Phosphorus-cycle disturbances during the Late Devonian anoxic events

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ABSTRACT

The Late Devonian was marked by repeated faunal crises and episodes of geographically widespread marine anoxia, and featured one of the 'Big Five' mass extinctions of the Phanerozoic Aeon during the Frasnian–Famennian transition. However, the processes responsible for causing the numerous anoxic events remain unclear. This study highlights the occurrence of disturbances to the phosphorus cycle during several Late Devonian crises by investigating sedimentary concentrations of the element (P_{tot}) as a tracer of nutrient influx, as well as its ratio with total organic carbon (TOC) to infer the recycling of the element from marine sediments. Increased TOC/P_{tot} ratios in the Frasnian–Famennian Lower and Upper Kellwasser horizons and upper Famennian Annulata and Hangenberg levels suggest that such nutrient recycling occurred across extensive areas of the marine shelf in Laurentia and both Rheic Ocean margins at those times, helping to sustain reducing conditions in those

environments. Elevated P_{tot} values in the Upper Kellwasser, Annulata, and Hangenberg levels are consistent with an enhanced nutrient influx as the initial trigger for the anoxia. Correlation of phosphorus trends with other geochemical indicators of weathering/detrital influx (osmium-isotope, silicon/aluminum, and titanium/aluminum ratios) support a scenario in which terrestrial runoff provided these nutrients both to marine shelves and the oceanic inventory. Upwelling of oceanic deep-water bodies may have then brought the phosphorus to areas that had not featured major direct inputs of terrigenous material. The exception is the Lower Kellwasser Event, during which there was no increase in phosphorus delivery to marine areas and no evidence for terrestrial influx at the studied sections, invoking a different mechanism for the development of water-column anoxia. Clearly, the Late Devonian marine realm was unusually susceptible to becoming anoxic through various possible triggers, including nutrient influx from land and/or deep-water upwelling, and the recycling of phosphorus from newly deposited sediments.

KEYWORDS

Phosphorus; Late Devonian; marine anoxia; nutrient recycling; Frasnian–Famennian extinction

1. Introduction

Numerous episodes of widespread marine anoxia occurred during the Late Devonian (~383–359 Ma; palaeogeography in Figure 1), and are marked in the geological record by the appearance of black shale horizons in Europe and elsewhere (reviewed in Bond and Grasby, 2017; see also: Walliser, 1984, 1996; Joachimski and Buggisch, 1993; Bond and Zatoń, 2003; Bond *et al*., 2004; Kaiser *et al*., 2006). The best known of these black shales appear just below and at the Frasnian–Famennian (F–F) Stage boundary (e.g., Buggisch, 1991), and mark the sedimentary expression of the

Lower (LKW) and Upper (UKW) Kellwasser events that culminated in one of the ‘Big Five’ mass extinctions of the Phanerozoic Aeon (e.g., Raup and Sepkoski, 1982; McGhee, 1996; Racki, 2005; Bond and Grasby, 2017). Other examples include the upper Famennian Annulata Shale (e.g., Walliser, 1996; Sandberg *et al*., 2002; Korn, 2010), and the Hangenberg Shale just below the Famennian–Tournasian (Devonian–Carboniferous) boundary that also marks a major biotic crisis (e.g., Walliser, 1996; Caplan and Bustin, 1999; see also review by Kaiser *et al*., 2016).

The anoxic facies exemplified by these black shales also record abundant geochemical and petrographic evidence for depleted water-column oxygen levels, in the form of enrichments in redox-sensitive trace elements, organic-biomarker compositions, pyrite framboid size populations, and perturbations to elemental isotope compositions (e.g., Joachimski and Buggisch, 1993; Joachimski *et al*., 2001; Bond and Zatoń, 2003; Bond *et al*., 2004; Racka *et al*., 2010; Marynowski *et al*., 2011, 2012; Song *et al*., 2017; White *et al*., 2018). Globally documented positive excursions in sedimentary carbon-isotope ($\delta^{13}C$) values of up to 4 ‰ also highlight that these events were associated with significant perturbations to the global carbon cycle (e.g., Joachimski and Buggisch, 1993; Joachimski *et al*., 2002; Stephens and Sumner, 2003; Chen *et al*., 2005; De Vleeschouwer *et al*., 2017). The association of these events with major biospheric crises might suggest that marine anoxia and euxinia had a profound, and possibly cumulative, effect on Devonian ecosystems (e.g., Buggisch, 1991; Bond *et al*., 2004). However, in some locations water-column deoxygenation is recorded as being either less severe (i.e., suboxic–dysoxic) or absent through the numerous Late Devonian events, suggesting that marine anoxia was certainly not truly global in extent, and was often intermittent, during those crises (e.g., Bond *et al*., 2004; Pujol *et al*., 2006; Marynowski *et al*., 2012; White *et al*., 2018). Consequently, abrupt climate cooling has also been proposed as an additional/alternative cause of faunal extinctions during the Kellwasser and Hangenberg crises (e.g., Copper, 1986; Streel *et al*., 2000; Joachimski and Buggisch, 2002; Kaiser *et al*., 2016; Song *et al*., 2017). Nonetheless, regions featuring marine anoxia clearly expanded geographically during the Late Devonian crises, and in this regard these episodes bear a superficial resemblance to the Mesozoic oceanic anoxic events (OAEs), which have been linked with warmer global climates, marine stagnation and/or stratification, weathering and nutrient runoff, and recycling of nutrients from sediments (see Jenkyns, 2010). However, whilst the Mesozoic OAEs are widely accepted to have been triggered by abrupt climate warming during hyperthermal events, the absence of evidence for similar temperature increases during the numerous Devonian anoxic episodes means that the ultimate trigger of those environmental perturbations remains unknown.

To date, alternative hypotheses for what caused the Late Devonian anoxic events have chiefly revolved around triggering oxygen depletion in the water column via an abrupt influx of nutrients to marine settings, resulting in enhanced levels of primary productivity and subsequent eutrophication (Wilder, 1994; Algeo and Scheckler, 1998; Averbuch *et al*., 2005). One potential source of these nutrients is from major upwelling of deep-water masses (e.g., Copper, 1986, 1998; Pujol *et al*., 2006). Alternatively, it has been proposed that an increase in continental weathering rates and associated runoff of terrigenous nutrients stimulated the enhanced primary productivity and subsequent marine anoxia (e.g., Wilder, 1994; Algeo and Scheckler, 1998; Averbuch *et al*., 2005). Increased terrestrial runoff associated with enhanced continental weathering during the Devonian crises has been documented by a number of proxies (e.g., strontium-isotopes, Chen *et al*., 2005; osmium-isotopes, Percival *et al*., 2019; silicon/aluminum (Si/Al), titanium/aluminium (Ti/Al), and zirconium/rubidium (Zr/Rb) ratios, Racki *et al*., 2002; Pujol *et al*., 2006; Riquier *et al*., 2006; Weiner *et al*., 2017; Paschall *et al*., 2019), with evidence of soil erosion and wildfires from organic-geochemistry studies further highlighting the contribution of terrestrial matter to the marine realm (Marynowski *et al*., 2012; Kaiho *et al*., 2013; Rimmer *et al*., 2015). Here, the distribution of nutrients in marine shelf basins during Late Devonian anoxic events, as well as their potential source, is further investigated, using phosphorus as a tracer of nutrient influx and recycling at a number of new records of Upper Devonian strata with a wide palaeogeographical coverage.

1.1. The marine phosphorus cycle

Phosphorus (P) is a key limiting nutrient for primary productivity in the marine realm, and surface waters typically contain a very low dissolved P content due to the rapid biological uptake of this element (see review by Filippelli, 2008, and references therein). There are no stable gaseous species of phosphorus in the atmosphere, and hydrothermal emissions and weathering of submarine lithologies represent a negligible source of the element to the marine realm. Consequently, continental weathering, and particularly the runoff of phosphorus bound within organic compounds (P_{org}) from soil erosion, provides the major influx of bioavailable P to the marine environment (Filippelli and Delaney, 1994; Föllmi, 1995). On geologically short timescales, phosphorus within the marine system is also returned to the shelf environment from deeper waters via the localized upwelling of nutrient-rich waters that have high P concentrations (see reviews by Froelich *et al*., 1982; Föllmi, 1996; Paytan and McLaughlin, 2007; and references therein).

At the point of initial deposition on the seafloor, the vast majority of the element is bound to organic matter (Delaney, 1998), with a smaller constituent composed of detrital material, iron-bound P, and the bones/teeth/scales of marine organisms such as fish (Froelich *et al*., 1982; Schenau and De Lange, 2000; Fantasia *et al*., 2018). Post burial, a large fraction of P_{org} can be converted into authigenic P phases such as carbonate-fluorapatite (CFA) and iron-bound P (Berner *et al*., 1993). Redox conditions can play an important role in these conversions, with formation of authigenic P phases potentially more prevalent in the presence of bioturbation (i.e., more oxygenated settings); furthermore, anoxic conditions may favour the formation of CFA over iron-bound P phases (see overviews of Algeo and Ingall, 2007; Dale *et al*., 2016). These early-diagentic transformations form a crucial aspect of long term P burial (the so-called 'sink switch'); however, whilst these processes will reduce the amount of P_{org} in the sediment, the P_{tot} content should remain unchanged, and in most marine settings the amount of detrital P is sufficiently small that the combined authigenic and organic P ($P_{reactive}$) will be close to the overall P_{tot} content (Algeo and Ingall, 2007). Consequently, whilst both the TOC/P_{org} and TOC/P_{tot} values should initially be close to the Redfield ratio of organic matter when P_{org} is deposited to sediments in oxic conditions, any subsequent conversion of P_{org} to authigenic species would elevate this ratio, although the ratio of TOC/P_{tot} will not be affected by this process.

In reducing conditions, interaction of sediments with oxygen-depleted bottom waters can result in liberation of P_{org} back into the water column (e.g., Van Cappellen and Ingall, 1994). Thus, in anoxic marine settings, sedimentary P is recycled very efficiently and can sustain elevated primary productivity in the overlying water column, whilst greatly reducing the efficiency of phosphorus burial (Van Cappellen and Ingall, 1994). This recycling of P_{org} will also elevate TOC/P_{org} values, but will additionally raise the TOC/P_{tot} ratio (although potentially to a lesser degree). Studies of the Mesozoic OAEs have highlighted the potential role played by this nutrient recycling in sustaining enhanced primary productivity and anoxic/euxinic conditions in marine shelf environments, where the onset of anoxia likely resulted from eutrophication associated with an external influx of nutrients to those areas (Mort *et al*., 2007; Kraal *et al*., 2010; Westermann *et al*., 2013; Fantasia *et al*., 2018).

Previous studies of the sedimentary phosphorus contents during the Late Devonian crises have indicated a likely influx of the element to the marine realm during the UKW Event, with a documented increase in total phosphorus content in the sediments at the base of the UKW Horizon in the West Valley Core (Appalachian Basin, New York, USA; Murphy, 2000; Sageman *et al*., 2003). Additionally, there is an elevated phosphate concentration in rocks from that stratigraphic level at the Boulongour Reservoir section in northwestern Xinjiang (NW China; Carmichael *et al*., 2014), with stratigraphically higher peaks documented at the F–F boundary itself in the Syv'yu River section in the subpolar Urals (Russia; Yudina *et al*., 2002), and a number of Polish sections (Racki *et al*., 2002). Sedimentary phosphate enrichments have also been noted in the Hangenberg shales just below the Devonian–Carboniferous boundary (Carmichael *et al*., 2016; Paschall *et al*., 2019). Furthermore, elevated organic carbon/organic phosphorus ratios from a single record (the West Valley Core) have been interpreted as indicating that once an oxygen-depleted water column had developed, recycling of nutrients from newly deposited sediments likely took place in the oxygen-depleted conditions during the LKW and UKW events, at least in that location (Murphy, 2000; Sageman *et al*., 2003; see also

Figure 2). Such nutrient recycling would have resulted in sustained high rates of primary productivity and a consequent prolongation of anoxic conditions. However, the occurrence of such nutrient recycling during the Kellwasser crises has not yet been demonstrated elsewhere, and the source of the increased sedimentary phosphate remains unresolved.

1.2. Study aims

In this study, six new datasets of total P concentrations (P_{tot}) are presented from records of the Frasnian–Famennian transition (see Figure 1 for geographic locations), spanning both the north-western (Steinbruch Schmidt, Germany; Kowala, Poland) and southern (Coumiac, France; Erfoud, Morocco) margins of the Rheic Ocean, and the Australian Canning Basin (South Oscar Range; Dingo Gap). The Steinbruch Schmidt, Kowala, and Coumiac samples were further studied for total organic carbon/total phosphorus (TOC/P_{tot}) ratios. The analyses are supplemented by combined new and previously published information on primary productivity and input of detrital terrigenous material to Steinbruch Schmidt, Kowala, Coumiac, and Erfoud, with the new aluminium data also used to normalise the P_{tpt} contents (P_{tot}/Al ratios) to determine whether changes in phosphorus were lithologically related. These data allow for an increasingly global picture to emerge of phosphorus cycling during the Frasnian–Famennian transition, particularly for recycling of sedimentary phosphorus in anoxic conditions, which has previously been tested in only one area. The results also allow investigation of the variability in interactions between regional disturbances to the P cycle and global/local environmental perturbations during the Kellwasser crises. Finally, sediments from Kowala spanning the upper Famennian Annulata and Hangenberg shales are investigated for P content and TOC/P_{tot} ratios, giving insight into whether the relationship between marine anoxia and P-cycle perturbations within a single marine basin varied across the different Late Devonian events.

2. Study areas

2.1. Steinbruch Schmidt (Germany, 51° 5' 12.1" N, 9° 7' 53.9" E)

The abandoned quarry "Steinbruch Schmidt" near the town of Bad Wildungen (Hesse, Germany) records the classic expression of the Kellwasser horizons as two distinct units of black carbonates and shales, interbedded with uppermost Frasnian and lowermost Famennian pelagic limestones (Schindler, 1990; Buggisch, 1991). The section also contains a bentonite that has been precisely uranium-lead dated to 372.36±0.053 Ma, helping to constrain the ages of the two Kellwasser crises (Percival *et al*., 2018). Two positive excursions are documented in bulk carbonate $\delta^{13}C$, characteristic of records of the Kellwasser events (Joachimski and Buggisch, 1993). These pelagic sediments were deposited on a submarine rise that was part of a large carbonate platform in northeastern Laurentia (also referred to as the southeastern part of Laurussia), indicating an environment distal from the palaeoshoreline (Meischner, 1971; Devleeschouwer *et al*., 2002). A minimal influx of detrital terrigenous material to this location is further suggested by decreased Ti/Al, Si/Al, and Zr/Rb ratios within the Kellwasser strata (Pujol *et al*., 2006; Weiner *et al*., 2017; and supplementary information therein), and potentially supported by a relatively low kaolinite/illite clay composition (Devleeschouwer *et al*., 2002).

The fossiliferous, bioturbated, carbonate-rich strata that envelope the Kellwasser horizons at Steinbruch Schmidt are interpreted as recording oxygenated marine conditions, and whilst it is accepted that the Kellwasser horizons mark times of a more oxygen-depleted water column, the degree of anoxia remains less clear. V/Cr and Th/U ratios from the Kellwasser horizons suggest that at least dysoxic conditions developed, but that sustained anoxia/euxinia probably did not (Pujol *et al*., 2006; Weiner *et al*., 2017). This conclusion is supported by ostracod fauna within the UKW Level, which also indicate variable degrees of oxygenation and that truly anoxic conditions were no more than intermittent (Casier and Lethiers, 1998). However, some nearby German sections have been interpreted as recording more sustained anoxia during the Kellwasser events (Bond *et al*., 2004; Pujol *et al*., 2006; Riquier *et al*., 2006), and whilst it is possible that redox changes across individual (but close) environments were variable during these crises, it cannot be discounted that the palaeoenvironment at Steinbruch Schmidt also featured prolonged anoxia at those times.

2.2 Kowala Quarry (Poland, 50° 47' 42" N, 20° 33' 43" E)

The Kowala Quarry (hereafter named Kowala) is an actively worked site near Kielce in Poland, which exposes a relatively expanded Frasnian through to basal Tournasian (lowest Carboniferous) succession from the Chęciny–Zbrza Basin (see Racki *et al*., 2002; and references therein). This intra-shelf basin was part of a very widespread carbonate platform that extended across more than 500 km of the northeastern part of Laurentia. The strata largely consist of organic-rich shales and limestones, often cyclically interbedded, allowing for the reconstruction of a cyclostratigraphic timescale for this record (De Vleeschouwer *et al*., 2013, 2017). This age model is well constrained by excellent conodont biostratigraphy (Szulczewski, 1996). The LKW Horizon is not clearly defined at Kowala. Percival *et al*. (2019) interpreted a set of laminated organic-rich shales from 12 m below the F–F boundary that featured both organic and inorganic geochemical indications of oxygen-depleted conditions as the LKW strata, and this interpretation is followed for this study, but there is no evidence of a positive excursion in δ^{13}C values in either bulk carbonate or organic material.

In contrast, the UKW Horizon is very well defined at Kowala, with euxinic conditions indicated by the appearance of finely laminated organic-rich micrites and shales, fine grained framboidal pyrite populations, and trace-metal content perturbations (Joachimski *et al*., 2001; Racki *et al*., 2002; Bond *et al*., 2004). A clear positive excursion in δ^{13}C is also documented in both organic matter and bulk carbonates in the UKW Horizon (Joachimski *et al*., 2001; Percival *et al*. 2019). However, unlike at Steinbruch Schmidt where non-Kellwasser strata record a continuously well-oxygenated water column, several studies indicate that redox conditions at Kowala outside of the times of the Kellwasser events were much more variable, alternating from suboxic at times all the way up to intermittent episodes of euxinia (e.g., Bond and Zatoń, 2003; Bond *et al*., 2004;

Marynowski *et al*., 2011). Increased levels of primary productivity and detrital input have also been reported from the UKW Horizon (Racki *et al*., 2002; Pujol *et al*., 2006), whilst shifts in reconstructed osmium-isotope compositions towards radiogenic values further support hypotheses that the Kellwasser horizons at Kowala were deposited during times of globally enhanced continental weathering (Percival *et al*., 2019).

The upper Famennian Annulata and Hangenberg shales are also currently well exposed at Kowala (e.g., Bond and Zatoń, 2003; Racka *et al*., 2010; Marynowski *et al*., 2012). Both horizons are marked by the appearance of black, organic-rich, laminated shales, although the Annulata unit also features more carbonaceous layers (Racka *et al*., 2010; Marynowski *et al*., 2012). Osmium-isotope data indicate that the Annulata Event coincided with a global-scale increase in continental weathering rates (Percival *et al*., 2019). However, detrital influx proxies suggest that the Chęciny–Zbrza Basin itself did not experience a major increase in the input of terrigenous material at that time, although there is evidence for locally enhanced primary productivity (Racka *et al*., 2010). In contrast, terrestrial organic-material that includes compounds indicative of wildfires is present in the Hangenberg shales, indicating that they were deposited relatively proximally to the palaeoshoreline, and supporting a large terrestrial influx to the marine environment during that later event (Marynowski *et al*., 2012). Trace-metal enrichments, framboidal pyrite size populations, and organic biomarkers have all been investigated for both levels. Photic-zone euxinia was probably prevalent throughout the early and later parts of the Annulata Event, but with a re-oxygenation event taking place mid-event; however, bottom-water conditions were probably more variably oxic-dysoxic during the early stages of the Annulata crisis, before becoming persistently deoxygenated during the later stages (Racka *et al*., 2010). Photic-zone euxinia appears to have also prevailed in the Chęciny–Zbrza Basin throughout the Hangenberg Event (Marynowski *et al*., 2012), but it is less clear how bottom-water conditions developed during this crisis (Marynowski *et al*., 2012, 2017; Derkowski and Marynowski, 2018).

2.3 Coumiac (France, 43° 27’ 40.7” N, 3° 2’ 25.1” E)

The Global Boundary Stratotype Section and Point (GSSP) for the base of the Famennian at Coumiac documents a well-oxygenated pelagic setting on the southern margin of the Rheic Ocean (Klapper *et al*., 1993). The strata are dominated by pale micritic carbonates that were deposited in a pelagic environment, which results in a very condensed stratigraphic succession due to the relatively starved influx of sediment. There is little facies evidence for prolonged marine anoxia during either Kellwasser event at that location, apart from a single thin shale layer preserved at the F–F boundary (Bond *et al*., 2004). TOC content is negligible throughout the section apart from in the boundary layer, where it reaches 0.3 wt% (*this study*, Figure 3C). Pyrite framboids are also only known from the F–F boundary, where their size distributions are consistent with the development of dysoxic, but not truly anoxic or euxinic, conditions in the water column (Bond *et al*., 2004). Dysoxic conditions during the Kellwasser crises are also supported by moderate increases in V/Cr ratios at those event levels (Pujol *et al*., 2006). Although the pelagic setting is suggestive of minimal terrestrial influence on this environment, an increase in detrital influx during the UKW Event might be indicated by enrichments in Si/Al, Ti/Al, and Zr/Al_2O_3 at the F–F boundary (Pujol *et al*., 2006). Despite the condensed nature of this record, the abundance of well-preserved conodonts allows for well constrained biostratigraphy; oxygen-isotope analysis of these fossils has also indicated cooling temperatures during and following the Kellwasser events (Balter *et al*., 2008).

2.4. Erfoud (Morocco, 31˚ 25' 52.7" N, 4˚ 13' 29.8" W)

Upper Devonian sequences in the Anti-Atlas area of Morocco record deposition on a carbonate shelf at the northwestern margin of Gondwana, which faced the southeastern part of the Rheic Ocean, (Wendt and Belka, 1991). Sedimentary samples spanning the stratigraphic record of the Kellwasser horizons and F–F boundary were collected near the town of Erfoud. The succession was deposited on a submarine rise between the Rheris and Tafilalt basins, in the eastern part of the Tafilalt Platform; thus, it is considered to have likely been quite distal from the palaeoshoreline. The lithology chiefly consists of limestones topped with condensed surfaces, which are rich in benthic, nektonic, and planktonic fauna. The LKW Horizon is marked by the appearance of laminated dark shales largely devoid of marine fossils, overlain by carbonate breccias and tempestites, which is interpreted here as indicating a marine transgression across the LKW Event followed by an abrupt regression in its aftermath. The UKW Horizon also features fossil-depleted laminated dark shales (with some more carbonaceous layers), but it is overlain by limestones that are also relatively impoverished, dominated by planktonic prasinophytes. A number of erosive horizons outcrop above this 'disaster' bed (50 cm above the top of the UKW Horizon) that may indicate another regressive event shortly after the F–F mass extinction. Thus, the record of water-column deoxygenation at Erfoud is superficially similar to settings in Germany, with transgressive black shales clearly marking the two Kellwasser horizons, and evidence for marine regressions following each crisis (see Bond and Wignall, 2008). Detailed biostratigraphy is lacking for the Erfoud section, but the known positions of the F–F boundary and Kellwasser levels (the latter supported by carbon-isotope data from this study) allow the approximate intervals of the Late *rhenana*, *linguiformis*, and *triangularis* zones to be inferred. Although the rocks clearly show that they have been significantly oxidized, featuring both a reddish appearance and a mineralogy depleted in reduced-iron species such as pyrite, the presence of 3–4 wt% goethite (the product of pyrite oxidation) in the Kellwasser levels suggests that those shales were indeed deposited in an oxygen-depleted water column. However, given the apparent variability in the degrees of anoxia that developed at the individual German records, it is not clear whether Erfoud records merely suboxic–dysoxic conditions during the Kellwasser crises, or if sustained anoxia/euxinia was a feature of this location. In addition to analysis of P contents in sediments, δ^{13}C values of organic matter were investigated in sediments from this site, in order to verify the stratigraphic positions of the Upper and Lower Kellwasser horizons.

2.5. South Oscar Range (Australia, 17° 54' 53.6" S, 125° 17' 57.0" E)

The South Oscar Range section is one of several stratigraphic successions recording a Late Devonian carbonate reef on the Lennard Shelf, at the edge of the Canning Basin. These records document a well-oxygenated environment on the shelf throughout the Late Devonian, with no indication from the preserved facies that marine anoxia developed in this area during either of the Kellwasser events (Playford, 1980). The section itself was deposited in an open marine environment on the fore-reef slope, with the lithology dominated by platform derived mega-breccias and limestone grainflows in the upper Frasnian strata, overlain by fine-grained limestones above the LKW Horizon (Hillbun *et al*., 2015). This facies change is consistent with a rise in sea-level during marine transgressions at the onset of both of the Kellwasser crises (Hillbun *et al*., 2015; Playton *et al*., 2016). Evidence of deep-water stromatolites observed in strata crossing the UKW Horizon and F–F boundary might support a transgression at that time (George, 1999). In the absence of organic-rich shales or any other evidence for sustained anoxia (such as trace-metal enrichments or organic biomarkers), the stratigraphic position of the Kellwasser horizons has been determined on the basis of two positive $\delta^{13}C$ excursions in bulk carbonate just below the F–F boundary (Hillbun *et al*., 2015; Playton *et al*., 2016). Although marine anoxia is not indicated by the appearance of organic-rich shales, uranium/thorium and vanadium/chromium ratios indicate the possibility of at least dysoxic conditions at the South Oscar Range during those crises (Hillbun *et al*., 2015).

2.6. Dingo Gap (Australia, 17˚ 40’ 0.2” S, 125˚ 12’ 1.3” E)

Dingo Gap represents a second section from the Lennard Shelf, about 100 km to the north west of the South Oscar Range transect. Upper Frasnian strata record an open-marine embayment within a fore-reef marginal slope environment, lithologically consisting of mega breccias and grainflows (George *et al*., 1997; Stephens and Sumner, 2003). The F–F boundary has been constrained to within 7 m on the basis of conodont biostratigraphy (George *et al*., 1997), and is marked by outcropping of the reef breccias, allochthonous blocks and/or bioherms, often overlain by deep-water stromatolites. In contrast, lower Famennian strata are made up of finer grained silty/sandy limestones (George *et al*., 1997; Stephens and Sumner, 2003). This change in lithology is thought to record a change in sea level, likely a rise during a transgressive event in the latest Frasnian, consistent with models from European records (Stephens and Sumner, 2003). As for the South Oscar Range, the Kellwasser horizons can only be defined on the basis of carbon-isotope chemostratigraphy. Two positive excursions in bulk carbonate $\delta^{13}C$ values within uppermost Frasnian strata have been interpreted as being time-equivalent to those associated with the Kellwasser levels in Europe and North America (Stephens and Sumner, 2003).

3. Methods

Chemical preparation and analyses of samples for phosphorus concentrations were carried out at the University of Lausanne using a UV/Vis Perkin Elmer Spectro-photometer LAMBDA 25 operating at a wavelength of 810 nm, following the methods in Eaton *et al*. (1995) and Fantasia *et al*. (2018). 100±5 mg of homogeneously powdered sample were weighed into a cleaned vial, and the precise mass recorded. 1 mL of 1 M $Mg(NO_3)_2$ was added to the powder, and roasted in an oven at 550 °C for 2.5 hr (following a stepwise temperature increase of 100 °C for 30 min and 250 °C for a further 30 min before being elevated to 550 °C). Once cooled, 10 mL of 1 N HCl were added to each sample, and the glass vials placed on a shaker for 16 hr to liberate the phosphorus from the dried residue. Samples were then filtered (0.45 μm) and transferred to HDPE scintillation vials, and refrigerated overnight before analysis. For clay-rich samples that likely had a high P_{tot} content, 40 μL of the refrigerated HCl-phosphorus solution was added to 3.95 mL of 0.1 M HCl in a plastic vial. For all other samples, 300 μL of the phosphorus solution was added to 2.75 mL of Milli-Q water. 100 μL of Mixing Reagent (a 2:1 mixture of ammonium molybdate solution and antimony potassium tartate sulphuric acid solution) and 100 μL of absorbic acid were added to all samples (Eaton *et al*., 1995). Repeated preparation and analyses of two internal standards and two carbonate samples indicate an analytical uncertainty of less than ±5%. A procedural blank and six PO_4^{3-}.HCl standard solutions (1, 2.5, 5, 10, 15, 20 μM) were used to calibrate the photometric measurements.

Total organic carbon (TOC) content was investigated using a Rock Eval 6 at the University of Lausanne, as described by Behar *et al*. (2001). The organic-carbon hydrogen index (HI), oxygen index (OI), and temperature of maximum hydrocarbon generation (T_{max}) parameters were also measured during these analyses. Aliquots of homogeneous powdered samples were weighed into crucibles, and their precise mass determined. 70±2 mg were weighed for very carbonate rich samples, with 60±2 mg weighed for less calcareous powders, and 50±2 mg for black shales with a likely high organic-matter content. Carbon-isotope values of bulk organic matter ($\delta^{13}C_{org}$ in ‰ vs VPDB) for Erfoud sedimentary rocks were determined on powdered samples that had been decarbonated with 10% HCl prior to analysis, using flash combustion on a Carlo Erba 1108 elemental analyser connected to a Thermo Fisher Scientic Delta V isotope ratio mass spectrometer. Other major-element analyses were conducted at the University of Lausanne, following the methods in Percival *et al*. (2019). New P, Si, Ti, and Al data were generated on a PANalytical PW2400 spectrometer using X-ray fluorescence (XRF) analyses of fused lithium tetraborate glass discs, with an analytical uncertainty lower than ±5% (Fantasia *et al*., 2018).

4. Results

4.1. Total organic carbon content and carbon-isotope data as a marker of the Kellwasser horizons

There is a significant increase in TOC content (<0.1 wt% to 2.93 wt%: Figure 3A) within the Kellwasser Horizons at Steinbruch Schmidt compared to the pale limestones that they are interbedded with, consistent with previously published data (Casier *et al*., 1999). Notably, the highest TOC values are within the black shale units; the black limestone layers that are also present within the Kellwasser horizons show a smaller increase in organic carbon content compared to background. The Rock-Eval analyses produced further information regarding the organic matter from within the Kellwasser strata, highlighting very low HI values, but very high OI and T_{max}. Such parameters indicate that the organic carbon currently consists of Type IV Kerogen (see Supplementary Tables and Peters, 1986); consequently, the organic matter at Steinbruch Schmidt is highly mature following oxidation and/or post-burial heating (see also Devleeschouwer *et al*., 2002) as well as significant surface weathering. Thus, the original TOC content at Steinbruch Schmidt was probably much greater than the quantity measured in the samples. In contrast, the high HI and relatively low OI and T_{max} values in black shales at Kowala are indicative of very immature, predominantly marine, organic matter, suggesting that the increased TOC contents recorded at the Kellwasser horizons there reflect original values. A small increase in TOC is also observed in the condensed UKW Horizon at Coumiac (<0.1 wt% to 0.3 wt%: Figure 3C), but even this maximum content is too low to provide meaningful HI, OI, or T_{max} parameters. The oxidized state of the Erfoud sediments means that their current organic content is extremely low, and consequently determination of the above parameters is difficult for that record.

New carbon-isotope data from the sediments at Erfoud highlight two positive $\delta^{13}C_{org}$ excursions in the black shales that are interpreted as being the Kellwasser horizons at that location (Figure 3D). The stratigraphically higher of the two shifts also continues above the UKW Horizon. Thus, the stratigraphic trends in $\delta^{13}C$ at Erfoud are consistent with a number of well-known records from Europe and elsewhere (see e.g., Joachimski and Buggisch, 1993; Joachimski *et al*., 2002).

4.2. Phosphorus concentrations and P_{tot}/Al ratios

Cross correlation of P_{tot} contents in samples investigated by both spectrophotometry and XRF analyses shows good comparability between the two methods (r^2 = 0.8110; see Supplementary Figure 1), and stratigraphic plotting of the data generated by the two methods also shows highly comparable trends, confirming this result (see data in supplementary information).

Stratigraphic patterns in P content (P_{tot}) in LKW strata show significant variation across the six studied sites (Figure 3). There is a clear increase (from 129 ppm to 839 ppm) in P_{tot} in LKW sediments at Steinbruch Schmidt (Figure 3A), and whilst there are also peaks up to 0.05 in P_{tot}/Al, they do not correspond to the same samples. Rather, the peaks in P_{tot}/Al occur where P_{tot} values are near background, but Al contents are also low; whereas the samples with high P_{tot} also feature elevated Al concentrations, leading to reduced P_{tot}/Al. Small increases in P_{tot} may also possibly be present at the top of the LKW Horizon at Kowala (from 297 to 644 ppm) and slightly below that level at the South Oscar Range (from 27 to 134 ppm), although those data are at low resolution (Figures 3B and 3E). Moreover, there is no deviation in P_{tot}/Al values across the LKW horizon at Kowala compared to either background values or the upper crustal average (Figure 3B). No enrichments in either P_{tot} or P_{tot}/Al are recorded in time-equivalent strata at Coumiac (Figure 3C), Erfoud (Figure 3D) or Dingo Gap (Figure 3F).

P_{tot} trends from Upper Kellwasser sediments show greater consistency across the studied sites. There is a clear peak in P_{tot} at the base of UKW Horizon at Kowala (to over 3500 ppm; Figure 3B) with additional spikes between the Kellwasser levels, and a similar enrichment in P_{tot} at Steinbruch Schmidt (168 ppm to 871 ppm; Figure 3A) beginning in the limestone bed just below the UKW Horizon. In both locations, the samples with elevated P_{tot} also feature increased P_{tot}/Al ratios, which in the case of Kowala greatly exceed the average upper crustal value (up to 0.15 at the base of or slightly below the UKW Level). A small increase in P_{tot} at the Kowala F–F boundary (to 917 ppm) is also reflected in a large peak in P_{tot}/Al ratio (to 0.167) but again, this peak is exaggerated by a significantly below-average Al content in that sedimentary layer. An elevation in P_{tot} values (to over 2000 ppm) is also recorded within UKW strata at Erfoud, with a single sample also showing a high P_{tot} content just below that level (Figure 3D), but only the peak just below the boundary is maintained as a high P_{tot}/Al ratio (of 0.149), suggesting that the P_{tot} enrichments within the UKW Horizon at Erfoud may be a product of the lithological change.

By contrast, P_{tot} values show a decrease at the F–F boundary and UKW Horizon at Coumiac (Figure 3C), but the P_{tot}/Al ratios at the boundary and just below are very elevated (up to 0.219). This result may partly be caused by the very low Al content of the Coumiac sediments (as carbonate-rich pelagic limestones); thus, it is not clear how truly representative of lithological changes these low Al contents might be. The low-resolution nature of the two Canning datasets means that neither record features P_{tot} results from the base of the UKW Horizon (Figures 3E and 3F), although a slight increase across the F–F boundary of the South Oscar Range section might hint at a possible P enrichment across UKW strata at that location.

A large increase in P_{tot} is also observed at the base of the Annulata (Figure 4B) and Hangenberg (Figure 4A) horizons at Kowala (from 282 ppm to 2270 ppm, and 285 ppm to 825 ppm, respectively). In the case of the Annulata, P_{tot} remains elevated throughout this unit before a second peak at the top of the level, whereas P_{tot} returns to background values or less above the base of the Hangenberg shale. Trends in P_{tot}/Al for both stratigraphic levels correlate very well with the P_{tot} variations (with enrichments from 0.004 to 0.05 across the Annulata Horizon, and 0.004 to 0.025 for the Hangenberg Level), strongly suggesting that these enrichments in P_{tot} are independent of lithological changes.

4.3. TOC/phosphorus ratios as evidence for nutrient cycling

The ratio of TOC/P_{org} in modern organic matter was initially proposed to be 106 (Redfield, 1958). Subsequent studies have revised this value to a global average of ~140 (e.g., Ho *et al*., 2003; Martiny *et al*., 2013) with significant variations between ~50 and ~2000 across different geographical regions and species (e.g., Ho *et al*., 2003; Algeo and Ingall, 2007; Martiny *et al*., 2013), but seldom exceeding ~115 in oxic marine sediments (Dale *et al*., 2016). The value of 115 is assumed here to have been the same during the Devonian. Whilst this relationship actually applies to TOC/P_{org} rather than the TOC/P_{tot} ratios presented here, most phosphorus is deposited through the water column in particulate organic form (Delaney, 1998). Thus, at the time of initial deposition prior to any conversion of P_{org} to authigenic phases, TOC/P_{org} should have been roughly equal to TOC/P_{tot}, with both ratios theoretically close to Redfield values. Over time, conversion of P_{org} to authigenic phases within the sediments will raise TOC/P_{org}, but leave TOC/P_{tot} relatively unchanged. Alternatively, liberation of sedimentary P_{org} under reducing conditions will inflate both TOC/P_{org} and TOC/P_{tot} (the latter by a lesser degree). Consequently, on the assumption that the content of detrital P is typically very low, it has been proposed that TOC/P_{tot} ratios elevated above the Redfield ratio represent a more reliable indicator of P_{org} liberation than TOC/P_{org}, unless P speciation analyses have also been undertaken that can rule out major conversion of organic P to authigenic species as the cause of elevated TOC/P_{org} (Algeo and Ingall, 2007; Kraal *et al*., 2010).

Sedimentary records of all four studied events highlight increases in TOC/P_{tot} ratios. A large increase in TOC/P_{tot} values is recorded within the LKW horizon at Kowala and Steinbruch Schmidt (38 mol/mol to 270 mol/mol, and 12 mol/mol to 222 mol/mol, respectively; Figures 3A and 3B). In comparison, there is only a slight elevation in TOC/P_{tot} associated with the LKW at Coumiac (5 mol/mol to 8 mol/mol; Figure 3C). Large increases in TOC/P_{tot} ratios are also observed in UKW strata across all of Kowala, Steinbruch Schmidt, and Coumiac, with an increase from 15 mol/mol to 573 mol/mol documented at Kowala (Figure 3B), from 3 mol/mol to 111 mol/mol at Steinbruch Schmidt (Figure 2A), and from 3 mol/mol to 39 mol/mol at Coumiac (Figure 3C). Finally, increased TOC/P_{tot} values are recorded within both of the Annulata and Hangenberg levels compared to the sediments below (25 mol/mol to 718 mol/mol for the Annulata, and 12 mol/mol to 978 mol/mol for the Hangenberg; Figure 4).

4.4. Major element proxies for terrestrial influx

Ti/Al ratios clearly decrease across the Kellwasser horizons at Steinbruch Schmidt; whilst Si/Al values are more variable within those strata, without showing any indications of enrichment above background Frasnian levels (Figure 5A). There is no deviation from background in either Si/Al or Ti/Al across the LKW at Kowala, but a pronounced spike in both proxies is observed at the Frasnian–Famennian boundary, with a possible slight increase in Ti/Al at the base of the UKW Horizon (Figure 5B). The Si/Al and Ti/Al data at Coumiac are at a low resolution, but appear to increase marginally just below the Frasnian–Famennian boundary and interpreted UKW Level (Figure 5C). However, it should be noted that Al contents are very low at Coumiac, and consequently, the trends in these ratios should be interpreted with caution. Similarly to Steinbruch Schmidt, there is no clear evidence for increased Si/Al or Ti/Al in either Kellwasser level recorded at Erfoud (Figure 5D). These results are generally very comparable with those of Pujol *et al*. (2006), and the Steinbruch Schmidt trends are also similar to the high-resolution data of Weiner *et al*. (2017; see supplementary information therein). Pujol *et al*. (2006) recorded more pronounced spikes in Si/Al and Ti/Al in the UKW Horizons of Kowala and Coumiac than are found here, but these discrepancies may be explained by the fact that these Kowala samples were drilled in a markedly different part of the quarry to the samples used by Pujol *et al*. (2006), and condensed nature of that record and low-resolution of both datasets at Coumiac.

A single data-point peak is noted in Si/Al in the lower part of the Hangenberg Shale at Kowala; by contrast, Ti/Al values fall across that level (Figure 6A). There are no clear deviations in either Si/Al or Ti/Al at the Annulata Level in Kowala (Figure 6B), consistent with the results of Racka *et al*. (2010).

5. Discussion

5.1. Nutrient recycling during the Devonian anoxic events

Elevations in TOC/P_{tot} to above 115 in both Kellwasser horizons at Kowala suggest that phosphorus has been lost from the sediments following deposition. In the modern, organic P is largely recycled from sediments to the water column in reducing conditions (Van Cappellen and Ingall, 1994), and this phenomenon has also been inferred as operating during the Mesozoic OAEs (e.g., Mort *et al*., 2007; Westermann *et al*., 2013; Fantasia *et al*., 2018). Alternatively, this change could result from a lower influx of authigenic or detrital P to sediments at Kowala during the Kellwasser crises. However, there is clear evidence for anoxic/euxinic conditions at Kowala during both Kellwasser events (e.g., Joachimski *et al*., 2001; Bond *et al*., 2004; Pujol *et al*., 2006; Percival *et al*., 2019), consistent with the hypothesis of recycling of sedimentary P to the water column under reducing conditions. In contrast, there is no clear negative correlation between P_{tot} or P_{tot}/Al and TOC/P_{tot} that might imply a lower influx of detrital or authigenic P (Figure 3B). Consequently, it is concluded that once oxygen-depleted settings developed at Kowala during the two Kellwasser crises, sedimentary phosphorus recycling became a major feature of the marine environment, consistent with conclusions drawn from the Appalachian Basin record in northeastern North America (Murphy *et al*., 2000; Sageman *et al*., 2003). Because phosphorus is often a strongly bio-limiting nutrient, such remobilization would have helped sustain a high level of primary productivity in the water column, aiding the prolongation of marine anoxia/euxinia during the Kellwasser crises.

The less clear TOC/P_{tot} peaks across the Kellwasser levels at Steinbruch Schmidt, with only one data point from each horizon exceeding 115 (Figure 3A), may indicate that recycling of sedimentary P_{org} was less efficient in the dysoxic conditions at that location during the crises (compared to the truly anoxic/euxinic environment at Kowala during those times; Pujol *et al*., 2006; Weiner *et al*., 2017). However, it is important to note the highly oxidized nature of the Steinbruch Schimidt sediments and likely reduction of sedimentary TOC content since the time of deposition. Thus, the original TOC/P_{tot} ratios in Kellwasser strata at Steinbruch Schmidt were likely higher and could have clearly exceeded 115, before being reduced following the maturation/weathering of organic carbon in that stratigraphic succession (sedimentary P_{org} is comparatively resilient to such processes so would have been less likely to be lost; see Kolowith and Berner, 2002). Consequently, it is interpreted that some degree of sedimentary P_{org} recycling took place at Steinbruch Schmidt during the Kellwasser crises and aided the maintenance of oxygen-depleted conditions at those times. Although, without knowing the original TOC content, it is unclear whether this phosphorus regeneration was truly sustained, or merely intermittent, during the two events. As noted above, significant post-depositional oxidation of the Erfoud sediments hinders accurate determination of TOC contents and TOC/P_{tot} ratios for that record. However, given the comparable appearance of laminated black shales within pale limestone facies at the Moroccan section compared to Steinbruch Schmidt and other German Frasnian–Famennian records, it is assumed that nutrient recycling in a similarly oxygen-depleted water column would also have taken place at Erfoud.

The very small TOC/P_{tot} increase at the Coumiac UKW Level might indicate a minor amount of phosphorus recycling in the dysoxic conditions proposed to have occurred at that location during the event (Bond *et al*., 2004; Pujol *et al*., 2006), potentially muted by more efficient retention of sedimentary phosphorus as iron-bound P. TOC/P_{tot} trends can also not be reconstructed for the South Oscar Range and Dingo Gap sections, due to the negligible organic-carbon content in sediments from those records. However, in the absence of evidence for anoxic conditions developing in the Canning Basin during the Frasnian–Famennian transition (Hillbun *et al*., 2015; Tulipani *et al*., 2015), and given the relatively high-energy environment under which the studied sedimentary records from that region formed, it is assumed that there would not have been significant recycling of nutrients from newly deposited sediments. This conclusion may be supported by the low P_{tot} content both within the South Oscar Range and Dingo Gap Frasnian–Famennian strata and other beds, suggesting that there was a minimal influx of the element to that region.

In addition, the elevated TOC/P_{tot} ratios recorded throughout the black-shale horizons associated with the Annulata and Hangenberg shales at Kowala strongly support a role for nutrient recycling in sustaining oxygen-depleted conditions during those environmental perturbations (Figure 4), consistent with the findings of Racka *et al*. (2010). Elevated TOC/P_{tot} ratios have been reported from black shale horizons that mark a number of earlier Devonian climate events, such as the

Givetian–Frasnian Frasnes Event and the early Frasnian Punctata Event (Sageman *et al*., 2003). Consequently, nutrient recycling associated with reducing conditions in the water column appears to have occurred at some locations during each of the Late Devonian crises, and in certain marine basins (e.g., the Chęciny–Zbrza Basin) were a common feature of all those environmental perturbations.

5.2. Phosphorus fluxes during the Devonian crises

There is no clear indication of elevated P influx during the LKW Event to the marine palaeoenvironments investigated in this study. No increase in P_{tot} or P_{tot}/Al is documented within LKW strata at Coumiac, Erfoud, or Dingo Gap (Figures 3C, 3D, and 3F). The high P_{tot} values do not correlate with peaks in P_{tot}/Al ratios at Steinbruch Schmidt (Figure 3A), indicating that they likely result from the change in lithology from organic-lean carbonates to black, clay-rich, shales. The very small increase in P_{tot} observed at the top of the LKW Horizon at Kowala occurs stratigraphically above the geochemical evidence for anoxia and P recycling (Figure 3B; see also supplementary figure 1); therefore, it cannot indicate a nutrient influx responsible for the stimulation of those processes. One data point at the South Oscar Range section suggests a P_{tot} increase correlative with the base of the LKW Horizon (Figure 3E), but even if there was an increase in nutrient influx to elevate primary productivity, there is no evidence that marine anoxia developed at that location. In addition to the lack of enriched P_{tot} contents, there is no evidence from the detrital proxies of Ti/Al or Si/Al for an increase in terrigenous material at any of Steinbruch Schmidt, Kowala, Coumiac, or Erfoud during the LKW Event (Figure 5).

However, a net-global increase in continental weathering rates prior to and during the onset of the LKW Event has been shown by stratigraphic trends in Sr and Os isotopes (Chen *et al*., 2005; Percival *et al*., 2019), and there is evidence for increased terrestrial runoff to other marine environments in North America and South China (Whalen *et al*., 2015). But whilst it is clear that anoxia may have been triggered by the direct runoff of terrestrial nutrients from proximal land masses in some marine settings during the LKW Event, this does not appear to be the case for any of the more distal environments studied here. Upwelling or alternative inputs of other bio-limiting nutrients (such as iron) to marine shelf environments may also have stimulated elevated primary productivity and consequent anoxic/euxinic conditions during the LKW Event (see Fung *et al*., 2000; Hutchins *et al*., 2002, for modern examples), or anoxic conditions may have arisen in the sites studied here via migration of expanded oxygen-minimum zones during a marine transgression (Bond *et al*., 2004). However, the absence of conclusive P_{tot} enrichments from most studied records is indicative that a perturbation of the phosphorus cycle was not the trigger of anoxia for that crisis.

In contrast to the absence of elevated phosphorus contents in LKW strata, a clear increase in P_{tot} and P_{tot}/Al is documented at the base of UKW Horizon at Kowala (Figure 3B), Erfoud (Figure 3D), Xinjiang in northwest China (Carmichael *et al*., 2014), and potentially also in basal UKW strata in the West Valley Core from Appalachian Basin (Sageman *et al*., 2003; see also Figure 2). Additional peaks in P_{tot}/Al are also recorded in strata between the two Kellwasser horizons at Kowala and correlate with slight increases in Si/Al and Ti/Al (Figure 5B), potentially indicating fluctuations in background terrigenous P influxes to that environment, although these increases might also reflect changes in burial efficiency of P under variable redox conditions (e.g., Algeo and Ingall, 2007). An increase in P_{tot}/Al is also observed within the UKW Horizon at Coumiac, which was also reported for excess P_2O_5 (phosphate/aluminum oxide compared to crustal average) concentrations by Pujol *et al.* (2006). However, it should be noted that there is no increase in P_{tot} content within the UKW Horizon at Coumiac, and the very low Al concentrations in those samples mean that these P_{tot}/Al tends should potentially be interpreted with caution. The elevated P_{tot} contents throughout UKW strata at Steinbruch Schmidt are only partially reproduced by high P_{tot}/Al ratios, suggesting that they are partly the result of the change in lithology, as for the LKW trends (Figure 3A). However, peaks in both P_{tot} and P_{tot}/Al near the top of and just below the UKW level might be equivalent to the enrichments recorded elsewhere. These results suggest that there was a major influx of phosphorus to the marine realm at the onset of the UKW Event. The P_{tot} peak at Kowala also stratigraphically correlates with a shift in osmium isotopes to very radiogenic values at the base of the UKW Horizon (Figure 5B), indicating that this phosphorus input coincided with enhanced continental weathering rates, and supporting terrestrial runoff as a source of the nutrient. This conclusion is supported by Si/Al and Ti/Al evidence for an increased detrital input to marine settings at Kowala, and potentially Coumiac, as well as elsewhere during the UKW Event (Figures 5B and 5C; see also data in Racki *et al*., 2002; Sageman *et al*., 2003; Pujol *et al*., 2006; Whalen *et al*., 2015). However, the absence of evidence for increased terrigenous input to the UKW palaeoenvironments at either Erfoud or Steinbruch Schmidt (Figures 5A and 5D; see also Pujol *et al*., 2006; Weiner *et al*., 2017), or for other German UKW settings (Pujol *et al*., 2006; Riquier *et al*., 2006; Weiner *et al*., 2017), suggests that there was a non-terrestrial nutrient source to some marine areas.

Whilst a record of elevated P_{tot} contents (and P_{tot}/Al ratios; Figure 4B) across the entire stratigraphic interval of the Annulata Horizon at Kowala is consistent with the findings of Racka *et al*. (2010), this trend is unexpected. Elevated TOC/P_{tot} ratios far in excess of 115 in the Annulata shales are interpreted as marking significant recycling of organic phosphorus from marine sediments at that time, which should have limited burial of the element. It is possible that there was a significant accumulation of detrital/authigenic P deposited in this area during the Annulata Event, as such species would not have been remobilized in the oxygen-depleted settings, allowing for an elevated P_{tot} content. However, neither this study or previous work suggests a major influx of terrigenous material or terrestrial organic matter to the Kowala palaeoenvironment during the Annulata Event, particularly during the later part of the crisis (Figure 6B; see also Racka *et al*., 2010), which does not support an enhanced input of detrital P to the area at that time. Alternatively, intermittent episodes of re-oxygenation during the anoxic episode may have allowed for retention of P alongside recycling during times of more reducing conditions. Such a scenario would still have required an external influx of P to the local marine environment. As for the UKW level, the elevations in P_{tot} and P_{tot}/Al correlates with a shift in osmium-isotope values to a more radiogenic composition (Figure 6B; see also Percival *et al*., 2019), suggesting that even if there was no direct increase in terrestrial runoff to the marine environment at Kowala, globally-enhanced continental weathering could have still delivered nutrients such as phosphorus to the global ocean. This phosphorus could then have been recycled via upwelling to locations that had not been affected by a terrestrial influx during the Annulata Event, such as Kowala.

The documentation of a peak in P_{tot} and P_{tot}/Al values (Figure 4A) at the base of the Hangenberg shale at Kowala is consistent with previously published P_2O_5 trends from Xinjiang in northwest China and Cat Co 3 in northeast Vietnam (Carmichael *et al*., 2016; Paschall *et al*., 2019), indicating that widespread marine anoxia was likely stimulated by enhanced primary productivity following an abrupt increase in the influx of nutrients, at least in those three areas. Carmichael *et al*. (2016) proposed that the nutrient input at Xinjiang was derived from runoff of terrigenous material. Documented evidence for nearby wildfires and a high fraction of terrestrial material in organic-matter studies of the Kowala Hangenberg level are indicative of this Polish sequence being deposited close to land (Marynowski *et al*., 2012), and an increase in Si/Al above background and average upper crustal values supports such an elevation in terrigenous influx, although Ti/Al ratios do not show such a change (Figure 6A). Similar observations regarding the influence of the proximal terrestrial realm have been made for Devonian–Carboniferous strata in both the Appalachian and Illinois basins of the western USA (Rimmer *et al*., 2015; see also Martinez *et al*., 2019). Consequently, it is likely that the development of anoxic conditions at Kowala during the Hangenberg Event was also triggered by the enhanced input of terrestrial nutrients, as postulated for Xinjiang and the Appalachian and Illinois basins (Rimmer *et al*., 2015; Carmichael *et al*., 2016). However, the Cat Co 3 palaeoenvironment lacked proximal land masses, leading Pascahall *et al*. (2019) to rule out a terrestrial nutrient influx for that location, and Martinez *et al*. (2019) have also postulated that a terrestrial nutrient influx may have been less important than a marine one in distal-deltaic settings in the area of modern day Cleveland (Ohio, USA).

5.3. Initiation of anoxia by various triggers

It is clear that the development of marine anoxia/euxinia during the Late Devonian events was stimulated by terrestrial runoff in some settings. Even where the direct input of terrigenous material was limited, the influx of continental runoff to the global ocean elsewhere (as evidenced by weathering/detrital proxies) likely increased the oceanic nutrient inventory. Consequently, upwelling of deep waters to marine shelves may have recycled the terrestrial nutrients to areas that did not experience major inputs of terrestrial runoff (as seen off the west coast of Peru today; Burnett, 1977; Burnett *et al.*, 1983 Hutchins *et al.*, 2002), extending the area of oxygen-depleted water bodies. Such a mechanism may explain the increased P contents for the UKW Horizon at Steinbruch Schmidt, the Annulata Shale at Kowala, and the Hangenberg Shale at Cat Co 3, despite no evidence of direct major terrestrial runoff to any of those settings. Marine transgressions associated with both Kellwasser crises and the Annulata Event may also have aided the spread of anoxic water masses at those times (e.g., Sandberg *et al*., 2002; Bond *et al*., 2004), and might have been particularly important during the LKW Event, for which there is little evidence of direct phosphorus influx to the marine environment. Further work is needed to determine which of direct terrestrial runoff to marine basins, recycling of those nutrients from deep waters, or spread of oxygen-depleted water masses during sea-level changes were most important on a global scale for each of the Late Devonian crises, and it is likely that all of those processes played some role in initiating the spread of anoxic conditions during those times.

Once anoxic/euxinic conditions had arisen in the water column, recycling of nutrients was likely a key factor in prolonging oxygen-depleted conditions in some marine areas (such as Kowala and the Appalachian Basin) by stimulating sustained high levels of primary productivity. Oxygen-isotope records from several sedimentary archives of the two Kellwasser events indicate that both Kellwasser crises were associated with global cooling, although spells of warming might have taken place superimposed upon those lower temperatures (Joachimski and Buggisch, 2002; Balter *et al*., 2008; Le Houedec *et al*., 2013; Huang *et al*., 2018). Moreover, sedimentary evidence for southern-hemisphere ice sheets have been dated to the latest Famennian on the basis of miospore biostratigraphy, suggesting that the Hangenberg Event also took place in a relatively cold global climate (e.g., Caputo *et al*., 1986; Streel *et al*., 2000; Kaiser *et al*., 2016). Cold temperatures might have helped enhance continental weathering rates and increase nutrient runoff through elevated erosive processes during glacial expansion and deglaciation (although there is currently no direct evidence for glaciation during the Kellwasser or Annulata crises), but climate cooling should also have encouraged a more oxygenated water column. By contrast, the Mesozoic OAEs are thought to have been associated with hyperthermal events that would have readily promoted oceanic stagnation, further aided by nutrient runoff and recycling associated with warming-driven weathering, all of which there is evidence for during the Mesozoic events (e.g., Mort *et al*. 2007; Kraal *et al*., 2010; Fantasia *et al*., 2018). Consequently, recycling of sedimentary phosphorus in an oxygen-depleted water column to sustain high levels of primary productivity and eutrophication may have been more important for the prolongation of anoxic conditions during the Devonian events than the later Mesozoic ones.

Whatever the precise trigger(s) of each of the individual Late Devonian anoxic events were, the fact that oxygen-depleted water columns developed on numerous occasions during the Frasnian and Famennian stages, likely caused by various mechanisms that may have had different triggers, suggests that the marine realm was particularly susceptible to deoxygenation during that time interval. Several long-term environmental systems experienced major changes throughout Middle–Late Devonian times, with repeated sea-level rises, gradual climate warming, the onset of the Eovariscan Orogeny, and the evolution of vascular-rooted land plants all known to have occurred (e.g., Algeo and Scheckler, 1998; Sandberg *et al*., 2002; Averbuch *et al*., 2005; Joachimski *et al*., 2009). Because soils play a key role in improving the bioavailability of phosphorus in the modern, it is possible that the long-term rise of vascular-root systems (which would have greatly increased soil masses and erosion of them) would have been particularly important. This development would have meant that there was not only a major influx of nutrients to the marine realm during the times of enhanced terrestrial runoff associated with many of the Devonian crises, but that the phosphorus was more bioavailable than it had been previously in Earth's history (see also Algeo and Scheckler, 1998). Although that specific scenario remains speculative, it is likely that one or more of the long-term changes listed above forced the global Devonian hydrosphere towards a state whereby oxygen depletion could easily occur across much of the marine shelf area and/or global ocean (Carmichael *et al*., 2014, 2016; Song *et al*., 2017; White *et al*., 2018).

6. Conclusions

New data from several geographically widespread Late Devonian stratigraphic records have revealed that the global phosphorus cycle was repeatedly disturbed during the numerous anoxic events that took place at that time. Carbon/phosphorus molar ratios of organic matter in excess of the modern global average value of ~115 indicate that recycling of nutrients from sediments deposited in oxygen-depleted conditions maintained enhanced levels of primary productivity and water-column deoxygenation in at least some marine settings during all four of the Late Devonian crises studied here. An increase in phosphorus contents in Upper Kellwasser, Annulata, and Hangenberg strata suggests that the marine anoxia/euxinia was initiated by the increased influx of that element (and potentially other nutrients) to the marine realm during those crises. Correlations of these phosphorus peaks with evidence for enhanced weathering rates suggest that this increased nutrient input resulted from significant runoff of terrigenous material to the marine realm, although delivery of these nutrients to some shelf settings potentially required subsequent oceanic cycling and upwelling. There is no equivalent enrichment in phosphorus associated with the Lower Kellwasser Horizon, despite clear indications of increased primary productivity and oxygen depletion in the water column in the same strata. Consequently, it is suggested that the environmental perturbations associated with the Lower Kellwasser Event largely did not result from a major influx of phosphorus to the marine realm, perhaps suggesting that this lesser biotic crisis likely had a profoundly different causal mechanism to the Upper Kellwasser anoxic event and other Devonian crises. It is concluded that the development of oxygen-depleted water columns for individual locations and events was likely stimulated via a number of different mechanisms throughout the Late Devonian, highlighting that the Late Devonian marine realm was particularly susceptible to the rise of anoxic conditions during that interval.

Ultimately, this tendency towards oxygen-depleted marine environments likely resulted from long-term processes such as repeated sea-level rises, orogenic episodes, magmatic activity, glaciation, and the evolution/geographical expansion of vascular rooted land-plants, that were taking place throughout Devonian–Carboniferous times.

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Figure Captions

Figure 1: Palaeogeographic map of the Late Devonian world, adapted from Percival *et al*., 2018. The locations of sedimentary sequences presented are as follows (white circles mark sites where the P_{tot} data are new for this study; the black circle indicates an area where P_{tot} data have been published previously): A = Steinbruch Schmidt, Germany; B = Kowala Quarry, Poland; C = Coumiac, France; D= Erfoud, Morocco; E = South Oscar Range, Australia, F = Dingo Gap, Australia; W = West Valley Core, New York, USA (Murphy *et al*., 2000; Sageman *et al*., 2003).

Figure 2: Previously published geochemical data plots of $\delta^{13}C$, TOC, P_{tot}, $TOC/P_{tot,}$ and Os-isotope trends for the West Valley Core (Murphy *et al*., 2000; Sageman *et al*., 2003; Turgeon *et al*.,

2007), with lithological and biostratigraphic information adapted from the same sources. All vertical scales are in meters. Fm., *ling*., and *triang*. indicate the Famennian Stage and *linguiformis* and *triangularis* conodont Zones, respectively. The TOC/P_{org} modern global average ratio is marked on all TOC/P_{tot} plots at 115 (Dale *et al*., 2016).

Figure 3: Geochemical data plots of δ^{13}C and P_{tot}, for all Kellwasser Horizons where new P data is presented for this study. P_{tot} concentrations normalized to Al contents (P_{tot}/Al), together with TOC and TOC/P_{tot} measurements, are also presented from sedimentary records of the Kellwasser horizons at (A) Steinbruch Schmidt, Germany, (B) Kowala, Poland (C) Coumiac, France, and (D) Erfoud, Morocco (P_{tot}/Al only). All vertical scales are in meters; the stratigraphic positions of the Lower (LKW) and Upper (UKW) Kellwasser horizons are indicated by the grey bars. Zone refers to conodont biostratigraphic Zones. Fm., *ling*., and *triang*. indicate the Famennian Stage and *linguiformis* and *triangularis* conodont Zones, respectively. The TOC/P_{org} modern global average ratio is marked on all TOC/P_{tot} plots at 115 (Dale *et al*., 2016), and the upper crustal average P/Al ratio (~0.01; Taylor and McLennan, 1995) is indicated on all P_{tot}/Al plots. All P_{tot}, P_{tot}/Al, and TOC/P_{tot} data are from this study. TOC data from Kowala are from Percival *et al*. (2019). TOC data from Steinbruch Schmidt and Coumiac, and δ^{13}C data from Erfoud, are from this study. Previously published carbon-isotope data are sourced as follows: Steinbruch Schmidt and Coumiac from Joachimski and Buggisch (1993); Kowala from Percival *et al*. (2019); South Oscar Range from Playton *et al*. (2016); Dingo Gap from Stephens and Sumner (2003). Biostratigraphic data are sourced as follows: Steinbruch Schmidt from Schindler (1990); Coumiac from Bond *et al*. (2004); Erfoud from this study; South Oscar Range from Playton *et al*. (2016). Lithological data are sourced as follows: Steinbruch Schmidt from Schindler (1990); Kowala from Percival *et al*. (2019); Coumiac from Bond *et al*. (2004); all other sites from this study. Osmium-isotope data from Kowala are from Percival *et al*. (2019); Note the variable scales for TOC, and the colour distinction between dark green for representing $\delta^{13}C_{org}$ and light green for $\delta^{13}C_{org}$.

Figure 4: Geochemical data plots for TOC, P_{tot}, P_{tot}/Al and TOC/P_{tot} measurements from sedimentary records of the (A) Hangenberg and (B) Annulata horizons at Kowala, Poland. All vertical scales are in meters; the stratigraphic positions of the Annulata and Hangenberg horizons are indicated by the grey bars. Zone refers to conodont biostratigraphic Zones. To. and *sul.* indicate the Tournasian Stage and *sulcata* conodont Zone, respectively. The TOC/P_{org} modern global average ratio is marked on all TOC/P_{tot} plots at 115 (Dale *et al*., 2016), and the upper crustal average P/Al ratio (~0.01; Taylor and McLennan, 1995) is indicated on all P_{tot}/Al plots. All data are from this study. Lithological data are sourced as follows: for the Hangenberg Horizon from Myrow *et al*. (2014); for the Annulata Horizon from this study. Biostratigraphic data are sourced as follows: for the Hangenberg Horizon from Myrow *et al*. (2014); for the Annulata Horizon from Racka *et al*. (2010).

Figure 5: Geochemical evidence for trends in global continental weathering, and local detrital influx to the settings recorded at (A) Steinbruch Schmidt, (B) Kowala, (C) Coumiac, and (D) Erfoud during the Kellwasser events. All vertical scales are in meters. Biostratigraphic, lithological, carbon-isotope, and P_{tot}/Al information as for Figure 3. Osmium-isotope data are from Percival *et al*. (2019); Si/Al and Ti/Al data are from this study. The upper crustal average Si/Al, Ti/Al, and P/Al ratios (Taylor and McLennan, 1995) are indicated.

Figure 6: Geochemical evidence for trends in global continental weathering, and local detrital influx to the settings during the (A) Hangenberg and (B) Annulata events recorded at Kowala. All vertical scales are in meters. Biostratigraphic, lithological, and P_{tot}/Al information as for Figure 4. Osmium-isotope data are from Percival *et al*. (2019); Si/Al and Ti/Al data are from this study. The upper crustal average Si/Al, Ti/Al, and P/Al ratios (Taylor and McLennan, 1995) are indicated.

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