Persistent dysoxia in very shallow seas across the Late Cambrian SPICE Event in the Durness Group, UK

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ABSTRACT

The Durness Group in north-west Scotland preserves a very shallow intertidal to subtidal marine carbonate record from SE Laurentia across the late Cambrian Steptoean Positive Isotopic Carbon Excursion (SPICE; ca. 495–492 Ma), which is considered to have been linked to a pulse of atmospheric oxygenation that in turn promoted biodiversification. We present integrated multi-proxy paleoredox data with the record of sea-level change, using combined Fe speciation, redox-sensitive trace element concentrations, and I/(Ca+Mg) ratios. We interpret the Durness SPICE peak to have occurred during an early highstand interval, and the depositional environment experienced episodic upwelling of deep, ferruginous, anoxic waters that followed high-frequency cycles. The combined data show that dysoxia, i.e., very low marine oxygen concentrations, persisted before, during and after the SPICE,

even in such shallow settings, confirming that a very shallow redoxcline was maintained in this region, and with no evidence for any sustained increase in oxygenation.

INTRODUCTION

The SPICE is a notable global event marked by a >10‰ positive carbon isotope ($\delta^{13}C$) excursion (CIE), culminating in peak values of carbonate carbon isotopes ($\delta^{13}C_{carb}$) in excess of +5‰, with an onset that acts as an auxiliary marker for the base of the late Cambrian Paibian Stage of the lower Furongian Series (ca. 495–492 Ma; Saltzman et al., 2000; Cothren et al., 2022). The onset of the SPICE broadly coincides with a major biotic turnover of trilobites, termed the end-Marjumiid Biomere extinction ('EMBE'; Palmer, 1984; Yang et al., 2024). The rising limb of the SPICE has been linked to a global deoxygenation event characterized by an expansion of low-oxygen oceanic conditions against a backdrop of generally low sulfate concentrations (Gill et al., 2011), and increasing organic carbon and pyrite burial (Saltzman et al., 2000).

The EMBE is characterized by the replacement of shallow-water taxa by those adapted to cold and deep-water environments, and is accompanied by oxygen isotope evidence for seawater cooling that supports hypotheses that link the EMBE with upwelling of colder deep waters onto shallow shelves (e.g., Elrick et al., 2011). The same oxygen isotope dataset also indicates a gradual increase in seawater temperature through the rising limb of the SPICE, potentially linked to decreasing thermohaline circulation and a temperature-related decrease in seawater oxygen concentrations (Elrick et al., 2011). The long-term burial of organic carbon and pyrite associated with the rising limb of the SPICE, in turn, is thought to have led to an increase in atmospheric pO_2 (Saltzman et al., 2011), so promoting an increase in phytoplankton diversity and, ultimately, potentially facilitating the Great Ordovician Biodiversification Event (e.g., Saltzman et al., 2011).

In Laurentian sections, the rising limb of the SPICE has been shown to correspond to an interval of coupled marine transgression-regression (Saltzman et al., 2004), that may suggest a link to tectonic changes (Glumac and Walker, 1998) and thus continental weathering (Pulsipher et al., 2021). Specifically, the onset of the SPICE rising limb coincides with transgression during the late Sauk II supersequence, which is recognized across the Laurentian continent (e.g., Saltzman et al., 2004). Increasing $\delta^{13}C_{carb}$ values during the SPICE rising limb correspond to gradual shallowing through the subsequent highstand, and the SPICE peak occurs approximately coincident with maximum regression near the Sauk II/III boundary (e.g., Saltzman et al., 2004; Cothren et al., 2022). Distinguishing transgressive deposition during late Sauk II from the onset of Sauk III transgression has resulted in different interpretations of sea level change coincident with key features of the SPICE (e.g., Schiffbauer et al., 2017; Yang et al., 2024). Crucially, however, eustatic sea level change is not always evident in single sections or basin settings due to the compounding effects of differences in regional subsidence rates. The majority of open marine sections that record the SPICE show transgressive deposition near the onset of the rising limb, and shallow (or shallower) deposition near the SPICE peak (e.g., Saltzman et al., 2004). The trigger for the SPICE, and other late Cambrian CIEs, remains elusive, but combined sedimentary mercury and osmium concentrations have been used to suggest that the SPICE was not externally triggered (i.e., via enhanced volcanism or weathering) but rather resulted from weak carbon-cycle feedbacks associated with inefficient silicate weathering (Frieling et al., 2024).

The shallow marine Durness Group, NW Scotland, exposes extensive Cambrian to Ordovician carbonates that formed part of the vast tropical-subtropical Great American Carbonate Bank of SE Laurentia (Fig. 1). Strata of the Eilean Dubh Formation archive the SPICE, and are composed of stromatolitic and thrombolitic limestones, and ribbon/laminated limestone and dolostones with occasional aeolian silts and evaporite pseudomorphs (Raine, 2010). There is no evidence for bioturbation and only a very limited body fossil record. Multiple high-frequency (m-scale) shallowing-upward cycles record subtidal (wavy bedding) to inter-tidal conditions (edge-wise conglomerates and fenestrae), within a sabkha, arid tidal-flat setting (Fig. 2A, Raine and Smith, 2017). Glauconite and Hg enrichments have been interpreted to track local redox, with low-oxygen conditions that were initiated during the rising limb of the SPICE reaching a peak during the falling limb, and being followed by a later transient, local oxygenation event (Pruss et al., 2019).

Here, we combine major element concentration data with multiple paleoredox proxy data, including Fe speciation, redox-sensitive trace elements (RSTE) and I/(Ca+Mg) ratios, and integrate these with interpretations of changes in local sea-level, to further constrain the dynamics of the SPICE event and its aftermath. Specifically, our multi-proxy approach allows a detailed assessment of the redox evolution of the Durness Group, revealing notably low-oxygen waters across the entire SPICE interval, despite the very shallow depositional setting.

METHODS

We collected samples at 1-2 m-scale intervals from the Eilean Dubh Formation. Carbonate powders were microdrilled from hand samples, and analyzed for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ using Continuous Flow Isotope Ratio Mass Spectrometry at Isoanaltyical Laboratories. Results are reported in permil relative to the Vienna Peedee belemnite (VPDB) standard in delta notation. Reproducibility of standards was 0.05‰ for $\delta^{13}C$ and 0.1‰ for $\delta^{18}O$. Major element concentrations were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher iCAP 7400), and trace element concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher iCAPQc) at the Cohen Laboratories, University of Leeds. Iron speciation analyses follow the established method of Poulton and Canfield (2005), and were performed at the Cohen Laboratories, University of Leeds. Measurement of I/(Ca+Mg) ratios followed the procedure of (Lu et al., 2018). Ca and Mg concentrations were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista Pro ICP-OES), and I concentrations were determined via inductively coupled plasma-mass spectrometry (High-resolution single collector ICP-MS, AttoM) at the University of Edinburgh, using a Tellurium internal standard (see Supplementary Materials for further details of methods and redox proxy systematics, and Tables S1 and S2 for all data).

RESULTS AND DISCUSSION

Consistent with the North American record, we interpret the study interval to reflect the end of the SAUK IIA (late highstand or lowstand systems tract), all of SAUK IIB [transgressive systems tract (TST), highstand systems tracts (HST), and the SAUK II/III sequence boundary], and the beginning of the SAUK IIIA [TST, HST and falling stage systems tract (FSST)] supersequences (Fig. 2A). This is broadly consistent with the interpretations of Raine and Smith (2017) but moves the position of the Sauk II/III boundary to match carbon isotope chemostratigraphic and lithostratigraphic observations from the North American record. Our $\delta^{13}C_{carb}$ data are consistent with previous records (Pruss et al., 2019), whereby the SPICE onset and rising limb occurs within the transgression to HST of SAUK IIB, reaching a maximum $\delta^{13}C$ value of +2.78‰ (Fig. 2B). Maximum regression across the Sauk II/III is recorded near the SPICE peak.

Samples through the entire interval prior to the SPICE have iron concentrations <0.32 wt% (Fig. S1), combined with very low TOC contents (<0.03 wt%; Fig. 2C). Iron concentrations then rise to 0.42 wt% just prior to the onset of the SPICE and become highly variable, from 0.15 wt% to 1.26 wt%, following m-scale sedimentary cycles (Fig. 2A). TOC concentrations also follow m-scale sedimentary cycles, and reach a maximum (but still <0.1 wt%) at the maximum relative water depth (the Maximum Flooding Surface) of SAUK IIB.

Samples with iron concentrations >0.5 wt% were analyzed for total iron/aluminium (Fe_T/Al), highly reactive/total iron (Fe_{HR}/Fe_T), and pyrite-bound iron/highly reactive iron (Fe_{py}/Fe_{HR}) ratios (Figs. 2D-F; Table S2; Clarkson et al., 2014). Samples with Fe_T >0.5wt%

and Al >0.5 wt% have Fe_T/Al ratios ranging from 0.33 to 2.44, with seven samples yielding Fe_T/Al >0.66, indicating Fe enrichment (Fig. 2D, Clarkson et al., 2014). Samples are also characterized by Fe_{HR}/Fe_T ratios that are persistently elevated above the anoxic threshold (Fe_{HR}/Fe_T >0.38; Fig. 2E; Poulton and Canfield, 2011), with Fe_{py}/Fe_{HR} ratios that are depleted relative to the lower limit for possible euxinia (Fe_{py}/Fe_{HR} <0.60; Fig. 2F; Poulton, 2021). The common occurrence of elevated Fe_{HR}/Fe_T and Fe_T/Al ratios across the SPICE indicates at least periodic anoxic mobilization of Fe^{2+} and subsequent precipitation, while low Fe_{py}/Fe_{HR} ratios suggest limited production of sulfide, even during diagenesis.

To provide further insight into redox conditions at the site of deposition, we use a refined approach for calculating enrichment factors (termed EF^*) for redox sensitive trace metals (e.g., U, Mo, Re) in carbonate-rich lithologies (Krewer et al., 2024; see Supplementary Materials). All resultant EF^*s are very low (Figs. 2G-I; Table S2), indicating limited anoxic enrichment (Tribovillard et al., 2012). A cross-plot of Mo_{EF}^*/U_{EF}^* (Fig. S2) also reveals two pathways for RSTE enrichment, with the majority of slightly elevated EF^* values resulting from delivery to sediments via a particulate shuttle.

We further measure I/(Ca+Mg) ratios to potentially reveal more subtle variations in oxygen availability through time (Fig. 2J; Table S2). I/(Ca+Mg) ratios are very low throughout the section (0.17–0.4 μmol/mol, mean = 0.24 μmol/mol) relative to the typical ‘oxic’ threshold of ~2.6 μmol/mol (Glock et al., 2014; Lu et al., 2016), including prior to, during and after the SPICE (Fig. 2J). These low values suggest limited iodide oxidation within the water column at the depth of carbonate formation (Lu et al., 2010). Calcite- and dolomite-bound iodine can be susceptible to diagenetic alteration (Hardisty et al., 2017), but here the absence of any correlation between the I/(Ca+Mg) ratios and TOC, $\delta^{18}O$ and Mg/Ca (Fig. S3), argues against any significant influence of diagenetic alteration or organically-bound iodine on I/(Ca+Mg) values.

The iodine data suggest low but non-zero oxygen concentrations, conducive to iodate reduction (i.e., the water column was likely predominantly manganous to nitrogenous). Carbonate I/(Ca+Mg) ratios of <2.5 μmol/mol (equivalent to IO_3^- <0.25 μmol/L in seawater) indicate seawater $[O_2]$ of <20–70 μM in modern and ancient oceans (Huang et al., 2022; Lu et al., 2016), suggesting that dysoxic conditions were prevalent at the site of carbonate formation throughout the Eilean Dubh Formation, consistent with the general lack of enrichment in U and Mo (Fig. 2), which would require anoxia. Significantly, there is no increase in I/(Ca+Mg) coincident during, or after, the SPICE, but there is a broad transition in the data from a lower interval (0–38.8 m, n = 24) where I/(Ca+Mg) values exhibit a higher mean (0.25 μmol/mol) and higher standard deviation (0.05 μmol/mol), to an upper interval (40.9–75.6 m, n = 18) that exhibits a slightly lower mean (0.21 μmol/mol) and lower standard deviation (0.02 = μmol/mol). Marginally elevated I/(Ca+Mg) values are largely restricted to two horizons in the lower interval, prior to the SPICE (ca. 20–25 m during the TST of SAUK IIB, and a short-lived peak represented by a singly sample at 32.8 m, during the HST of SAUK IIB, Fig. 2J).

Intervals of elevated Re_{EF*} (max = 7.57, Fig. 2I) are consistent with low but non-zero iodine, suggesting the occasional development of dysoxic conditions which would effectively draw down Re. Samples over an interval higher in the section (ca. 62–66 m) record appreciable U_{EF}^* values that more likely reflect redox-related enrichment (Fig. S2) corresponding to short-lived development of anoxic conditions at the sediment-water interface, consistent with elevated TOC (Fig. 2C) and Re_{EF}^* (Fig. 2I), and muted I/(Ca+Mg) (Fig. 2J). In sum, the combined multi-proxy paleoredox data indicate dominantly dysoxic conditions at the site of deposition, with persistent enrichments in Fe_{HR} being due to oxidation of Fe^{2+} sourced from upwelling of ferruginous deeper waters.

COMPARISON WITH COEVAL RECORDS ACROSS THE SPICE

In Durness, we interpret the onset of the SPICE rising limb to correspond with a TST and the peak of the SPICE with the HST, which is consistent with the overall pattern of sea level change recorded in sections of northeastern Utah and southeastern Idaho (Saltzman et al., 2004). This stratal stacking pattern mirrors the lithostratigraphic descriptions of most sections that record the SPICE, and also matches patterns noted for many other sections that precede positive CIEs, including the Ediacaran pre-Shuram and ‘Omkyk’ intervals, the Cambrian Terreneuvian peaks 5p/ZHUCE and 6p, and Cambrian Series 2 to Miaolingian peaks IV, VII, and XI/X (Hawke Bay regression peak) (Bowyer et al., 2024). There will, however, be different lithostratigraphic expressions of relative sea level change regionally. Given the very shallow nature of the Eilean Dubh Formation, smaller scale flooding associated with a generally very low global sea level between Sauk II and III may be absent, and the full SPICE record is expressed in only ca. 20 m of strata (Fig. 2). This results in a

SPICE peak that appears to be very 'abrupt', further suggesting that there may be cryptic hiatuses within the section (Nicholas, 1994). Assuming the utility of $\delta^{13}C$ for global chemostratigraphic correlation, then the FSST recorded by Raine and Smith (2017) may correlate to the post-SPICE *Saukiella* Zone in Laurentia (Sauk III). This FSST may be related to local accommodation space changes during the early Sauk IIIA rather than a reflection of the status of eustatic sea level at the Sauk II/III boundary as defined in North American sections. This interpretation is suggested by the $\delta^{13}C$ record, although no biozone data are available in the Eilean Dubh Formation to further support this.

Existing data have also shown that widespread anoxia, or a shallow redoxcline, was pervasive across the continental shelves of western Laurentia during the pre-and early-SPICE interval (He et al., 2024). The low values of I/(Ca+Mg) recorded in this study, which remain within a narrow range during the whole interval studied, indicate relatively invariable low-oxygen conditions and notably a shallow marine redoxcline throughout the entire pre- to post-SPICE interval in SE Laurentia. By contrast, far higher mean I/(Ca+Mg) values have been recorded from other regions, including sections of Australia and the Great Basin of Laurentia (Fig. 3). These sites also record increasing I/(Ca+Mg) values either coincident with, or after the SPICE, interpreted to reflect increasing local marine (and possibly atmospheric) oxygen concentrations driven by progressive organic carbon and pyrite burial (Fig. 3, He et al., 2024). Such an increase in atmospheric oxygen concentrations would be expected to impact the shallow marine redox state directly, and so it is noteworthy that the very shallow setting represented by the Eilean Dubh Formation does not record clear evidence for this increase.

Shelf and slope oceanic waters around the Iapetan and Laurentian continental margins during the entire latest Cambrian to early Ordovician have been shown to be generally poorly oxygenated with shallow redoxclines or expanded oxygen minimum zones (OMZs) (e.g., (Kozik et al., 2023). The ambient greenhouse climate of the late Cambrian would have favored the expansion of OMZs (e.g., Elrick et al., 2011), and ocean circulation would also have created heterogenous distribution of nutrients and redox conditions (e.g., LeRoy et al., 2021).

Our data confirm that, unlike the shallow marine records of SPICE events observed in other margins of Laurentia (UK, USA), South China and Australia, the shallow waters of SE Laurentia did not experience any significant post-SPICE rise in oxygen (Fig. 3). It is possible that this could be due to seawater cooling, stimulating global ocean circulation (Zhang et al., 2024), so accentuating continental margin upwelling (Stouffer et al., 2006), so augmenting local productivity and thereby expanding oxygen minimum zones (OMZ) (Zhang et al., 2024). Such cooling is consistent with upwelling at the onset of the rising limb of the SPICE during the TST. But as the Durness carbonates were deposited in very shallow, tropical-subtropical settings, they were likely to have experienced only modest temperature fluctuations.

CONCLUSIONS

The Durness Group in northern Scotland preserves a very shallow marine carbonate record from SE Laurentia across the late Cambrian SPICE, and highlights the significant regional expression of this event, which was closely coupled to global sea-level change. Multi-proxy paleoredox data using Fe speciation, redox-sensitive trace element concentrations, and I/(Ca+Mg) ratios show that the Durness SPICE interval was characterized by the episodic upwelling of deep, ferruginous, anoxic waters into dysoxic shallow waters. The onset of the SPICE rising limb coincides with transgressive deposition, consistent with other Laurentian sections, whilst the remainder of the rising limb corresponds to deposition during the highstand. Significantly, we show that very low marine oxygen conditions persisted before, during and after the SPICE, even in shallow waters, confirming that this region, unlike others around Gondwana, retained a shallow redoxcline and experienced no increase in oxygenation post-SPICE, confirming significant regional differences in expression of the SPICE event.

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Figure captions

Figure 1. Geological map of the Cambrian-Ordovician Durness Group, NW Scotland, showing the study area south-west of Balnakeil Bay, Durness (modified after Raine, 2010).

Figure 2. Summary of redox dynamics through the late Cambrian SPICE event (shaded), recorded by the Eilean Dubh Formation (A) Composite stratigraphy and tentative correlation of Sauk supersequences (with modified sequence stratigraphic information from Raine, 2010). Horizontal grey dashed line marks the Maximum Flooding Surface. TST = Transgressive Systems Tract. HST = Highstand Systems Tract. FSST = Falling Stage Systems Tract. (B) C isotope ($\delta^{13}C_{carb}$) record (this study). (C) TOC. (D) Fe_T/Al

for samples with >0.5 wt% Fe_T and >0.5 wt% Al. Vertical dashed lines in (D) bracket the range of normal oxic values (0.44–0.66) for carbonates and shales (Clarkson et al., 2014). (E) Fe_{HR}/Fe_T ratios, where vertical dashed lines represent empirically-derived 'oxic' (<0.22) and 'anoxic' (>0.38) threshold ratios, separated by an equivocal zone (Poulton and Canfield, 2011). (F) Fe_{Py}/Fe_{HR} ratios, where vertical dashed lines represent the empirically-derived ferruginous (<0.60) and euxinic (>0.80) thresholds, separated by an equivocal zone that may represent euxinia (Poulton, 2021). (G) Mo enrichment factors (Mo_{EF*}). (H) U enrichment factors (U_{EF*}). (I) Re enrichment factors (Re_{EF*}). (J) I/(Ca + Mg).

Figure 3. Comparison of global and regional geochemical expression of the SPICE event constrained within a common age model in the records of (A) $\delta^{13}C_{carb}$, (B) $\delta^{34}S_{CAS}$, and (C) I/(Ca+Mg) in the context of late Cambrian paleogeography (Gill et al., 2011; He et al., 2024; Pruss et al., 2019; Zhang et al., 2024). Biomere extinctions are constrained within the age model through integration of carbon isotope and paleontological records of Zhang et al. (2024). Detrital zircon U-Pb data from Cothren et al. (2022); Re-Os age from Rooney et al. (2022). MDAs – maximum depositional ages; ORMs – organic rich mudrocks.