABullion Canyon section shelf / slope; carbonates; clasticsshallow continental shelf / slope; carbonates; clasticsmarly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABurbank Hills section, Utah, USAshallow continental shelf; carbonatesmarly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, 	Laurussia - North America: Pennsylvania, USA	Tioga section (TCB), Appalachian Basin, PA, USA	deep continental basin (clastic)	black shale (LKE); UKE not exposed	N/A	Beard et al. (2017); Bush et al. (2015)
Laurussia - North America: Utah, USABullion Canyon section shelf / slope; carbonates; clasticsmarly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/AMorrow et al. (2011)Laurussia - North America: Utah, USABurbank Hills section, Utah, USAshallow continental shelf; carbonateslaminated siltstone (UKE), dark gray limestone (LKE); Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/A(Giles et al., 2002)Laurussia - North America: Utah, USACR4 section, Confusion Range, Utah, USAdeep continental 	Laurussia - North America: Utah, USA	Buckhorn Canyon section	shallow continental shelf / slope; carbonates; clastics	marly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Morrow et al. (2011)
Laurussia - North America: Utah, USABurbank Hills section, Utah, USAshallow continental shelf; carbonateslaminated siltstone (UKE), dark gray limestone (LKE); Kellwasser Events not differentiated, UKE and LKE lithologies not notedN/A(Giles et al., 2002)Laurussia - North America: Utah, USACR4 section, Confusion Range, Utah, USAdeep continental basin (clastic)black shale (LKE?); Kellwasser Events not differentiated, UKE and LKE lithologies not notedtrace element evidence for anoxiaBratton et al. (1999)	Laurussia - North America: Utah, USA	Bullion Canyon section	shallow continental shelf / slope; carbonates; clastics	marly sandstone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Morrow et al. (2011)
Laurussia - North America: Utah,CR4 section, Confusion Range, Utah, USAdeep continental basin (clastic)black shale (LKE?); Kellwasser Events not differentiatedtrace element evidence for anoxiaBratton et al. (1999)	Laurussia - North America: Utah, USA	Burbank Hills section, Utah, USA	shallow continental shelf; carbonates	laminated siltstone (UKE), dark gray limestone (LKE); Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	(Giles et al., 2002)
	Laurussia - North America: Utah, USA	CR4 section, Confusion Range, Utah, USA	deep continental basin (clastic)	black shale (LKE?); Kellwasser Events not differentiated	trace element evidence for anoxia	Bratton et al. (1999)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - North America: Utah, USA	WMO section, Confusion Range, Utah, USA	deep continental basin (clastic)	mudstone/chert; Kellwasser Events not differentiated	trace element evidence for anoxia	Bratton et al. (1999)
Laurussia - North America: Utah, USA	Whiterock Canyon section, Monitor Range, Nevada, USA	foreland basin; deep; clastic	dolomitized siltstone (UKE?) shale (LKE?); Kellwasser Events not differentiated	trace element, pyrite framboid evidence for anoxia at UKE only	Bond and Wignall (2005); Bratton et al. (1999)
Laurussia - North America: Virginia, USA	Norton section, Appalachian Basin, VA, USA	foreland basin; deep; clastic	black shale and mudstone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Over (2002)
Laurussia - Urals: Russia	Akkyr, southern Urals, Russia	shallow continental shelf; carbonates	fossiliferous limetones; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	positive $\delta^{13}$ C excursion	Abramova and Artyushkova (2004); Izokh (2009); Tagarieva (2013)
Laurussia - Urals: Russia	Bol'shaya Barma, southern Urals, Russia	shallow continental shelf; carbonates	fossiliferous limetones; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Abramova and Artyushkova (2004); Tagarieva (2013)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Urals: Russia	Kuk-Karauk, southern Urals, Russia	shallow continental shelf; carbonates	fossiliferous limetones; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Tagarieva (2013)
Laurussia - Urals: Russia	Lemezinsky section, southern Urals, Russia	shallow continental shelf; carbonates	bituminous black limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Abramova and Artyushkova (2004)
Laurussia - Urals: Russia	Ryauzyak, southern Urals, Russia	shallow continental shelf; carbonates	fossiliferous limetones; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Abramova and Artyushkova (2004); Tagarieva (2013)
Laurussia - Urals: Russia	Syv'yu River, Timan- Pechora Basin, Urals, Russia	shallow continental shelf; carbonates / clastics	silty limestone (UKE), limestone (LKE)	positive $\delta^{13}$ C excursion (pronounced excursion for UKE, LKE less certain); with trace element evidence for anoxia	Gharaie et al. (2007); Racki et al. (2018); Yudina et al. (2002)
Laurussia - Urals: Russia	Chut' River outcrop, Ukhta anticline, Timan- Pechora Basin, Urals, Russia	shallow lagoon; carbonates	limestone and evaporates; UKE and LKE lithologies not noted	N/A	House et al. (2000)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
Laurussia - Urals: Russia	Ukhta-Sosnogorsk, Urals, Russia	clastic/carbonate basin, continental shelf	clay, limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Lukševičs et al. (2017)
Siberia: Russia	Kosoy Utyos section, Kuznetsk Basin, Siberia, Russia	shallow continental shelf; carbonates / clastics	clayey limestone (UKE); LKE not exposed	negative $\delta^{13}$ C excursion (negative towards F-F boundary; positive through triangularis zone)	Izokh (2009); Izokh et al. (2009)
Siberia: Russia	Stolb Island, Lena River Delta, Siberia, Russia	shallow continental shelf; carbonates / clastics	black clay and limestone (UKE); LKE not exposed	N/A	Yazikov et al. (2013)
Inthanon Zone: Thailand	Mae Sarang section, northwestern Thailand	deep shelf	limestone (UKE and LKE)	positive $\delta^{13}C$ excursion	Dopieralska et al. (2012); Königshof et al. (2012); Racki et al. (in revision); Savage (2019)
Sibumasu Terrane: Yunnan, China	Bancheng secton, Yunnan Province, China	Basin; clastic deposition	shale and chert (UKE); LKE not noted	N/A	Ma et al. (2016)
Sibumasu Terrane: Thailand	Thong Pha Phum secton, Satun Province, Thailand	outer continental shelf	limestone (UKE and LKE)	positive $\delta^{13}C$ excursion	Racki et al. (in revision); Savage et al. (2006)
South China: Guangxi, China	Baisha section, Yangshuo Basin, Guangxi, China	shallow continental shelf; carbonates	black limestone (UKE and LKE)	positive $\delta^{13}C$ excursion	Chen et al. (2005); Chen et al. (2002); Du et al. (2008); Gong et al. (2002); Song et al. (2017a)
South China: Guangxi, China	Baqi section, Yangshuo Basin, Guangxi, China	shallow continental shelf / slope; carbonates	limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
South China: Guangxi, China	Du'an section, Guangxi, China	shallow continental shelf; carbonates	nodular limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008); Gong et al. (2002)
South China: Guangxi, China	Lali section, Guangxi, China	shallow continental shelf; carbonate trough	black limestone (UKE and LKE)	N/A	Zhang et al. (2019)
South China: Guangxi, China	Liujing section, Guangxi, China	shallow continental shelf / slope; carbonates	limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	negative $\delta^{13}$ C excursion (coupled with negative $\delta^{18}$ O excursion), trace element evidence for anoxia	Du et al. (2008); Gharaie et al. (2007); Gong et al. (2002)
South China: Guangxi, China	Luoxiu section, South China	shallow continental shelf / slope; carbonates / clastics	nodular limestone and black shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	negative $\delta^{13}$ C excursion	Du et al. (2008); Zheng et al. (1993)
South China: Guangxi, China	Ma'anshan section, Yangshuo Basin, Guangxi, China	shallow continental shelf; carbonates	limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008); Ma et al. (2016)
South China: Guangxi, China	Mangchang section, Yangshuo Basin, Guangxi, China	shallow continental shelf; carbonates	limestone and shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
South China: Guangxi, China	Nandong section, Guangxi, China	shallow continental shelf; carbonates	dark marly shale (UKE and LKE)	positive $\delta^{13}$ C excursion (UKE only; is negative at LKE)	Du et al. (2008); Gong et al. (2002); Huang et al. (2018b); Song et al. (2019)
South China: Guangxi, China	Nayi section, Guangxi, China	shallow continental shelf; carbonates / clastics	shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008)
South China: Guangxi, China	Sanli section, Guangxi, China	shallow continental shelf; carbonates / clastics	shale; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Du et al. (2008)
South China: Guangxi, China	Shenwanli section, Guangxi, China	shallow continental shelf; carbonates	limestone (partially dolomitized); Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A (sampling interval does not provide sufficient information)	Gong et al. (2002)
South China: Guangxi, China	Xiangtian section, Yangshuo Basin, Guangxi, China	shallow continental shelf; carbonates	black shale/marl; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	negative $\delta^{13}$ C excursion. trace element evidence for anoxia	Du et al. (2008); Wang et al. (1991)
South China: Guangxi, China	Xikuangshan section, Yangshuo Basin, Guangxi, China	shallow continental shelf; carbonates	limestone and black shale (UKE); LKE lithology not noted	N/A	Ma et al. (2016); Ma and Bai (2002); Wang et al. (1986)

Paleocontinental Region	Section Name and Location	Paleoenvironment	Kellwasser Event lithology	isotopic and geochemical signatures	References
South China: Guangxi, China	Yangdi (also referred to as Fuhe), Guangxi, China	shallow continental shelf / slope; carbonates	nodular limestone and calcareous turbidites (UKE); limestone (LKE)	positive δ <sup>13</sup> C excursion (UKE only)	Chen et al. (2005); Chen et al. (2013); Du et al. (2008); Gong et al. (2002); Gong et al. (2007); Huang and Gong (2016); Huang et al. (2018a); Ma et al. (2016); Ma and Bai (2002); Song et al. (2019); Wang et al. (2018); Whalen et al. (2015); Xu et al. (2008); Xu et al. (2012); Zeng et al. (2011); Zhang et al. (2017)
South China: Guilin, China	Dongcun, Guilin, China	shallow continental shelf; carbonates	black limestone (UKE and LKE)	positive $\delta^{13}$ C excursion	Xu et al. (2008); Xu et al. (2003); Xu et al. (2012)
South China: Vietnam	Si Phi section, Vietnam	shallow continental shelf; carbonates / clastics	limestone and thin brownish shale; ongoing debate over biostratigraphic control	positive $\delta^{13}$ C excursion in <i>triangularis</i> Zone (UKE) only, LKE not well defined	Dzik et al. (2018); Komatsu et al. (2019); Königshof et al. (2017)
South China: Vietnam	Xom Na section, Vietnam	shallow continental shelf / slope; carbonates	limestone; Kellwasser Events not differentiated, UKE and LKE lithologies not noted	N/A	Thanh et al. (2013)
Uralian Arc: Russia	Pershino Platform, East Urals, Russia	oceanic island arc; narrow shallow belt- carbonates	limestone (UKE); LKE not exposed	slight positive $\delta^{13}$ C change across F-F boundary, trace element evidence of anoxia	Mizens et al. (2015); Mizens et al. (2014)

Note: We have attempted to be as thorough as possible in compiling a table with >150 sections involving >300 citations with >140 references, in a number of different languages; any errors or omissions are entirely unintentional.

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