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Linking the progressive expansion of reducing conditions to a stepwise mass extinction event in the late Silurian oceans

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ABSTRACT

The late Ludlow Lau Event was a severe biotic crisis in the Silurian, with resurgent microbial facies and faunal turnover rates otherwise only documented with the "big five" mass extinctions. This asynchronous late Silurian marine extinction event preceded an associated positive carbon isotope excursion, the Lau CIE, although a mechanism for this temporal offset remains poorly constrained. Here we report thallium isotope data from locally reducing late Ludlow strata within the Baltic Basin to document the earliest onset of global marine deoxygenation. The initial expansion of anoxia coincides with the onset of the extinction and therefore precedes the Lau CIE. Additionally, sulfur isotope data record a large positive excursion parallel to the Lau CIE, interpreted to indicate a major increase in pyrite burial associated with the widely documented carbon isotope excursion. This suggests a possible global expansion of euxinia (anoxic and sulfidic water-column) following deoxygenation. These data are the most direct proxy evidence of paleo-redox conditions that link the known extinction to the Lau CIE through the progressive expansion of anoxia, and most likely euxinia, across portions of the late Silurian oceans.

INTRODUCTION

High rates of evolutionary turnover and severe, punctuated extinctions of marine taxa were a hallmark of the Silurian (e.g., Jeppsson, 1998; Crampton et al., 2016). This interval occurred during the transition from the Late Ordovician icehouse to Devonian greenhouse worlds when a dynamic ocean-atmosphere system oscillated between cool and warm conditions (e.g., Jeppsson, 1998). Recurrent extinctions in graptolites and conodonts were associated with the transitions between the alternating climate states, the most notable being the globally-documented late Ludlow Lau extinction (Jeppsson, 1998; Calner, 2005; Crampton et al., 2016). This extinction was first recognized using conodonts from carbonate platform successions (termed the Lau event; e.g. Jeppsson and Aldridge, 2000) and then in graptolite studies of deeper-water shale sequences (termed the Kozlowskii event; Koren', 1993; Urbanek, 1993), herein referred to as the Lau/Kozlowskii extinction (LKE). The LKE is at least the tenth largest extinction event in Earth history with ~ 23% loss of genera (e.g., Bond and Grasby, 2017 and references therein). In addition to conodonts and graptolites, it affected a wide range of marine taxa including brachiopods (Talent et al., 1993), fishes (Eriksson et al., 2009), and acritarchs (Stricanne et al., 2006). Extinctions of individual taxonomic groups are asynchronous, with documented extinctions in benthic and nektonic groups preceding the planktic organisms (e.g., Munnecke et al., 2003; Stricanne et al., 2006; Calner, 2008). The LKE shares similar characteristics to the "big five" mass extinctions such as the

survival of disaster fauna and a resurgence of microbially-mediated sedimentary facies (e.g., Talent et al., 1993; Jeppsson, 2005; Calner, 2005, 2008; Eriksson et al., 2009).

Despite the magnitude and complexity of the LKE, its mechanistic underpinnings are not well-constrained. An expansion of reducing conditions has been implicated as a potential driver of the observed temporal-stepwise extinction (e.g. Munnecke et al., 2003; Stricanne et al., 2006). This hypothesis is also used to explain the possibility of extensive burial of organic carbon, resulting in the Lau positive carbon isotope excursion (CIE; e.g. Saltzman, 2005), but this cannot explain the temporal offset between the LKE and the Lau CIE. Further, organic carbon burial can be affected by other factors (e.g., Canfield, 1994). Variations in eustatic sea level and carbonate weathering rates have also been invoked as a potential mechanism for driving positive CIEs (e.g., Hirnantian CIE; Kump et al., 1999). However, a global expansion of reducing conditions provides a kill mechanism and can be tested using combined traditional and novel paleo-redox proxies.

This study investigates the relationship between the LKE and Lau CIE in the context of changing marine redox conditions in upper Silurian (Ludfordian Stage) strata from the Baltic Basin. In order to reconstruct the evolution of global marine redox conditions we measured thallium (Tl) isotopes, manganese (Mn) concentrations, and pyrite sulfur isotopes ($\delta^{34}S_{pyr}$) from a distal shelf/slope setting (Latvia) and carbonate-associated sulfate (CAS) sulfur isotopes ($\delta^{34}S_{CAS}$) from a shallow shelf setting (Gotland, Sweden; Fig. 1). This multi-proxy, multi-lithology approach aims to establish a first-order link between the fossil record of stepwise extinction, carbon burial, and the progression from more oxygenated to more reducing conditions in the late Silurian seas.

GEOLOGIC SETTING

The Baltic Basin was located in a tropical, epicratonic seaway on the southern margin of the paleocontinent Baltica (e.g., Eriksson and Calner, 2008; Fig. 1; Fig. DR1). In the late Silurian, the northern and eastern edges of the basin were delineated by rimmed carbonate shelves with parallel facies belts ranging from lagoonal deposits in the north to deep-shelf shales and marls in the south, deepening towards the Rheic Ocean (Eriksson and Calner, 2008). The Uddvide-1 drill core and nearby outcrops on the island of Gotland, Sweden are predominantly carbonates from the shallow shelf area of the basin (for more details see Eriksson and Calner, 2008). The Priekule-20 drill core from southwestern Latvia is predominantly shales and marls from a correlative deep shelf setting (details in Kaljo et al., 1997).

METHODS AND RESULTS

Two study localities were analyzed for $\delta^{13}C$ records, organic or inorganic (micrite), to investigate carbon cycle dynamics. Pyrite sulfur was extracted from shale samples using a widely accepted chromium reduction method, and CAS was extracted from carbonates following standard methods. Full details of all analytical methods are given in the GSA Data Repository[1]. Sulfur isotopes were analyzed to investigate global pyrite burial ($\delta^{34}S_{CAS}$) and the potential imprints on local signatures ($\delta^{34}S_{pyr}$). Sedimentary Tl isotopes ($\varepsilon^{205}Tl = [(R_{sample}/R_{reference})-1] \times 10^4$) have been used to investigate the earliest onset of global marine deoxygenation during Mesozoic CIEs (Ostrander et al., 2017; Them et al., 2018). During Mn-oxide precipitation, Tl is adsorbed with a large positive isotope fractionation, thus leaving seawater isotopically lighter (as reviewed in Nielsen et al., 2017). Precipitation and burial of Mn-oxides require oxic bottom-water conditions, the expanse of which represents the dominant seawater control of Tl-isotope composition on time scales < ~5 million years (Nielsen et al., 2017; Owens et al., 2017). The global seawater Tl-isotope signal is recorded in euxinic marine settings and in anoxic waters with sulfide near the sediment-water interface from basins that are well-connected to the open ocean (Owens et al., 2017). Consequently, reconstructing the Tl isotope composition of late Silurian seawater provides evidence for initial changes in global marine oxygenation by tracking the burial flux of Mn-oxides relative to the extinction, CIE, and additional redox proxies (e.g., Ostrander et al., 2017; Them et al., 2018). Importantly, a large Tl isotope fractionation is not associated with the burial of other Mn-bearing minerals (e.g., sulfides, carbonates). Constraining locally reducing conditions using an independent geochemical proxy is necessary to interpret Tl isotopes as a temporal seawater signature and to avoid

contamination via local Mn-oxides (Owens et al., 2017). Low total Mn concentrations [Mn] are indicative of locally reducing conditions (e.g. Boyer et al., 2011) and, thus, utilized in this study.

The Lau CIE is documented in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records from the outer shelf setting (Fig. 2A), with values increasing within the upper part of the *Bohemograptus bohemicus tenuis-Neocucullograptus kozlowskii* zones, reaching peak values of +5.7‰ and -23.5‰, respectively, in the Nova Beds of the Dubysa Formation (Fm). The $\delta^{13}C$ records return to baseline values in the overlying Engure Fm. There is a positive ~40‰ excursion in $\delta^{34}S_{pyr}$ data (baseline values ~-22‰ shift to peak values of up to ~+15‰) that coincides with the Lau CIE within the upper Nova Beds and basal Engure (Fig. 2B). [Mn] are low throughout the section with average values of 363 and 552 ppm in the lower to middle Dubysa and Engure, respectively (Fig. 2C). The $\varepsilon^{205}Tl$ record shows baseline values in the lower to middle Dubysa of -4.1 to -4.6 (Fig. 2D). This is followed by a positive excursion in $\varepsilon^{205}Tl$ values that peaks at -2.6 and averages -3.3 throughout the rest of the drill core.

The Lau CIE is also documented in both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records from the inner shelf carbonates (Fig. 3A), with values beginning to rise in the upper När Fm and peaking in the overlying Eke Fm (*Icriodontid* Zone) at +7.5‰ and -24.0‰. Within the Burgsvik Sandstone, $\delta^{13}C_{carb}$ values decline to ~+4.0‰, while $\delta^{13}C_{org}$ values increase to -22.9‰, which is followed by a return to peak $\delta^{13}C_{carb}$ values of +7.5‰ in the overlying Burgsvik Oolite (*Ozarkodina snajdri* Zone). The overlying Hamra Fm and Sundre Fm record the falling limb of the CIE, but not post-excursion baseline values. There is a positive ~30‰ excursion in the $\delta^{34}S_{CAS}$ record (Fig. 3B), with initial values ~+11‰ in the När that rise through the Eke to values of ~+22‰. The $\delta^{34}S_{CAS}$ values then continue rising through Burgsvik Oolite, Hamra, and Sundre to +40.6‰.

DISCUSSION

The [Mn] from the Latvia deep shelf setting (Fig. 2C) are all below the average crustal values and suggest depleted local Mn deposition, and therefore locally reducing conditions throughout the studied interval (Boyer et al., 2011). Cross-plotting [Mn] and Tl isotopes shows no significant correlation (Fig. DR2I). Thus, it is unlikely that local Mn-oxide burial has influenced the Tl-isotope seawater signature. The observed positive shift in Tl isotopes from ~-4.6 to -2.6 begins within the Ludfordian *B. bohemicus tenuis* graptolite biozone (Fig. 2D) and signifies a decline in the global burial of Mn-oxides. The reduction in Mn-oxide burial is likely due to significant bottom-water deoxygenation as anaerobic microbial metabolisms kept pace with carbon export, reducing bottom water oxidants such as oxygen and Mn-oxides, but not yet reducing enough to increase widespread organic carbon preservation and burial (e.g., Ostrander et al., 2017; Them et al., 2018). This early onset of deoxygenation coincides with the initial phase of extinction (e.g., brachiopods, fish, and conodonts) that predates the Lau CIE (Fig. 4; e.g. Calner, 2008). Extinctions in these nektonic and benthic taxa coincide with the rising limb of the positive Tl-isotope excursion, which begins ~ 8 m before the Lau CIE. This suggests that deoxygenation and subsequent spread of anoxia was responsible for the initial phases of extinction in fauna living at/near the sediment-water interface and within deeper waters ~175 to 270 kyr prior to the Lau CIE (see GSA Data Repository for calculations). For the first time in the Paleozoic, this stratigraphic relationship of extinction/turnover, and C- and Tl-isotopes is observed. A similar progression of events has been suggested for two Mesozoic oceanic anoxic events or OAEs (Ostrander et al., 2017; Them et al., 2018), but with varying magnitudes and durations.

The positive C- and S-isotope excursions (Figs. 2 and 3) are consistent with transient increases in the amount of reduced C and S buried globally as organic matter, pyrite, and possibly organic sulfur compounds (e.g., Gill et al., 2011; Owens et al., 2013; Raven et al., 2019). Sea level may also have been a contributing, but secondary, factor to the Lau CIE (see GSA Data Repository for further discussion). This suggests the Lau CIE began as export and burial of organic carbon to the seafloor outpaced consumption via remineralization, which was likely dependent on a sufficiently large portion of shelf and other marine environments being affected by deoxygenation and expansion of anoxia. The excess organic matter available fueled microbial sulfate reduction (MSR) and ultimately increased pyrite burial as MSR-

produced H_2S reacted with reactive iron minerals in sulfidic environments. The burial fractions of reduced C and S were preferentially enriched in ^{12}C and ^{32}S due to fractionations associated with biological processes, and the remaining seawater was enriched in ^{13}C and ^{34}S. Euxinic conditions possibly expanded into a greater portion of the oceans at the onset of the Lau CIE as denoted by positive excursions in $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ (Fig. 2B, 3B). This onset of euxinia temporally coincides with the second wave of extinctions that affected planktic groups (i.e., ~75% loss in biodiversity of graptolites) and the rising limb of the CIE (Fig. 4A). Phytoplankton (i.e. acritarchs) actually increased in abundance immediately prior to and during the rising limb of the Lau CIE (Stricanne et al., 2006) as reducing conditions expanded, likely due to a lack of predation as zooplankton and larger marine taxa experienced earlier extinctions. Acritarchs finally declined with an associated ~95% drop in abundance during the peak of the CIE just before the global extent of euxinia reached a maximum, which is inferred by the rising limb nearing the peak of the $\delta^{34}S_{CAS}$ values.

In both the Gotland and Latvia $\delta^{34}S$ records, peak excursion values post-date the corresponding peak $\delta^{13}C$ values in the Lau CIE. The offset in these records suggests that organic carbon burial fueled high MSR rates, but may also be related to differences in oceanic residence times and/or continued pyrite burial post-CIE (e.g., Owens et al., 2013). The falling limb of the $\delta^{34}S_{pyr}$ record also lags the falling limb of the CIE, perhaps indicating the continued consumption of previously exported organic carbon after the termination of the burial event, which is corroborated by Tl isotopes not returning to baseline values (cf., Them et al., 2018). Regardless of the C-S offset and isotopic magnitudes, these large-magnitude S-isotope excursions that span ~ 1 Myr require a reduction in the marine sulfate reservoir, which was likely significantly lower than modern seawater (e.g., Gill et al., 2011).

CONCLUSIONS

The integrated paleontological and geochemical records suggest a stepwise extinction for the LKE was associated with the progressive expansion of reducing marine conditions. Increased anoxic and euxinic conditions likely shoaled from deeper shelf/slope areas to shallow platform settings during the Lau CIE. Our Tl-isotope data provide detailed evidence for expanding marine deoxygenation in the interval that preceded the Lau CIE, coinciding with the initial phase of extinction. This was followed by global C- and S-isotope perturbations that coincide with continued marine extinction. This study highlights the role of oxygen depletion (i.e., non-sulfidic anoxia) near the onset of biotic change and provides a mechanism for the previously documented stepwise extinction event. The progressive expansion of oceanic anoxia leading to euxinia is a potential mechanism for extinction due to significant stress on marine ecosystems (Meyer and Kump, 2008), which might be similar to at least two Mesozoic OAEs. More broadly, this study indicates that global marine redox dynamics were a major driver in the evolution of the late Silurian biosphere, and potentially other Paleozoic biotic crises. The multi-proxy redox approach provides a more holistic global view of redox changes and supports recent evidence suggesting prevelant low oxygen conditions in the upper oceans of the Paleozoic (Lu et al., 2018).

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FIGURES

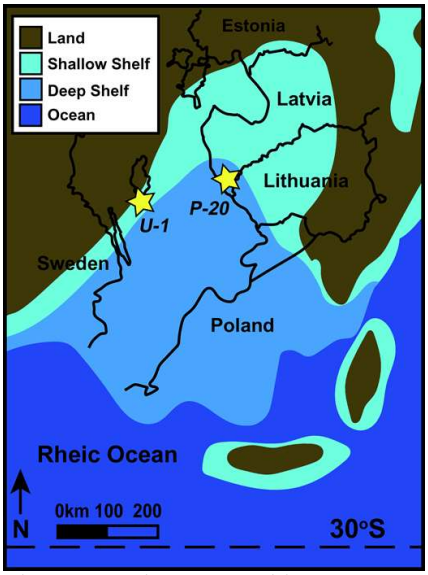

Figure 1. Paleogeographic reconstruction of the late Silurian Baltic Basin region (modified from Blakey Europe Series, Silurian ca. 425 Ma; https://www2.nau.edu/rcb7/). Locations of the Gotland, Sweden localities and the Latvian Priekule-20 drill core are marked by yellow stars. Detailed discussion of correlation and biostratigraphy of the two localities can be found in the GSA Data Repository[1].

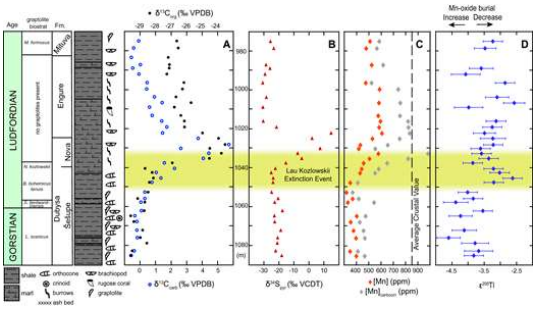

Figure 2. Geochemical data from the Priekule-20 drill core, near Priekule, Latvia. Graptolite biozones after Kaljo et al. (1997). The Lau/Kozlowskii extinction interval is shaded in yellow. Panel A: Carbonate and organic carbon isotope data. Panel B: Pyrite sulfur isotope data. Panel C: Manganese concentration data with the dashed line representing average crustal values. Panel D: Thallium isotope data plotted with 2σ error bars.

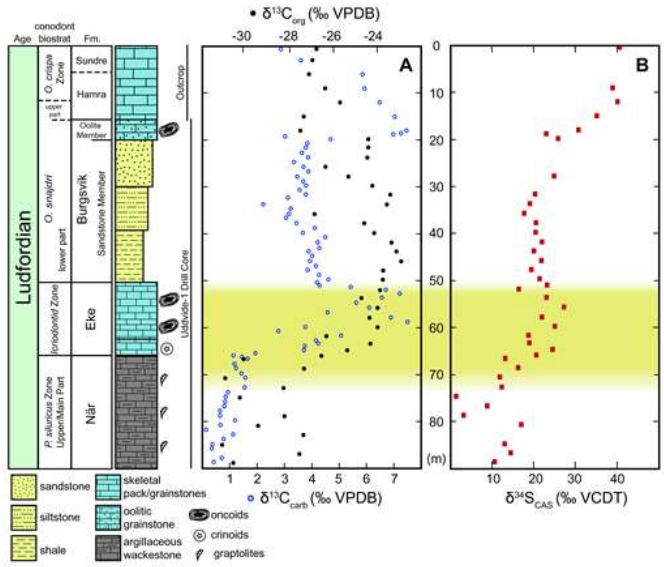

Figure 3: Geochemical data from the Uddvide-1 drill core and nearby outcrops on Gotland, Sweden. Conodont biozones after Jeppsson (2005). The Lau/Kozlowskii extinction interval is shaded in yellow. Panel A: Carbonate and organic carbon isotope data. Panel B: Carbonate associated sulfate (CAS) sulfur isotope data.

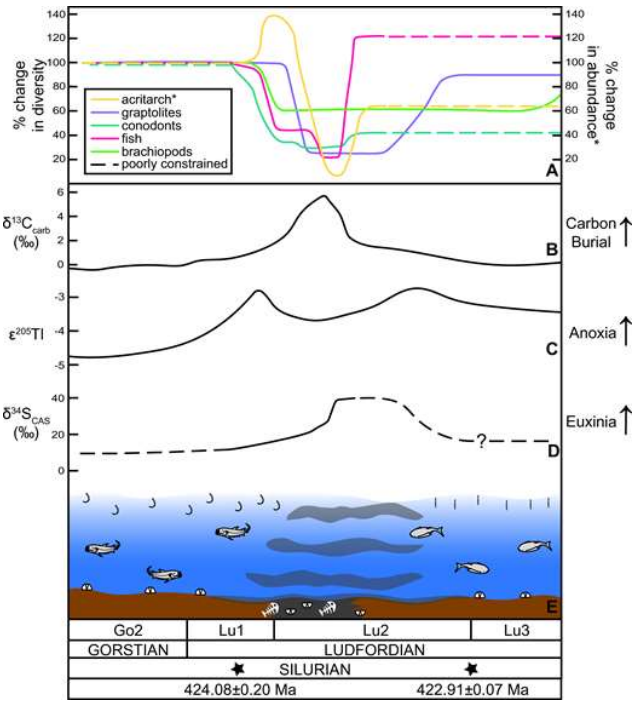

Figure 4: Summary figure of biotic, geochemical, and oceanographic events in the late Silurian that culminated in the LKE and Lau CIE. (A) Biotic data for acritarch (Stricanne et al., 2006), graptolite (Manda et al., 2012), conodont (Calner, 2008), fish (Eriksson et al., 2009), and brachiopod (Talent et al., 1993) extinctions. (B) Carbonate carbon isotope record. (C) Thallium isotope record indicating increased oceanic anoxia. (D) CAS sulfur isotope record suggesting increased euxinia; dashed portions are

expected, but currently unconstrained trends. € Depiction of the biotic and marine redox changes throughout the Gorstian and Ludfordian. Stars mark ~ positions of U-Pb zircon dates on K-bentonite ash beds from Podolia, Ukraine (Cramer et al., 2015). Construction of this figure detailed in the GSA Data Repository[1].

[1]GSA Data Repository item 201Xxxx, including analytical methods, geochemical data, and cross plots, is available online at www.geosociety.org/pubs/ft20XX.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.