



RESEARCH ARTICLE

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Geochemical Records Reveal Protracted and Differential Marine Redox Change Associated With Late Ordovician Climate and Mass Extinctions

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Key Points:

- Newly paired iodine and sulfur geochemistry highlight the role of shelf anoxia during the Late Ordovician Mass Extinction
- Iodine records show pervasive local anoxia, while sulfur records reveal waning then waxing sulfidic conditions in Late Ordovician oceans
- Combination of reducing marine conditions, cooling, habitat reduction, and glacioeustasy caused the first mass extinction in the Phanerozoic

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract The Ordovician (Hirnantian; 445 Ma) hosts the second most severe mass extinction in Earth history, coinciding with Gondwanan glaciation and increased geochemical evidence for marine anoxia. It remains unclear whether cooling, expanded oxygen deficiency, or a combination drove the Late Ordovician Mass Extinction (LOME). Here, we present combined iodine and sulfur isotope geochemical data from three globally distributed carbonate successions to constrain changes in local and global marine redox conditions. Iodine records suggest locally anoxic conditions were potentially pervasive on shallow carbonate shelves, while sulfur isotopes suggest a reduction in global euxinic (anoxic and sulfidic) conditions. Late Katian sulfate-sulfur isotope data show a large negative excursion that initiated during elevated sea level and continued through peak Hirnantian glaciation. Geochemical box modeling suggests a combination of decreasing pyrite burial and increasing weathering are required to drive the observed negative excursion suggesting a ~3% decrease of global seafloor euxinia during the Late Ordovician. The sulfur datasets provide further evidence that this trend was followed by increases in euxinia which coincided with eustatic sea-level rise during subsequent deglaciation in the late Hirnantian. A persistence of shelf anoxia against a backdrop of waning then waxing global euxinia was linked to the two LOME pulses. These results place important constraints on local and global marine redox conditions throughout the Late Ordovician and suggest that non-sulfidic shelfal anoxia—along with glacioeustatic sea level and climatic cooling—were important environmental stressors that worsened conditions for marine fauna, resulting in the second-largest mass extinction in Earth history and the only example during an icehouse climate.

Plain Language Summary Changes in ocean oxygen contents have had major impacts on marine biodiversity since the rise of animals 600 million years ago. Here we use paired iodine concentrations and sulfur isotope data to constrain marine oxygenation surrounding the Late Ordovician Mass Extinction (LOME; ~445 Ma), the second-largest mass extinction in Earth history, and the only of the “Big 5” that has been traditionally associated with short-lived icehouse conditions. Despite previous work, the role of oxygen deficiency during the LOME remains controversial and under-constrained. To our knowledge, this study presents the first multi-basinal and multiproxy datasets to specifically reconstruct local and global marine redox conditions surrounding the two LOME pulses. These results suggest that a unique and vacillating combination of anoxic and euxinic (anoxic and sulfidic water column) marine conditions. Thus, redox variability tied with climatic cooling, and glacioeustasy were potential mechanisms leading to the first mass extinction in the Phanerozoic.

1. Introduction

The Ordovician Period hosts one of the largest marine biodiversification events in Earth history, the Great Ordovician Biodiversification Event (GOBE). After this proliferation of marine fauna, however, the second-largest mass extinction in Earth history occurred, the Late Ordovician Mass Extinction Event (LOME; (Harper et al., 2014)). The LOME resulted in the loss of ~85% of marine species between two distinct extinction pulses, with the first occurring at the Katian–Hirnantian boundary, and the second in the late Hirnantian (Brenchley et al., 2001; Harper et al., 2014; Jabolinski, 1991). Traditionally, the first LOME pulse has been associated with rapid global cooling and widespread glaciation that resulted in major eustatic sea-level fall, creating widespread

marine habitat loss and ecologic shifts (Harper et al., 2014). The second LOME pulse has been associated with sea-level rise and an expansion of anoxic (potentially euxinic: anoxic and sulfidic water column) conditions (Dahl et al., 2021; Hammarlund et al., 2012). However, recent studies have invoked widespread anoxia/euxinia for both LOME pulses, indicating that the redox conditions surrounding this event might be more complex than initially understood (Zou et al., 2018). Associated with the LOME was a major perturbation in the global carbon cycle, recorded as a positive excursion in the marine carbon isotope record known as the Hirnantian carbon isotope excursion (HICE) (Brenchley et al., 2003).

The primary causal mechanisms for the HICE has previously been attributed to changes in carbonate weathering regimes during eustatic sea-level fall (Kump et al., 1999) and/or enhanced burial of organic matter associated with increased preservation resulting from decreased marine oxygenation (Brenchley et al., 2003; Hammarlund et al., 2012; Jones & Fike, 2013). Traditional sulfur (S) isotope approaches have investigated the dynamics and extent of euxinic marine conditions during the LOME. Pyrite sulfur isotope ($\delta^{34}\text{S}_{\text{pyr}}$) profiles across multiple globally distributed paleobasins show nearly synchronous positive excursions, suggesting a global perturbation, albeit with local overprints to explain the variable enrichments between 15–40‰. Overall, the positive $\delta^{34}\text{S}_{\text{pyr}}$ shift may reflect increased pyrite burial under widespread sulfidic conditions (Hammarlund et al., 2012; Jones & Fike, 2013). However, the single reported seawater sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) record shows little variation in this global redox proxy throughout the HICE, suggesting a minimal change in global pyrite burial rates over this interval and thus a limited global expansion of euxinic conditions (Jones & Fike, 2013).

Additionally, non-traditional paleoredox proxies have been applied to assess the extent of widespread reducing conditions as a potential kill mechanism for both LOME pulses. Specifically, uranium and molybdenum ($\delta^{238}\text{U}$ and $\delta^{98}\text{Mo}$) stable isotope records have been interpreted to reflect global to regional changes in marine redox, and have identified possible shifts towards more reducing conditions—but at differing times during the Hirnantian (Bartlett et al., 2018; Dahl et al., 2021; Zhou et al., 2015). Models based on $\delta^{238}\text{U}$ data from eastern Laurentia suggest up to 15% of the total seafloor area experienced anoxic conditions just before the end of the Ordovician (Bartlett et al., 2018). Meanwhile, $\delta^{98}\text{Mo}$ data from South China have been interpreted to record local shifts from suboxic to euxinic conditions prior to and during the early Hirnantian (Zhou et al., 2015). However, each of these marine redox interpretations is based on singular datasets within widely different depositional environments. Moreover, delineating the timing of these inferred changes in redox relative to one another remains problematic, as the lack of a universally accepted, fully integrated Upper Ordovician biostratigraphic scheme limits the resolution of correlations (see Supporting Information S1). Additionally, these two paleoredox proxies have different specific responses due to their position on the redox ladder, that is, changes in increasingly reducing marine conditions, which creates additional complications for understanding the onset of non-sulfidic anoxia ($\delta^{238}\text{U}$) versus euxinia ($\delta^{98}\text{Mo}$).

To better elucidate critical gaps in our understanding of the mechanistic underpinnings for the LOME, we present new $I/(\text{Ca} + \text{Mg})$ ratios and $\delta^{34}\text{S}_{\text{CAS}}$ datasets from three low-latitude but widely distributed Upper Ordovician carbonate successions. Our study localities were deposited in different paleocean basins and record the HICE along with major fluctuations in eustatic sea level (Finney et al., 1997; Ghienne et al., 2014; Kiipli & Kiipli, 2020; Young et al., 2010). These new-paired geochemical datasets provide a more comprehensive understanding and specificity of marine redox conditions (local and global) and climate that led to the second-largest extinction event in Earth history.

2. Background

2.1. Geologic Setting

Epeiric seaways were widespread throughout much of the Late Ordovician as a result of elevated eustatic sea levels (Rasmussen et al., 2019). Widespread carbonate deposition dominated these epeiric seaways with carbonate successions found even within sub-tropical regions such as the paleocontinent of Baltica (Figure 1). Subsequently, nearly every marine setting records a major decrease in sea level during the latest Katian and Hirnantian marked by subaerially exposed carbonate platforms and significantly reduced shallow-water marine habitats.

The first study site is a thick succession outcropping in the Monitor Range, Nevada, where high-resolution $\delta^{13}\text{C}_{\text{carb}}$ records have previously documented the HICE (Finney et al., 1997, 1999; Jones et al., 2016). This section consists of the Late Ordovician Hanson Creek Formation as well as the early Silurian Roberts Mountain Formation

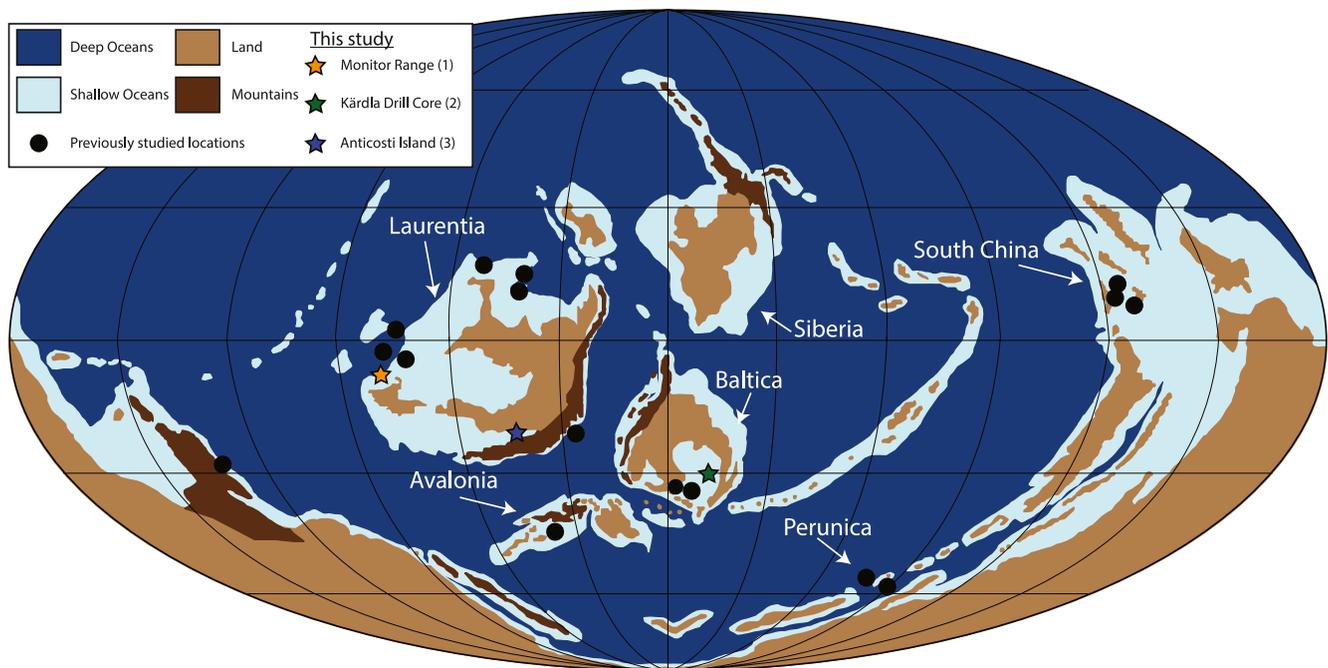


Figure 1. Paleogeographic reconstruction of the Late Ordovician (Sandbian-Katian). Modified from Melchin et al., 2013. Study site localities are marked as stars, with the locations of other study areas shown in black circles.

(Finney et al., 1997). These marine carbonates were deposited in an upper slope setting on the western passive margin of Laurentia in the Panthalassic Ocean and contain facies that range from deep water thinly laminated lime mudstones and bedded cherts to wave agitated cross-laminated oolitic grainstones (Finney et al., 1997). The second study site is a thick succession recorded within the Kärđla drill core, southern Estonia consisting of the Late Ordovician Jonstorp, Halliku, Kuldiga, and Saldus formations, and the early Silurian Öhne Formation (Kaljo et al., 2001). These carbonates were deposited along the southern margin of Baltica with direct connection to the Iapetus Ocean and contain facies ranging from offshore argillaceous wackestones to shallow water oolitic grainstones (Kiipli & Kiipli, 2020). Last, the Point Laframboise section on Anticosti Island, Quebec, contains the Late Ordovician Ellis Bay and early Silurian Becscie formations. This is a mixed siliciclastic and carbonate succession deposited on a storm-dominated ramp in a foreland basin on eastern Laurentia (Desrochers et al., 2010). Facies range from distal bioturbated mudstones through shallow patch reef limestones. Each of our study localities has been the subject of extensive biostratigraphic and $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphic studies, allowing for correlation between the sections (Figure S1 in Supporting Information S1).

However, detailed correlations of stratigraphic sections from hydrographically separate paleobasins remain difficult in any study, especially when comparing sections with biostratigraphic zonation based on different taxonomic groups. Here we base our Late Ordovician-early Silurian stratigraphic correlations on available graptolite, conodont, and chitinozoan biostratigraphy, as well as the high-resolution $\delta^{13}\text{C}_{\text{carb}}$ trends. The Monitor Range section contains diagnostic Late Ordovician graptolites (e.g., *Metabolograptus extraordinarius* and *Metabolograptus persculptus* biozones) and conodonts (*Amorphoganathus ordovicicus* biozone) (Finney et al., 1997, 1999; Murphy et al., 1979), which provide direct and reliable high-resolution integration of this section with the latest calibrated Ordovician Time Scale 2020 (Goldman et al., 2020). Unfortunately, neither the western Anticosti Island nor Kärđla drill core successions contain the diagnostic *M. extraordinarius* or *M. persculptus* graptolites (Melchin, 2008) which are found in correlative shale-dominated sequences, and thus direct integration with the Ordovician Time Scale 2020 is not as straightforward. However, these two carbonate-dominated sequences do contain diagnostic chitinozoans (Achab et al., 2011; Brenchley et al., 2003; Young et al., 2010) which allows them to be integrated into the most recent global Ordovician biostratigraphic framework (Goldman et al., 2020). Both the western Anticosti Island and Kärđla drill core sections contain the chitinozoan *Belonechitina gamachiana* and *Spinachitina taugourdeau* biozones, allowing for the precise correlation between these two localities. Because of the lack of a common biostratigraphic scheme, we also rely on the carbon isotope stratigraphy previously

documented from each study site to augment some issues in integrating differing biostratigraphic schemes from these three successions (see Supporting Information S1).

2.2. Local and Global Redox Proxies

Iodine-to-calcium ($I/Ca + Mg$) ratios in carbonate minerals are thought to capture local changes in water column oxygen contents (Lu et al., 2010). When discussing concentration patterns, iodine abundances are normalized to carbonate contents and magnesium (Mg) concentrations are included to account for varying carbonate mineralogy (Hardisty et al., 2014, 2017; Lu et al., 2018). Although iodine has a relatively long residence time in the modern ocean (~ 300 kyr), iodine responds rapidly to changes in local reducing conditions due to its redox potential (Hardisty et al., 2021; Rue et al., 1997). Under well-oxygenated local conditions, iodate (IO_3^-) is the dominant species of iodine, while under reducing conditions iodate is converted to iodide (I^-) (Rue et al., 1997). The redox potential of iodate to iodide is similar to that of O_2 , Mn^{2+} , and NO_3^- , thus high iodate concentrations in foraminifera ($>2.6 \mu\text{mol/mol}$) tend to correlate with well-oxygenated portions of the modern surface oceans and predictably decrease in oxygen minimum zones (OMZs; $0.5\text{--}2.5 \mu\text{mol/mol}$) (Lu et al., 2010; Rue et al., 1997). A recent study on the Eastern Tropical Northern oxygen-deficient zone has shown that I/Ca ratios $<1.5 \mu\text{mol/mol}$ are likely to have been precipitated within local water masses with local O_2 concentrations of $<7 \mu\text{mol/L}$ (Hardisty et al., 2021). Within this framework, concentrations of iodate within carbonate minerals can be used to track local paleoredox conditions, as iodate readily substitutes for the carbonate ion, while iodide is excluded from the lattice structure (Lu et al., 2010). Furthermore, iodine has a higher reduction potential than more widely used U, and S proxies within carbonates, as well traditional shale-based proxies (Fe, V, Mo), and thus responds more readily to local low-oxygen conditions (Lu et al., 2010).

Sulfate-S isotope compositions and concentrations in the global oceans are controlled by the input and output fluxes of sulfur to and from the oceans. The two major input fluxes are riverine sulfate and volcanic outgassing, which have a combined value of 1.5×10^{18} mol/Myr, and both have isotopic compositions that range between 0% to $+9\%$ (Burke et al., 2018). Important output fluxes for sulfur are the burial of sulfate-evaporites (0.83×10^{18} mol/Myr), which has a minor isotopic fractionation, and sedimentary pyrite with a flux of 0.67×10^{18} mol/Myr (Burke et al., 2018). Pyrite formation via microbial sulfate reduction (MSR) records up to a -70% sulfur isotope fractionation between sulfate and the product sulfide, (approximated by $\Delta^{34}S$; $\Delta^{34}S = \delta^{34}S_{SO_4} - \delta^{34}S_{H_2S}$) and thus leaves residual sulfate isotopically heavier, compared to isotopically light sulfide (Lang et al., 2020; Pasquier et al., 2021). This process occurs in anaerobic environments and is dependent on the availability of labile organic matter, reactive iron, and sulfate (Gomes & Hurtgen, 2015; Sim, 2019). Sulfur isotopes of carbonate-associated sulfate ($\delta^{34}S_{CAS}$) are commonly used to generate high-resolution spatiotemporal records of global marine sulfate-sulfur isotope compositions. Since marine sulfate throughout the Phanerozoic had a significantly longer residence ($10^5\text{--}10^7$ yrs) time than inter-ocean mixing timescales (10^3 yrs) and thus is homogenous throughout ocean basins, $\delta^{34}S_{CAS}$ values are generally representative of the global seawater reservoir. Pyrite sulfur ($\delta^{34}S_{pyr}$) isotopes, in contrast, are best used as a local proxy for MSR activity and the associated factors that control the magnitude of fractionation, such as rates of sulfate reduction, iron availability for pyrite formation, and interplays between open and closed system dynamics (Lang et al., 2020; Pasquier et al., 2021).

3. Materials and Methods

Weathered surfaces, when present, were removed from samples via a water-cooled saw to ensure the fresh material was utilized for geochemical analysis. In-depth details regarding sample processing and purification for carbonate-associated sulfate (CAS), pyrite sulfur, and $I/(Ca + Mg)$ are described in the Supporting Information S1.

Extracted CAS precipitated as $BaSO_4$ and sedimentary pyrite as Ag_2S were weighed into tin capsules with excess V_2O_5 and analyzed for their $\delta^{34}S$ values using a ThermoFisher Delta V at the University of California Riverside or a Finnigan MAT 252 at Indiana University. All sulfur isotopic ratios are reported in standard per mil ($\%$), using delta notation (δ) relative to Vienna Canyon Diablo Troilite (V-CDT) with reproducibility for all sulfur analyses better than $\pm 0.2\%$ based on replicates of the samples and standards. Standards used for sulfur isotopic analysis include the international standards NBS-127 = 21.1% ; IAEA S-1 = -0.30% ; IAEA S-2 = 22.7% ; IAEA S-3 = -32.3% ; and EMR-CP = 1.07% an internal lab standard at Indiana University. $I/(Ca + Mg)$ ratios were analyzed using an Agilent 7500cs inductively coupled-plasma mass spectrometer (ICP-MS) at the National

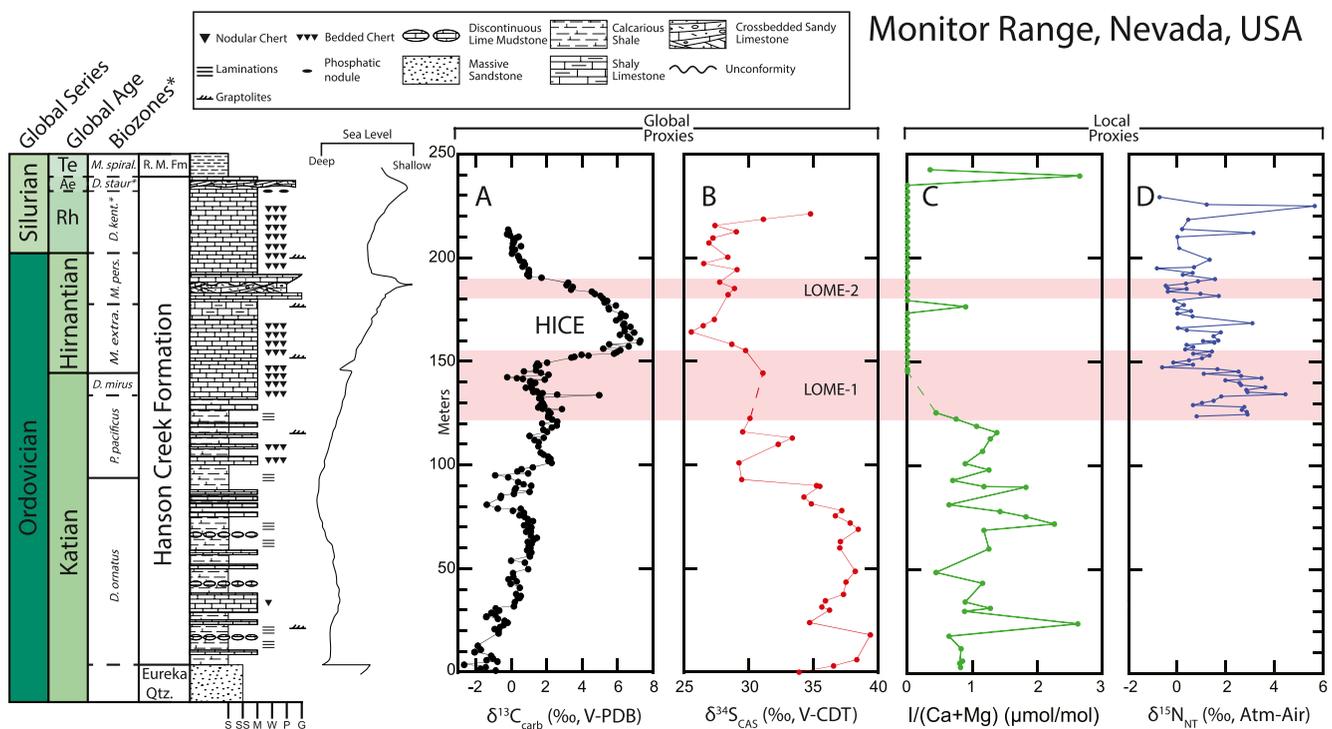


Figure 2. Geochemical and lithologic profile of Monitor Range, Nevada. Biozones, lithologic profile and sea level curve are from Finney et al., 1997, 1999 and Murphy et al., 1979 (* indicates conodont biozone). (a) $\delta^{13}\text{C}_{\text{carb}}$ replotted from Jones et al., 2016. (b) $\delta^{34}\text{S}_{\text{CAS}}$, this study. (c) $I/(\text{Ca} + \text{Mg})$ ratios, this study. (d) $\delta^{15}\text{N}_{\text{NT}}$ replotted from LaPorte et al., 2009. *D. kent.** = *D. kentuckyensis*, *D. staur.** = *D. staurognaethoides* R.M. Fm = Roberts Mountains Formation.

High Magnetic Field Laboratory at Florida State University following standard methods (Lu et al., 2010). Internal standard curves were made fresh daily from high purity standards and compared to in-house and previously published geo-standards KL 1–2 and KL 1–4 from Hardisty et al. (2017) and were found to be within $\pm 0.5\%$ of the reported value. The precision of duplicate samples and replicate analysis were within $\pm 0.08 \mu\text{mol/mol}$ or better.

4. Results

4.1. Monitor Range, Nevada, USA

Detailed carbon isotope data have been published from the Monitor Range section, documenting the HICE and other minor excursions (Finney et al., 1999; Jones et al., 2016; Murphy et al., 1979). The new $I/(\text{Ca} + \text{Mg})$ ratios from this section show relatively low values throughout the Katian and Hirnantian (Figure 2), with average values in the *Dicellograptus ornatus* graptolite biozone at $\sim 1.5 \mu\text{mol/mol}$, declining to $0 \mu\text{mol/mol}$ in the *Paraorthograptus pacificus* to *Diceratograptus murnis* biozones and remaining at $0 \mu\text{mol/mol}$ to the uppermost part of the section where values rise to an average of $\sim 1.5 \mu\text{mol/mol}$. $\delta^{34}\text{S}_{\text{CAS}}$ data from this section show an average of $+36\%$ throughout much of the lower Hanson Creek Formation, with a protracted fall beginning in the late Katian *D. ornatus* biozone and reaching minimum values of $+26\%$ in the early Hirnantian *M. extradinarius* biozone. Within the late Hirnantian *M. persculptus* biozone, $\delta^{34}\text{S}_{\text{CAS}}$ values increase to an average of $+29\%$ and continue to increase to $+35\%$ in the Silurian Rhuddanian *Distomodus kentuckyensis* conodont biozone.

4.2. Kärđla Drill Core, Estonia

A detailed carbon isotope record has also been published from the Kärđla core, Estonia, where the HICE was also identified (Kaljo et al., 2001; Young et al., 2010). Unfortunately, due to the limited amount of core material available and the relatively large sample amounts required for sulfur isotope analyses, $I/(\text{Ca} + \text{Mg})$ analyses were not possible below the uppermost Halliku Formation. The $I/(\text{Ca} + \text{Mg})$ values within the upper Halliku Formation show a consistent absence of iodine ($0 \mu\text{mol/mol}$) but begin to increase within the Kuldiga Formation

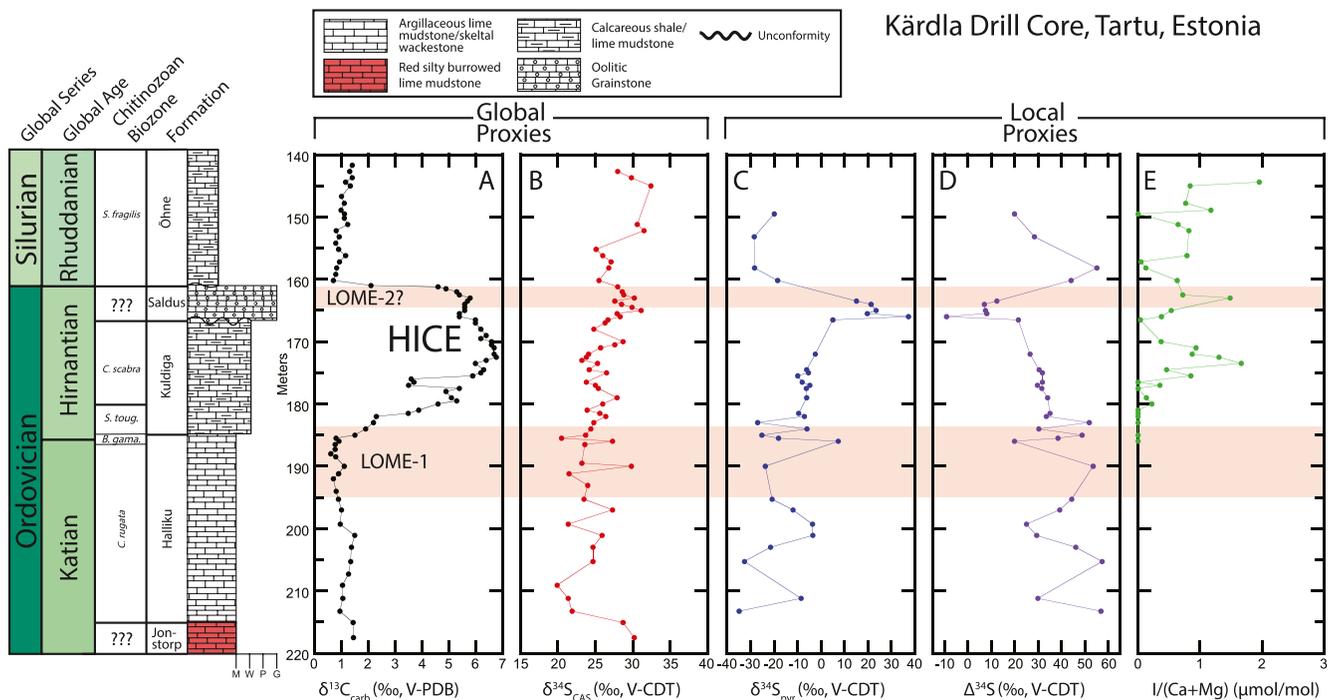


Figure 3. Geochemical and lithologic profile of the Kärddla Drill Core, Estonia. Chitinozoan biozones and lithologies are modified from Brechley et al., 2003 and Young et al., 2010. (a) $\delta^{13}\text{C}_{\text{carb}}$ replotted from Young et al., 2010. (b) $\delta^{34}\text{S}_{\text{CAS}}$ this study. (c) $\delta^{34}\text{S}_{\text{pyr}}$ this study. (d) $\Delta^{34}\text{S}$, this study. (e) $\text{I}/(\text{Ca} + \text{Mg})$ ratios, this study.

(*Conochitina scabra* biozone) to a maximum value of $1.6 \mu\text{mol/mol}$. The values fall to near zero ($<0.1 \mu\text{mol/mol}$) at the top of the formation (Figure 3). Iodine contents increase again within the Saldus Formation to a maximum of $1.5 \mu\text{mol/mol}$ and then decline to near-zero values within the basal Öhne Formation. Finally, $\text{I}/(\text{Ca} + \text{Mg})$ ratios increase steadily throughout the Öhne Formation (*Spinachitina fragilis* biozone) to a maximum of $2 \mu\text{mol/mol}$. The $\delta^{34}\text{S}_{\text{CAS}}$ data from the Kärddla core show a negative perturbation in the lowermost Halliku Formation, within the Katian lower *Conochitina rugata* chitinozoan biozone, from maximum values of $+30\text{‰}$ to minimum values of $+20\text{‰}$. Subsequently, $\delta^{34}\text{S}_{\text{CAS}}$ values remain relatively invariant, ranging between $+20\text{‰}$ to $+25\text{‰}$ into the Hirnantian (upper *C. rugata* through *S. scabra* biozones), where average values trend to $+30\text{‰}$ in the upper Kuldiga through Öhne formations (*S. fragilis* biozone). The corresponding $\delta^{34}\text{S}_{\text{pyr}}$ values range between -35‰ and $+7\text{‰}$, with an average of $\sim -17\text{‰}$ within the Halliku Formation. The overlying Kuldiga and Saldus formations record $\delta^{34}\text{S}_{\text{pyr}}$ values that steadily increase to a maximum value of $+37\text{‰}$, and these values return to a new baseline of $\sim -30\text{‰}$ in the overlying Öhne Formation.

4.3. Anticosti Island, Canada

The Point Laframboise section on western Anticosti Island has been studied extensively, including previously published geochemical data for carbon, sulfur, and uranium isotopes in addition to carbonate clumped- and conodont paleothermometry (Jones et al., 2011; Finnegan et al., 2011; Jones & Fike, 2013; Bartlett et al., 2018). Previous studies have documented the HICE in detail from this section in addition to cooling trends in sea-surface temperatures and increases in global marine anoxia. The placement of the Katian–Hirnantian boundary within the upper Ellis Bay Formation (Figure 4) is based upon previous high-resolution $\delta^{13}\text{C}$ chemostratigraphy (i.e., HICE) that has been integrated with detailed biostratigraphic studies from this section and other Upper Ordovician successions globally (Bergström et al., 2020; Jones et al., 2011; Young et al., 2010). This chronostratigraphy differs from Bartlett et al. (2018) who assign the entire Ellis Bay Formation to the Hirnantian Stage. The placement of the Katian–Hirnantian boundary on Anticosti Island is still the subject of much debate, however, this interpretation is consistent with the global chitinozoan biozones, which are documented from this section and integrated into the recent Ordovician Time Scale 2020 (Goldman et al., 2020; see Supporting Information S1).

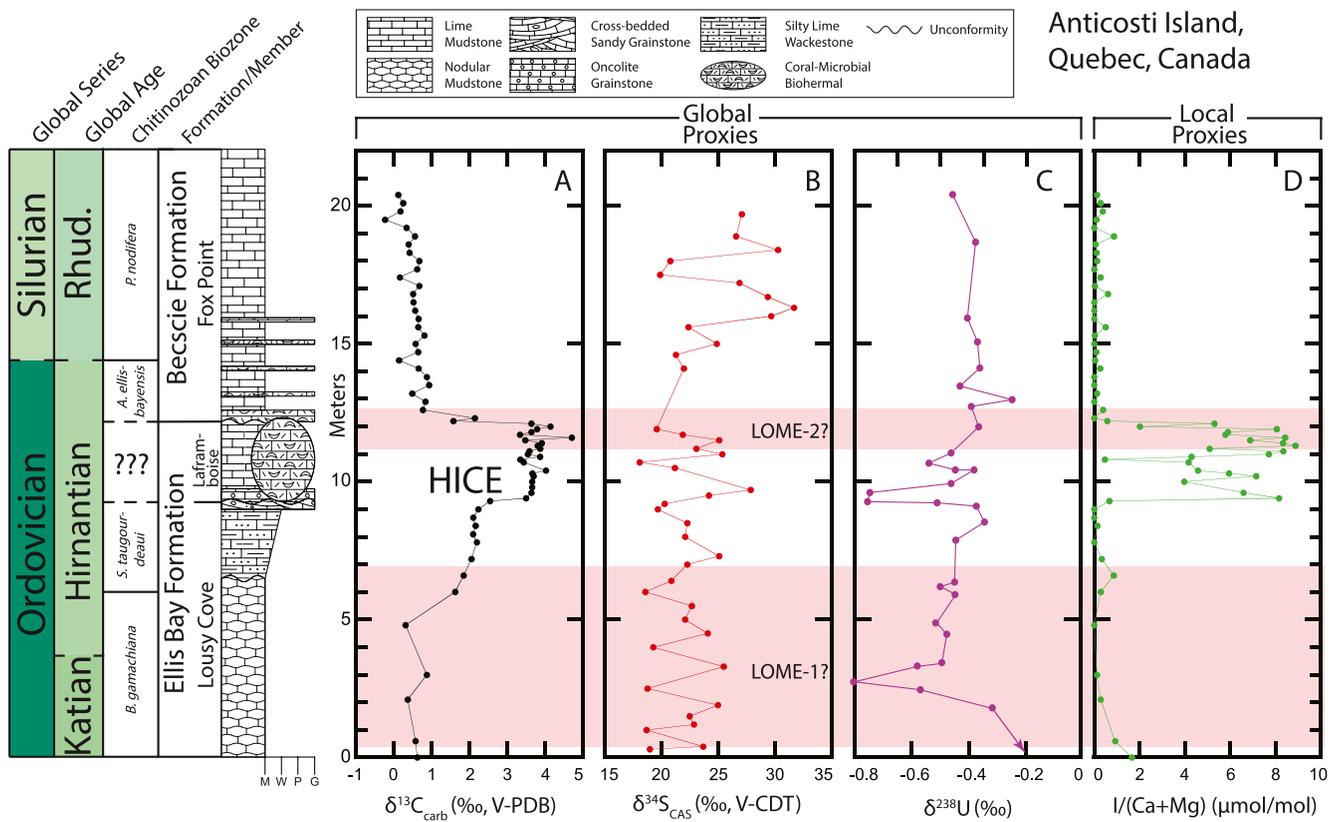


Figure 4. Geochemical and lithologic profile of Anticosti Island, Canada. Lithofacies are modified Jones & Fike, 2013. (a) $\delta^{13}\text{C}_{\text{carb}}$ replotted from Young et al., 2010. (b) $\delta^{34}\text{S}_{\text{CAS}}$ replotted from Jones & Fike, 2013. (c) $\delta^{238}\text{U}$ replotted from Bartlett et al., 2018. (d) $I/(\text{Ca} + \text{Mg})$ ratios, this study. Placement of Katian–Hirnantian boundary is based on detailed chitinozoan biostratigraphy that is calibrated to the Ordovician Time Scale 2020 (Achab et al., 2011; Goldman et al., 2020).

Our new $I/(\text{Ca} + \text{Mg})$ data set (Figure 4) from this section shows low values ($<2 \mu\text{mol/mol}$) within the *B. garmachiana* and *S. taugourdeau* biozones of the mid-inner ramp facies of the Lousy Cove Member, but values increase rapidly to an average of $6 \mu\text{mol/mol}$, ranging from ~ 0.5 to $9 \mu\text{mol/mol}$, within the patch reef facies of the Laframboise Member. Subsequently, $I/(\text{Ca} + \text{Mg})$ ratios within the early Silurian inner-mid ramp carbonates of the overlying Becscie Formation (*Ancyrochitina ellisbayensis* and *Plectochitina nodifera* biozones) show a return to consistently low values ($<1 \mu\text{mol/mol}$).

5. Discussion

5.1. Evaluation of Diagenetic Influences

Assessing $I/(\text{Ca} + \text{Mg})$ and $\delta^{34}\text{S}_{\text{CAS}}$ values for potential diagenetic overprints is paramount to ensure the recorded signals represent primary changes in seawater. Importantly, a recently published study using $\delta^{44}\text{Ca}$ and Sr/Ca ratios addressed the extent of diagenetic influence on both the Monitor Range and western Anticosti Island sections (Jones et al., 2020). This study suggests that deeper water settings like that of Monitor Range and western Anticosti Island, generally retain primary seawater geochemical signatures (i.e., sediment buffered), while strata deposited in shallower water settings are more likely to reflect geochemical signatures akin to sediment porewaters (Jones et al., 2020). Unfortunately, extensive diagenetic studies have not been performed on the Kärö drill core, however, this section is interpreted to be deposited in a deeper shelf setting (albeit shallower than the upper slope setting of the Monitor Range section), suggesting that this section likely preserves mostly primary geochemical signatures (Kaljo et al., 2011). Importantly, if the Kärö drill core were diagenetically altered, there would be a lack of co-varying trends that can be correlated to other sections and regions (i.e., the absence of the HICE, significantly lighter or heavier carbon and/or sulfur isotopes, etc.), as well as extensive karstic features and low statistical variation within cross-plots (see below).

Meteoric diagenesis has been shown to decrease the concentrations of both iodine (Hardisty et al., 2017; Lu et al., 2010) and sulfate in carbonates, as freshwater typically contains lower concentrations of these ions. However, there are no known processes that can increase iodine in carbonates, and in the case of CAS, meteoric diagenesis itself imparts a negligible isotopic effect (Gill et al., 2008). However, other early diagenetic processes (i.e., non-meteoric processes) can still impart isotopic effects, such as authigenic carbonate formation (see below for further discussion). While there is an abundance of low $I/(Ca + Mg)$ values recorded in our datasets, we interpret these as predominantly primary seawater signatures as significant diagenetic alteration cannot explain the very high $I/(Ca + Mg)$ ratios, some of the highest in the early Paleozoic (Lu et al., 2018), recorded within the shallow marine patch reef facies of the western Anticosti Island section. These high $I/(Ca + Mg)$ values were recorded during a lower stand of sea level in the Hirnantian, a stratigraphic interval, and carbonate facies that would have been most susceptible to extensive diagenesis (Figure S3b in Supporting Information S1). Studies of Cenozoic carbonates from the Great Bahamas Bank have shown that iodine concentrations may also be reduced during early diagenesis in carbonate settings (Hardisty et al., 2017). Intervals that were affected by meteoric diagenesis contained $I/(Ca + Mg)$ values close to 0 $\mu\text{mol/mol}$ (Hardisty et al., 2017), likely reflecting alteration by reducing fluids rather than primary seawater values. While it is possible that processes similar to these may have contributed to lowering general iodine concentrations in carbonates from this study if fluid migration were to greatly affect primary geochemical signals it would be in the units that would have originally contained the highest porosity and lowest permeability (i.e., the shallow-water facies). In other words, the Lamframboise Member-Ellis Bay Formation, Anticosti Island, and the Saldus Formation, Estonia, by this prediction would have low $I/(Ca + Mg)$ values. However, these respective intervals within our carbonate successions contain the highest $I/(Ca + Mg)$ values, while the lowest values are found in fine-grained carbonate and clay-rich facies where porosity and permeability would have likely inhibited significant fluid migration. Additionally, these Bahamian drill cores have shown other evidence for meteoric diagenesis in these intervals with near-zero $I/(Ca + Mg)$ values, including carbon isotopic signatures that are significantly more negative compared to the original aragonitic sediments that passively record primary seawater (Swart & Oehlert, 2018), whereas the Late Ordovician carbon isotopic data from our study sections do not show these types of signatures even surrounding intervals of glacioeustatic exposure (Brenchley et al., 2003; Desrochers et al., 2010; Jones et al., 2016; Young et al., 2010).

Geochemical crossplots are also a widespread tool used to assess the fidelity of geochemical signatures, where correlating trends with high R^2 values can point to mixing of primary marine signal with those from diagenetic alteration. Recrystallization of carbonates during diagenesis can yield $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ and $I/(Ca + Mg)$ signatures that deviate from primary seawater values, reflecting a mixture of primary and secondary sources and producing linear or asymptotic relationships among the geochemical parameters (Ahm et al., 2018; Swart & Oehlert, 2018). Here we have cross-plotted $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$, [CAS], $\delta^{34}\text{S}_{\text{CAS}}$, and $I/(Ca + Mg)$ datasets, and these show weak to no correlations, indicating that complete diagenetic overprint is absent from our datasets (Figure S3 in Supporting Information S1). The only crossplots that show significant correlation are $I/(Ca/Mg)$ versus $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ versus $\delta^{13}\text{C}_{\text{carb}}$ from Anticosti Island, however, these trends simply reflect two distinct data populations that within each population do not correlate. Further, clear trends that continue across formational boundaries and major facies changes suggest that geochemical signatures found in these successions are largely primary and contain limited diagenetic alteration.

The likelihood of bulk CAS to faithfully record primary seawater sulfur isotope values has previously been called into question. Bulk $\delta^{34}\text{S}_{\text{CAS}}$ may incorporate sulfate from both primary and secondary carbonate phases potentially leading to more “noise” in isotopic datasets, while $\delta^{34}\text{S}_{\text{CAS}}$ from well-preserved brachiopod carbonate components in the same section show more invariant values (Present et al., 2015). Unfortunately, abundant and well-preserved brachiopods at regularly spaced and high-resolution intervals are not present throughout all the studied sections and thus were not a viable option for performing high-resolution component-specific CAS measurements. Studies comparing early Cenozoic bulk CAS, planktonic foraminiferal CAS, and authigenic barite found that while species-specific foraminiferal data yielded vital effects up to $\pm 1\%$ versus barite, bulk CAS faithfully follow the recorded changes in secular $\delta^{34}\text{S}_{\text{sulfate}}$ in both duration and magnitude (Toyama et al., 2020; Yao et al., 2020). Other studies have shown that fine-grained carbonate sediments, similar to those found in this study, may preserve a combination of primary seawater-derived CAS as well as MSR-derived porewater sulfates preserved as secondary cements (Edwards et al., 2019; Present et al., 2019). Present et al. (2019) showed that strata with low porosity and fine-grained texture are more likely to preserve extensive early diagenetic MSR-derived

overprints, reflecting the residual sulfate pool, resulting in a more positive $\delta^{34}\text{S}_{\text{CAS}}$ record compared to coarse-grained, low porosity equivalent strata.

The heavy $\delta^{34}\text{S}_{\text{CAS}}$ values found in Katian strata of the Monitor Range section could be the result of early diagenetic MSR-derived authigenic carbonates precipitation, facilitated by organic matter remineralization, which increases pore-water alkalinity, subsequently incorporating isotopically heavy sulfate, as they are more positive than the few previously published, roughly time-equivalent, middle to late Katian $\delta^{34}\text{S}_{\text{CAS}}$ values (Kampschulte & Strauss, 2004; Present et al., 2020). If the positive $\delta^{34}\text{S}_{\text{CAS}}$ values at the Monitor Range reflect early diagenetic MSR-derived authigenic cements (e.g., Present et al., 2019), then the sulfur isotope compositions should correspond to the lowest $I/(\text{Ca} + \text{Mg})$ values. Sulfate reduction is further down the marine redox ladder than iodate reduction, and unlike iodate, the product iodide does not incorporate readily into the carbonate lattice (Lu et al., 2010). Within the Monitor Range section, most of the highest $I/(\text{Ca} + \text{Mg})$ values occur alongside the heaviest $\delta^{34}\text{S}_{\text{CAS}}$ values, and the lowest $I/(\text{Ca} + \text{Mg})$ values occur with the most negative $\delta^{34}\text{S}_{\text{CAS}}$ values (Figure 2). Other studies have suggested that sedimentation rates may be the most important factor for modulating MSR and subsequent control on fractionation factors between porewater sulfate and sulfide due to the increased disconnection between porewater and water column sulfate (Pasquier et al., 2021). Sea-level reconstructions and previous biostratigraphic studies of the Monitor Range section indicate that sedimentation rates were mostly stable throughout the late Katian at this locality, which would limit the extent of fluctuations in sulfur isotope fractionation between sulfate and sulfide due to a more constant diffusive length between porewaters and water column sulfate. This relationship in our Monitor Range datasets are thus not consistent with an MSR-driven sulfate model as the principle explanation for the positive $\delta^{34}\text{S}_{\text{CAS}}$ values. Furthermore, if MSR-derived authigenic carbonates were largely responsible for our Monitor Range $\delta^{34}\text{S}_{\text{CAS}}$ values, then we should expect isotopically light $\delta^{13}\text{C}_{\text{carb}}$ profiles via concomitant organic matter oxidation throughout the section that significantly deviate from other $\delta^{13}\text{C}_{\text{carb}}$ records interpreted to reflect the global DIC reservoir (Schrag et al., 2013). In contrast, the Monitor Range $\delta^{13}\text{C}_{\text{carb}}$ records show no significant and widespread carbon isotope deviations from other previously published time equivalent $\delta^{13}\text{C}_{\text{carb}}$ records (Bergström et al., 2010; Jones et al., 2016; Kump & Arthur, 1999; LaPorte et al., 2009; Saltzman & Young, 2005).

Lastly, if the $\delta^{34}\text{S}_{\text{CAS}}$ values of the Monitor Range were significantly affected by MSR-derived authigenic carbonate formation during diagenesis, then positive $\delta^{44}\text{Ca}$ values would be expected from this succession, as was shown from Miocene offshore carbonates purported to have formed within sedimentary intervals with extensive MSR (Blättler et al., 2015). In contrast, however, a recent $\delta^{44}\text{Ca}$ study of the Upper Ordovician carbonate successions in the Monitor Range revealed the most negative $\delta^{44}\text{Ca}$ values throughout the Great Basin (Jones et al., 2020). While it is certainly possible that some early diagenetic mechanisms (e.g., MSR-derived authigenic carbonates) could have contributed to our positive $\delta^{34}\text{S}_{\text{CAS}}$ values, it is unlikely that these processes were the primary factors controlling the first-order trends observed in these datasets.

Additionally, $\delta^{34}\text{S}_{\text{CAS}}$ records presented here across multiple paleobasins on separate paleocontinents from variable bathymetric depths show biostratigraphically, well correlated first-order trends (i.e., the fall $\delta^{34}\text{S}$ in the late Katian and a return to more positive values within the late Hirnantian-Rhuddanian) also suggest preservation of primary seawater signatures (Figures 2–4). While local diagenetic processes may have influenced the $\delta^{34}\text{S}_{\text{CAS}}$ data, it is very unlikely that each of the study sections would experience similar early and late diagenetic histories that resulted in similar first-order trends. These local diagenetic histories can more likely explain the smaller magnitude variations ($\sim 2\text{--}4\%$) within and between $\delta^{34}\text{S}_{\text{CAS}}$ records from the study sites.

5.2. Modeling the Sulfur Cycle

Our $\delta^{34}\text{S}_{\text{CAS}}$ trends recorded from the Monitor Range documents an $\sim 10\%$ fall leading into the Hirnantian. The data at the base of the Kärö core appear to capture the very end of this fall and, when taken with the Monitor Range data, suggest this represents a global perturbation in the sulfur cycle. Here we constructed a forward sulfur isotope mass balance box model to reproduce the magnitude of the isotope perturbation and to provide quantitative constraints on global pyrite burial and weathering fluxes. We prescribed initial conditions based on modern estimates of weathering and pyrite burial rates (Kurtz et al., 2003), and sensitivity tests were explored for all fluxes (for initial parameters and values explored see Table S1 in Supporting Information S1). All forcings were changed as a multi-step function rather than a pulse to simulate progressive changes (see Figure S4 in Supporting Information S1 for graphical representation of model forcings). While this type of modeling

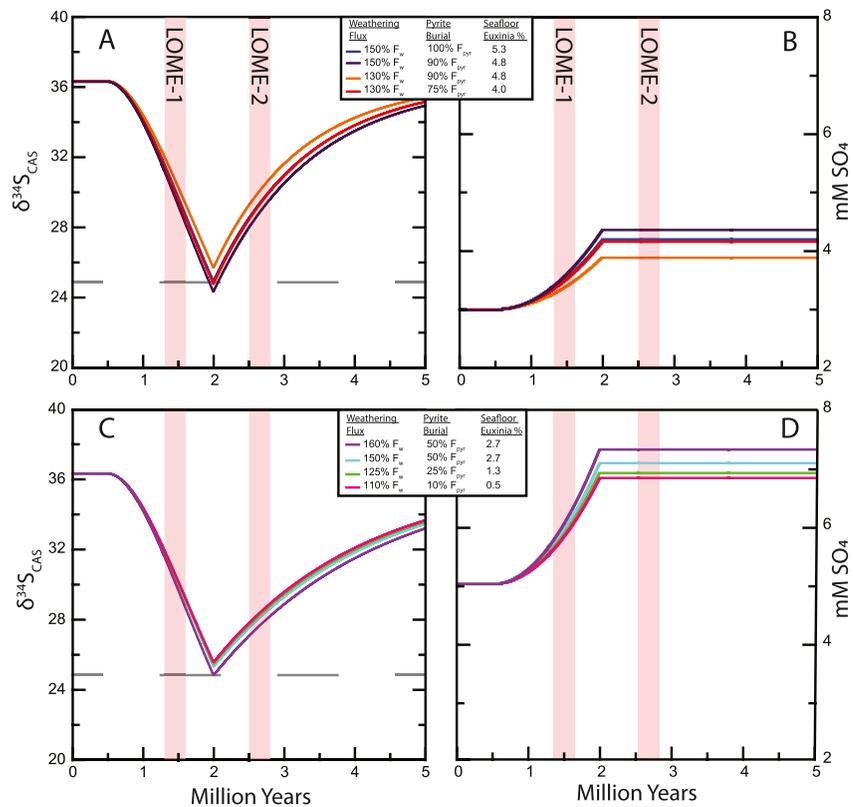


Figure 5. Results of geochemical box modeling showing changes in pyrite burial (F_{pyr}), weathering fluxes (F_w) needed to reproduce seen CAS trends in Monitor Range for a 3 mM SO_4^{2-} scenario (panels A and B) and a 5 mM SO_4^{2-} scenario (panels C and D). Also shown are changes in sulfate concentrations resulting from the associated weathering and pyrite burial fluxes (panels B and D). Dashed line indicates (a) 10‰ excursion for all scenarios. For additional sensitivity tests, see Supporting Information S1.

cannot provide a single unique solution from the changes in the sulfur cycle, it does provide a range of plausible first-order quantifications for these various parameters. It is important to note that all model runs presented here (Figure 5) were prescribed with a change in the sulfur isotope fractionation ($\Delta^{34}\text{S}$). We start with an initial value of +35‰ and decrease it to +20‰ during the perturbation, consistent with a global average of previously published $\Delta^{34}\text{S}$ values (see Table S2 in Supporting Information S1) and those determined in this study. The starting seawater sulfate-S isotope composition for the late Katian of $\sim+35\text{‰}$ is based on our $\delta^{34}\text{S}_{\text{CAS}}$ data set from the Monitor Range. We have used recent Sr isotope weathering models for the Late Ordovician (Hu et al., 2017) and previously published Late Ordovician-Silurian global redox studies (Bartlett et al., 2018; Stockey et al., 2020) for further model constraints for changes in the pyrite burial flux. The time interval adopted for all model runs is 5 Myr for the duration of the negative $\delta^{34}\text{S}_{\text{CAS}}$ excursion based on graptolite biostratigraphy of the Monitor Range section that can be well integrated into the latest calibrated Ordovician Time Scale 2020 (Goldman et al., 2020; see Supporting Information S1 for more details on age constraints). Any model run that does not return to near baseline conditions within the prescribed 5 Myr timeframe is unlikely to explain the observed stratigraphic trend.

Importantly, no single model parameter was able to reproduce the fall in $\delta^{34}\text{S}_{\text{CAS}}$ in the required timeframe (Supporting Information S1). However, model runs assuming moderate decreases in pyrite burial in concert with an increase in weathering can generate the observed $\delta^{34}\text{S}_{\text{CAS}}$ drop (Figure 5). A 50%–75% reduction in pyrite burial (i.e., 50% F_{pyr} and 25% F_{pyr} of initial burial rate, respectively) combined with a 25%–60% increase in the weathering flux (i.e., 125% F_w and 160% F_w , respectively) produces a $\sim 10\text{‰}$ negative excursion using an initial marine sulfate concentration of 5 mM. This scenario is the most parsimonious with the initiation of sea-level fall, which would reduce shelf area and thus the total aerial extent of pyrite burial, as well as increase the weathering inputs. This change in sea level is a result of changes in global climate and associated changes in thermohaline circulation

at this time (see Section 5.3 below) may have increased marine oxygenation of the Late Ordovician oceans, and further reduced global pyrite burial. These combined effects would both contribute to the observed $\delta^{34}\text{S}_{\text{CAS}}$ drop.

A starting marine sulfate concentration of 5 mM is consistent with previous estimates for Late Ordovician seawater (Horita et al., 2002; Jones & Fike, 2013). Model simulations starting with 3 mM marine sulfate concentrations require smaller changes in the weathering and pyrite burial fluxes (i.e., 25% reduction yields a value of 75% F_{pyr}) to simulate the negative excursion (Figure 5a). However, we do not favor an initial marine sulfate concentration of 3 mM or less due since it is the low end of estimates based on fluid inclusions and previous Late Ordovician sulfur isotope modeling (Hammarlund et al., 2012; Horita et al., 2002; Jones & Fike, 2013). Furthermore, sensitivity tests with an initial 3 mM oceanic reservoir show changes in seawater sulfate sulfur isotopes that are faster than those documented from Upper Ordovician records in terms of reaching the minimum value and the later return to baseline. Additionally, our model places an upper constraint on Late Ordovician marine sulfate concentrations, as our simulations with initial values of 10 mM or greater cannot reproduce the observed sulfur isotope records unless unreasonable changes in weathering and pyrite burial fluxes are prescribed (Supporting Information S1).

Most significantly, the observed negative $\delta^{34}\text{S}_{\text{CAS}}$ perturbation requires a major decrease in pyrite burial, thus potentially requiring a reduction in the global extent of euxinic conditions (since pyrite burial is highly efficient under such conditions). Thus, if we assume that most reduced sulfur is buried as pyrite in euxinic settings, we can calculate a maximum estimate of euxinic seafloor area. This approach is an oversimplification since pyrite is also formed in reducing sediments overlain by oxic and anoxic non-sulfidic waters. However, since pyrite burial in these settings is less efficient, an even greater reduction in the area of the seafloor subject to reducing conditions is required. Initial pyrite burial flux for the late Katian required a F_{pyr} of 1.1×10^{18} mol of S/Myr, compared to the modern global rate of 0.67×10^{18} mol of S/Myr (Kurtz et al., 2003). The extent of euxinic conditions in the modern oceans is estimated at $\sim 0.15\%$ of the global seafloor (Reinhard et al., 2013), with reduced sulfur burial flux that would equate to $\sim 3.1 \times 10^{16}$ mol of S/Myr, most of which occurs in the Black Sea (Neretin et al., 2001). This reduced sulfur burial flux includes pyrite burial and any intermediate valence reduced S species, as well as organically bound S, and is thus a maximum estimate for reduced sulfur burial. Given this data from modern oceans and the estimated late Katian pyrite burial rates, we can estimate the extent of euxinic conditions in the late Katian at most was $\sim 35 \times$ more than the modern, equating to an aerial extent of approximately 5.3% ($35 \times 0.15\%$ of the modern). We estimate that a subsequent 75% to 50% reduction in pyrite burial—corresponding to the minimum $\delta^{34}\text{S}_{\text{CAS}}$ values—would reduce the maximum global estimate for the extent of euxinia to ~ 1.3 –2.7% within the Hirnantian. We observe a shift back to more positive $\delta^{34}\text{S}_{\text{CAS}}$ values in the late Hirnantian–early Silurian, likely signaling a return to more reducing conditions with the oceans.

Due to the susceptibility of carbonate-associated sulfate data to be possibly compromised from various diagenetic processes (see above Section 5.1) that can lead to some variability within the recorded $\delta^{34}\text{S}_{\text{CAS}}$ values, we performed a series of sensitivity tests allowing for some degree of overprinting of primary $\delta^{34}\text{S}_{\text{CAS}}$ values (Figures S4–S6 in Supporting Information S1). These tests reveal that our fundamental conclusions of decreased seafloor euxinia do not change within a range of reasonable $\delta^{34}\text{S}_{\text{CAS}}$ variations and possible diagenetic overprinting, but simply affects estimated ranges of total seafloor euxinia. Through careful sample selection and laboratory treatment (i.e., preference of less permeable, low porosity micrite over pack/grainstone, careful extraction procedures to avoid pyrite oxidation) we have generated robust $\delta^{34}\text{S}_{\text{CAS}}$ datasets that are in good agreement with correlative and previously published $\delta^{34}\text{S}_{\text{CAS}}$ datasets (Jones & Fike, 2013; Present et al., 2015). However, it is important to acknowledge that diagenetic overprints are still possible but given the results of our sensitivity tests, agreement of trends among sections, and large-scale ($>5\%$) trends within a section these secondary processes cannot be the primary mechanisms responsible for the major trends in data recorded from these study sites. Ultimately these model results have produced conservative estimates for the extent of seafloor euxinia in the Late Ordovician oceans.

5.3. Late Ordovician Cascade of Redox, Environmental, and Biotic Change

The negative excursion in $\delta^{34}\text{S}_{\text{CAS}}$ recorded from the late Katian is interpreted to indicate a reduction in global euxinia, which is counter to the occurrence of undifferentiated “anoxic” black shales (i.e., anoxic, ferruginous, or euxinic) found at many locations across the globe during this interval (Melchin et al., 2013). Our I/(Ca + Mg) trends indicate that sub-oxic to anoxic conditions were locally pervasive at least in the sections we studied and by inference may have been widespread in the late Katian oceans and persisted into the Hirnantian. The explanation

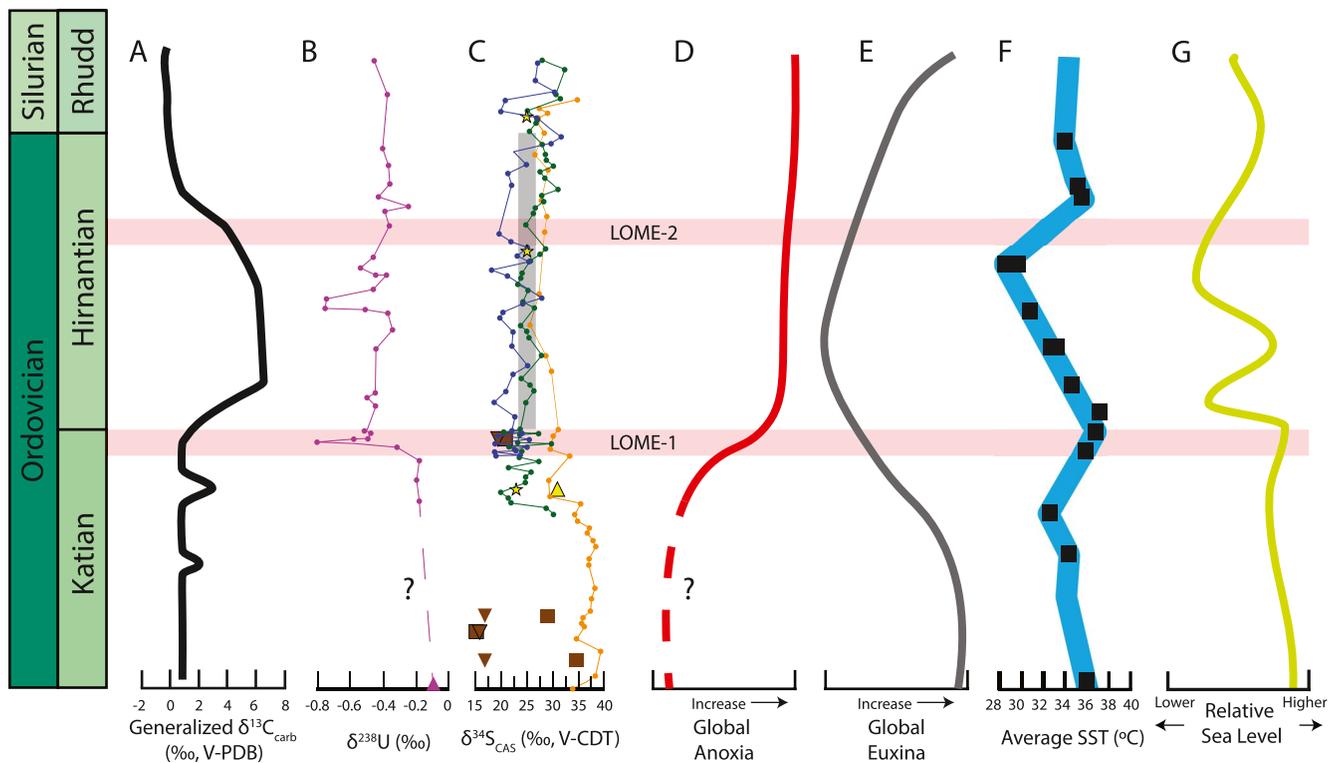


Figure 6. The generalized geochemical trends of Late Ordovician-Silurian global marine redox proxies from carbonates ($\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{238}\text{U}$) and the relationship to mass extinction pulses, climate, and sea level. (a) Generalized late Katian-early Rhuddanian $\delta^{13}\text{C}_{\text{carb}}$ trends. (b) The $\delta^{238}\text{U}$ data are replotted from Bartlett et al., 2018 (purple dots) and Lu et al., 2017 (purple triangle). (c) The $\delta^{34}\text{S}_{\text{CAS}}$ datasets from this study are the green dots/line representing the Kärldla drill core and the orange dots/line representing the Monitor Range section. The blue dots/line are from the western Anticosti Island section (replotted from Jones & Fike, 2013); brown inverted triangles are brachiopod-CAS; brown squares are bulk-CAS data from Kampschulte and Strauss (2004); yellow stars are brachiopod-CAS; and yellow triangles are bulk-CAS from Present et al. (2015). Note the clear overlap in $\delta^{34}\text{S}_{\text{CAS}}$ values from bulk- and brachiopod-CAS datasets throughout the upper Katian-Hirnantian stages. (d) Generalized changes in the extent of global marine anoxia. (e) Generalized changes in the extent of global marine euxinia. (f) Average Sea Surface Temperatures data replotted from Finnegan et al. (2011). (g) Eustatic sea level from Goldman et al. (2020).

for this apparent contradiction may lie with the fact that iodine and sulfur respond to different types of reducing conditions, with iodine responding to changes in redox near O_2 reduction (i.e., non-sulfidic anoxia), while sulfate reduction occurs in more reduced settings further down the redox ladder (Froelich et al., 1979; Lu et al., 2010; Rue et al., 1997). Additionally, these two proxies reflect different spatiotemporal relationships, with iodine reflecting local water-column conditions, while $\delta^{34}\text{S}_{\text{CAS}}$ values record changes in sulfur cycling in the global oceans. In the discussion that follows we focus on this new level of paleoredox specificity for the Late Ordovician oceans in the context of coincident changes in the environment, eustatic sea level, and the marine biosphere.

Significant changes in local and global marine redox conditions began in the late Katian and were coincident with high sea level, elevated sea surface temperatures (SSTs), and generally high levels of marine biodiversity (Figure 6; Finnegan et al., 2011; Finney et al., 1999; Haq & Schutter, 2008; Rasmussen & Harper, 2011; Trotter et al., 2008). There is growing evidence from clumped oxygen isotopes and conodont paleothermometry that global average SSTs began declining in the latest Katian with the initiation of Gondwanan ice sheet expansion (Finnegan et al., 2011; Trotter et al., 2008). This relationship suggests that the negative $\delta^{34}\text{S}_{\text{CAS}}$ excursion and the implied changes in global average temperature were initiated by the intensification of thermohaline circulation as a result of increased deep-water formation around Gondwanan margins, consistent with sedimentary indicators of upwelling in the Monitor Range section (i.e., bedded cherts and phosphates; Figure 2) (Pope, 2003). Increased thermohaline circulation would have led to cooler globally averaged SSTs and increased renewal of dissolved deep marine O_2 , thus ventilating portions of previously euxinic environments along continental margins, shifting the sulfidic chemocline deeper and likely into the sediments in many regions. The ultimate result was a reduced global pyrite burial flux. Thus, euxinic water column conditions may have decreased globally in the latest Katian. Changes in global ocean circulation patterns similar to ones proposed here, have also been proposed as a driver

for the main phases of the GOBE (Rasmussen et al., 2016). However, these changes in the Late Ordovician global circulation patterns may have driven a decrease in biodiversity of the deep-water *Foliomena* fauna in the latest Katian (Finnegan et al., 2016), as well as major changes in geographic and bathymetric range of the *Hirnantia*/Edgewood-Cathay Fauna (Rong et al., 2020). Widespread sulfidic sediment pore waters may help explain the mild enrichments in molybdenum concentrations and iron speciation records of anoxic, sulfide limited, water-column conditions leading into the Hirnantian as recorded in black shales/deep basinal settings on Laurentia, Baltica, Avalonia, and peri-Gondwana (Hammarlund et al., 2012; Hardisty et al., 2018).

The collective data suggest that a combination of cooling temperatures, reduction of habitable space on shelves and in epeiric seaways due to eustatic sea-level fall (Figure S3 in Supporting Information S1), and our new evidence for possibly widespread non-sulfidic anoxic marine conditions in many local basins culminated in the first LOME pulse near the Katian–Hirnantian boundary. Consistent with this hypothesis, the first appearance of bedded chert in the Monitor Range section, suggesting an increase in local upwelling, coincides with indicators of local sea-level fall (Finney et al., 1997) and expansion of a local OMZ recorded in a drop in $I/(Ca + Mg)$. There is also evidence within previously published bulk nitrogen data (LaPorte et al., 2009) for a shift toward more reducing conditions. This data shows a trend to more negative $\delta^{15}N$ values after our $I/(Ca + Mg)$ ratios drop to near 0 $\mu\text{mol/mol}$ (Figure 4d) where it is attributed to a local increase in denitrification. Denitrification occurs after iodine reduction on the redox ladder (Lu et al., 2010), consistent with the observed relationship to our iodine data. Together these local redox proxies suggest a progressive loss of oxygen in this local environment before the Katian–Hirnantian boundary. Although many Hirnantian localities show evidence of locally reducing conditions, the anomalously high $I/(Ca + Mg)$ ratios recorded from western Anticosti Island are likely due to lowered local sea level allowing for changes in surface currents and nutrient dynamics. The net result was well-oxygenated conditions in very shallow waters that supported patch reef environments in this region. Given the similarities in the iodine data across multiple basins and our inferred global signatures in $\delta^{34}S_{CAS}$, we suggest that euxinia likely decreased globally while, paradoxically, less severe anoxia expanded globally in shallow settings thus non-sulfidic anoxia impacted marine life leading into the first LOME pulse. This reduction in euxinic conditions may be attributed to the observed global cooling of surface waters and subsequent increased solubility of O_2 , combined with enhanced thermohaline circulation, thus ventilating previously euxinic portions of Late Ordovician oceans. This enhanced ocean circulation may have in turn intensified local upwelling around continental margins throughout the globe, thus leading to more local primary productivity, enhancing global carbon burial and local anoxia, as evidenced by $I/(Ca + Mg)$ trends. These climatic and oceanographic conditions during the late Katian–Hirnantian may have provided a unique balance that resulted in expansion of anoxic non-sulfidic water masses, but the increased oxygen solubility and circulation may have prevented these water masses from being pervasively euxinic. Ultimately, these marine redox conditions would have had a major impact on marine life in productive continental margins and remaining shallow seaways.

Changes in global marine redox conditions associated with eustatic sea-level rise have been invoked as a causal mechanism for the second LOME pulse in the late Hirnantian (within the *M. persculptus* graptolite biozone) (Harper et al., 2014). As Gondwanan ice sheets melted and the late Hirnantian climate warmed (Finnegan et al., 2011), marine stratification and chemocline migration during eustatic sea-level rise likely played an important role in the second LOME pulse. The $\delta^{238}U$ records from carbonates on western Anticosti Island (Bartlett et al., 2018)—along with $\delta^{98}Mo$ and $\delta^{238}U$ data, Mo concentrations, and iron speciation from organic-rich shale successions (Hammarlund et al., 2012; Stockey et al., 2020; Zhou et al., 2015; Zou et al., 2018)—indicate a return to widespread reducing conditions in global oceans during this time. Our iodine and sulfur isotope datasets are consistent with a shift to more reducing conditions. Specifically, late Hirnantian–early Silurian $I/(Ca + Mg)$ values indicate local anoxia at all three sections, and $\delta^{34}S_{CAS}$ profiles from all sites trend positively by $\sim 7\%$ (Figure 5), indicating a return to increased global pyrite burial. Increased reducing conditions along continental margins during this time would have largely tracked eustatic sea-level rise, warming sea surface temperatures would have led to decreased O_2 solubility and circulation. As OMZs expanded from deep shelf/slope to shallower areas on the continental shelf during the late Hirnantian–early Silurian this increased the overall areal extent of seafloor overlain by anoxic and euxinic bottom waters.

6. Conclusions

Paired iodine and sulfur isotope geochemistry reveal new spatiotemporal relationships between marine non-sulfidic anoxia and euxinia associated with the Late Ordovician Mass Extinction. Our I/(Ca + Mg) ratios are low throughout this time interval in all sections, except for a set of high values (average of 6 $\mu\text{mol/mol}$) recorded from the shallow patch reef facies on western Anticosti Island. At the same time, our new $\delta^{34}\text{S}_{\text{CAS}}$ records show a large negative excursion of $\sim 10\%$ magnitude over the late Katian–Hirnantian. Modeling of these $\delta^{34}\text{S}_{\text{CAS}}$ records suggests that the negative excursion was driven by moderate decreases in the pyrite burial rates combined with small increases in weathering. The implications include a reduction of global pyrite burial, which equates to a maximum decline of seafloor euxinic conditions by $\sim 3\%$ from the late Katian into the Hirnantian. This decrease is roughly consistent with recent models of Hirnantian to early Silurian global redox conditions (Bartlett et al., 2018; Stockey et al., 2020) based on different proxies ($\delta^{98}\text{Mo}$, $\delta^{238}\text{U}$) with different redox sensitivities. Importantly, this transition does not preclude the possibility of increasing oxygen deficiency as recorded in iodine data in marginal settings due to enhanced upwelling as seen in the Monitor Range. Additional data from redox-sensitive elements are needed from multiple paleobasins to constrain the extent of these non-sulfidic reducing conditions.

In sum, our multiproxy data and modeling indicate widespread ventilation of marine environments followed by enhanced weathering during the late Katian–early Hirnantian. This sequence of events likely resulted from enhanced thermohaline circulation and growth of Gondwanan ice sheets that cooled sea surface temperatures and potentially increased deeper ocean oxygenation, therefore reducing euxinic conditions in the global oceans. However, non-sulfidic anoxic conditions remained pervasive throughout shallow shelf settings due to attendant increases in productivity resulting from increased upwelling and ocean circulation. These relationships indicate that a unique combination of reducing marine conditions, climatic cooling, falling sea level and narrowing ecospace led to the first LOME pulse. Subsequently, deglacial eustatic sea-level rise during the late Hirnantian that coincided with warming temperatures, deoxygenation, and decreased ocean circulation led to an expansion of global euxinic conditions, broadly coincident with the second LOME pulse. Our study sheds new light on the possibility of a complex and evolving redox landscape reflecting the interplay of multiple interrelated controls—with severe biotic turnover as a consequence. More generally, these results hint at the improved perspective that can come by integrating multiple local and global proxies from a wide distribution of locations.

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Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data used in this study is made available in this article and its Supporting Information S1. All geochemical data processed in this study is submitted to the EarthChem Database (Kozik et al., 2021).

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