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Calcium isotope constraints on the marine carbon cycle and $CaCO_3$ deposition during the late Silurian (Ludfordian) positive $\delta^{13}C$ excursion

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ABSTRACT

This study investigates calcium isotope variations ($\delta^{44/40}Ca$) in late Silurian marine carbonates deposited in the Prague Basin (Czech Republic), which records one of the largest positive carbon isotope excursion (CIE) of the entire Phanerozoic, the mid-Ludfordian CIE, which is associated with major climatic changes (abrupt cooling) and global sea-level fluctuations. Our results show that during the onset of the CIE, when $\delta^{13}C$ increases rapidly from $\sim$0‰ to $\sim$8.5‰, $\delta^{44/40}Ca$ remains constant at about 0.3 ± 0.1‰ (relative to NIST 915a), while $^{87}Sr/^{86}Sr$ in well-preserved carbonates are consistent with a typical Ludfordian seawater composition (ranging from $\sim$0.70865 to $\sim$0.70875). Such decoupling between $\delta^{13}C$ and $\delta^{44/40}Ca$ trends during the onset of the CIE is consistent with the expected order-of-magnitude difference in the residence times of Ca ($\sim 10^6$ yr) and C ($\sim 10^5$ yr) in the open ocean, suggesting that the mid-Ludfordian CIE was caused by processes where the biogeochemical pathways of C and Ca in seawater were mechanistically decoupled. These processes may include: (i) near shore methanogenesis and photosynthesis, (ii) changes in oceanic circulation and stratification, and/or (iii) increased production and burial of organic C in the global ocean. The latter, however, is unlikely due to the lack of geological evidence for enhanced organic C burial, and also because of unrealistic parameterization of the ocean C cycle needed to generate the observed CIE over the relatively short time interval. In contrast, higher up in the section where $\delta^{13}C$ shifts back to pre-excursion baseline values, there is a correlated shift to higher $\delta^{44/40}Ca$ values. Such coupling of the records of Ca and C isotope changes in this part of the study section is inconsistent with the abovementioned differences in oceanic Ca and C residence times, indicating that the record of $\delta^{44/40}Ca$ changes does not faithfully reflect the evolution of the oceanic Ca reservoir, but rather some local processes in the Prague Basin. These can be related to *restricted elemental/sediment cycling* involving mixing of isotopically distinct Ca sources and carbonate polymorphs (calcite vs. aragonite), and/or possible *kinetic Ca isotope effects* due to changes in the rate of marine carbonate formation. Evidence supporting the 'kinetic' effect in the studied mid-Ludfordian carbonates is indicated by correlated $\delta^{44/40}Ca$ and Sr-concentration data ($r_s = -0.76$, $p < 0.001$, $n = 41$) yielding a slope of -0.00097, which is indistinguishable from the 'kinetic' slope of abiotic calcite precipitation. Kinetic processes are integral to the model of rapid carbonate precipitation recently proposed by Kozłowski (2015), to explain the origin of the mid-Ludfordian CIE, involving intense methanogenesis/photosynthesis in near shore settings coupled with rapid $CaCO_3$ precipitation (i.e., massive whitings events) and eustatically-controlled *carbonate hypersaturation* of seawater. More Ca isotope studies are needed to shed light on the question of whether *kinetics* or *mineralogy* controls the coupled variations in carbonate $\delta^{44/40}Ca$ and $\delta^{13}C$ records observed in this study and other large positive CIEs in geological record.

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1. Introduction

Stratigraphic records of carbon isotope values ($\delta^{13}C$) in marine sedimentary rocks of Silurian age show a number of positive carbon isotope excursions (CIE), typically associated with severe biological crises, and synchronized paleo-climatic and sea level changes driven by plausible ice sheet advances and retreats in Gondwana (Munnecke et al., 2003; Loydell, 2007; Calner, 2008; Trotter et al., 2016). The most prominent is the late Silurian (mid-Ludfordian) CIE with associated faunal crises, dated at about 424 million years ago, which is documented globally from different paleo-continents (Fig. 1A), including Baltica (Kaljo et al., 1997; Calner, 2008), Gondwana (Australia, Carnic Alps, cf., Talent et al., 1993; Brett et al., 2009; Jeppsson et al., 2012), Laurentia (Barrick et al., 2010), Perunica (Lehnert et al., 2007a, 2007b; Manda et al., 2012), and Avalonia (Loydell and Frýda, 2011). This globally recognized mid-Ludfordian CIE lasted for about 120 000 yrs (Kozłowski and Sobień, 2012) and reached typical magnitudes of up to +9‰ (Fig. 1B, cf. Frýda and Manda, 2013), with few records from very shallow-water settings showing extreme values up to +11‰ (Jeppsson et al., 2012). Overall, the mid-Ludfordian $\delta^{13}C$ event is the largest positive CIE of the entire Phanerozoic (Munnecke et al., 2003) and is predated by two asynchronous faunal crises: the *Lau conodont Bioevent* and *Kozlowskii graptolite Bioevent* (Jeppsson, 1987; Urbanek and Teller, 1997), also associated with a global scale marine regression and climate cooling (Lehnert et al., 2007a).

The cause of this late Silurian CIE is not yet known. The shear magnitude of this excursion, coupled with the lack of evidence for increased organic carbon deposition in coeval marine sediments (e.g., Frýda and Manda, 2013), argues against increased marine productivity and burial of organic carbon on a global scale as the primary driver of the mid-Ludfordian CIE. The problem is reminiscent of the stratigraphically older (i.e., late Ordovician) Hirnantian CIE, which also recorded extremely positive $\delta^{13}C$ values of up to +7‰ in carbonate sections that are organically lean compared to overlying and underlying sediments (Melchin and Holmden, 2006). Similarly, the Hirnantian CIE is associated with climate cooling, sea level lowstands, and biotic extinctions.

Numerous conceptual models have been offered to explain these early Paleozoic large positive CIEs, stemming from detailed sedimentological investigations of the potential role played by glaciation, sea level, and seawater circulation as factors influencing stratigraphic variation in sedimentary $\delta^{13}C$ values (Jeppsson, 1990; Holmden et al. 1998, 2012a; Bickert et al., 1997; Kump et al., 1999; Panchuk et al., 2006; Melchin and Holmden, 2006; Calner, 2008; LaPorte et al., 2009; Kozłowski and Sobień, 2012; Kozłowski, 2015). Assuming that the positive CIEs indeed reflect primary marine signals, there is also the aspect of *global* vs. *local scale* nature of the inferred C cycle perturbations to consider (cf., Swart, 2008; Swart and Kennedy, 2011), particularly in the Paleozoic where secular records of inferred seawater $\delta^{13}C$ changes are typically reconstructed from the sedimentary deposits of epeiric seas. These shallow marine environments were subject to a variable degree of circulation restrictions with respect to an open ocean (cf., Holmden et al., 1998), which created local conditions that may have influenced the carbonate chemistry of seawater, $CaCO_3$ precipitation rate, mineralogy, and the composition of calcifying biota; all leading to the preservation of spatial and temporal patterns in sedimentary $\delta^{13}C$ records (e.g., Holmden et al., 1998; Immenhauser et al., 2003; Panchuk et al., 2006; Fanton and Holmden, 2007; Swart, 2008; LaPorte et al., 2009).

Thus far, there is no agreed-upon explanation for the origin and primary cause(s) of the mid-Ludfordian CIE, and the available published research presents numerous hypotheses that could be classified based on their *global* vs. *local scale* significance, and the expected degree of coupling between marine C and Ca cycle perturbations. In this context, *global* refers to processes that have the potential to perturb the isotopic composition of the massive oceanic C and Ca reservoirs. Hypotheses offered in this category include: (1) changes in the global ocean stratification and circulation linked to climatic changes (Jeppsson, 1990; Bickert et al., 1997), (2) increased rate of organic carbon burial in the oceans (Kump and Arthur, 1999), (3) increased low latitude weathering of carbonate platforms due to a eustatic marine regression (Kump et al., 1999), (4) changes in the structure of marine primary producers (Calner, 2008; Kozłowski and Sobień, 2012), and/or (5) the burial of authigenic carbonate in anoxic deep ocean sediments (Schrag et al., 2013). In contrast, hypotheses of *local scale* significance refer to the effects of more spatially constrained processes, such as local C and Ca cycling effects in circulation restricted epicontinental seas, vital effects related to changes in marine carbonate producers (i.e., kinetic effects and mineralogical effects), and diagenetic effects. These local-scale processes involve smaller C and Ca reservoirs that respond more quickly, and produce larger isotopic effects, compared to perturbations of the more

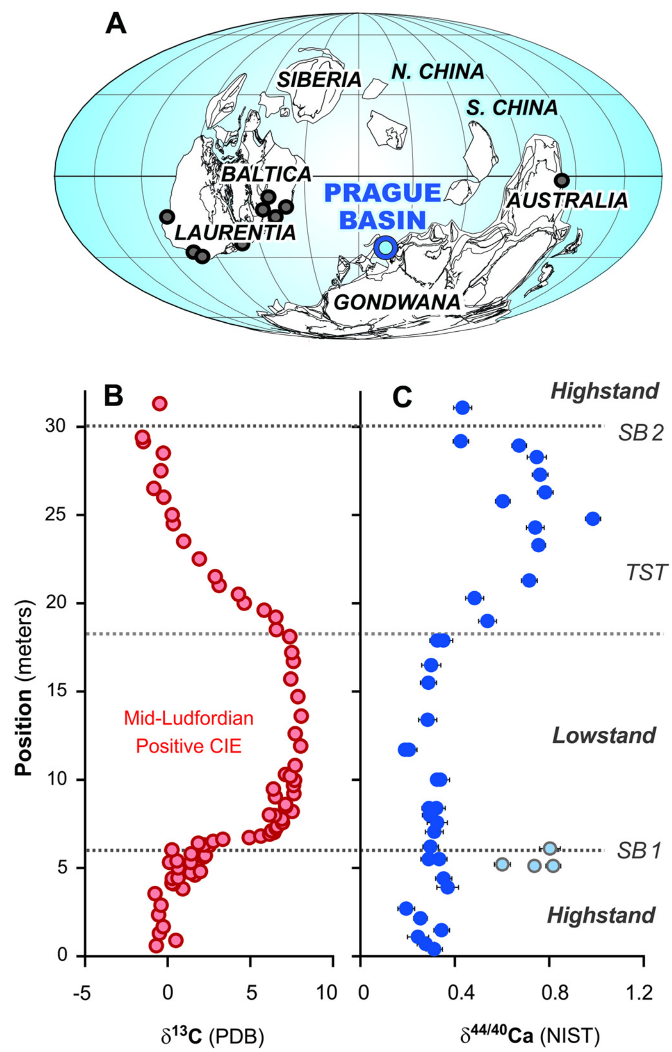

Fig. 1. (**A**) Paleogeographic map showing our study site, i.e., the Prague Basin, and also distribution of other localities (black circles) with published $\delta^{13}C$ records of the mid-Ludfordian carbon isotope excursion (CIE) (modified after Frýda and Manda, 2013; and Torsvik, 2009). (**B**) The $\delta^{13}C$ record across the mid-Ludfordian CIE from the Prague Basin, the Kosov section No. JF195 (data from Frýda and Manda, 2013). (**C**) $\delta^{44/40}Ca$ record across the mid-Ludfordian CIE measured on identical samples that were used for the $\delta^{13}C$ record (see above). Abbreviations used: SB = Sequence Boundary; TST = Transgressive System Track; MFS = Maximum Flooding Surface (after Frýda and Manda, 2013; Kozłowski and Sobień, 2012).