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Uranium isotopes distinguish two geochemically distinct stages during the later Cambrian SPICE event

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Abstract

Anoxic marine zones were common in early Paleozoic oceans (542–400 Ma), and present a potential link to atmospheric pO₂ via feedbacks linking global marine phosphorous recycling, primary production and organic carbon burial. Uranium (U) isotopes in carbonate rocks track the extent of ocean anoxia, whereas carbon (C) and sulfur (S) isotopes track the burial of organic carbon and pyrite sulfur (primary long-term sources of atmospheric oxygen). In combination, these proxies therefore reveal the comparative dynamics of ocean anoxia and oxygen liberation to the atmosphere over million-year time scales. Here we report high-precision uranium isotopic data in marine carbonates deposited during the Late Cambrian ‘SPICE’ event, at ca. 499 Ma, documenting a well-defined –0.18‰ negative $\delta^{238}\text{U}$ excursion that occurs at the onset of the SPICE event’s positive $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursions, but peaks (and tails off) before them. Dynamic modelling shows that the different response of the U reservoir cannot be attributed solely to differences in residence times or reservoir sizes - suggesting that two chemically distinct ocean states occurred within the SPICE event. The first ocean stage involved a global expansion of euxinic waters, triggering the spike in U burial, and peaking in conjunction with a well-known trilobite extinction event. During the second stage widespread euxinia waned, causing U removal to tail off, but enhanced organic carbon and pyrite burial continued, coinciding with evidence for severe sulfate depletion in the oceans (Gill et al., 2011). We discuss scenarios for how an interval of elevated pyrite and organic carbon burial could have been sustained without widespread euxinia

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Appendix A. Supplementary material

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in the water column (both non-sulfidic anoxia and/or a more oxygenated ocean state are possibilities). Either way, the SPICE event encompasses two different stages of elevated organic carbon and pyrite burial maintained by high nutrient fluxes to the ocean, and potentially sustained by internal marine geochemical feedbacks.

Keywords

carbonates; uranium isotopes; paleoredox; oceanic anoxic events; anoxic marine zones; SPICE event

1. Introduction

The O₂ content of the Earth's atmosphere and oceans has changed dramatically through Earth history (Canfield, 2005; Holland, 2006). Oxygen began to accumulate in appreciable amounts after the "Great Oxidation" some 2.3-2.4 billion years ago, but ocean-oxygenation proxies show that anoxic water masses remained common well into the Paleozoic Era (Berner and Raiswell, 1983; Berry and Wilde, 1978; Dahl et al., 2010; Gill et al., 2011). Indeed, before the Late Silurian appearance of charcoal (requiring pO₂ > 15 atm% (Belcher and McElwain, 2008)), atmospheric oxygen levels were likely lower and continental shelf anoxia more extensive than today (Bergman et al., 2004; Berry and Wilde, 1978; Dahl et al., 2010; Raiswell and Berner, 1985).

Burial of the fraction of reduced organic carbon that escapes oxidation is a net source of atmospheric oxygen, as is burial of pyrite produced after sulfate reduction (Garrels and Perry, 1974). Increases in the magnitude of these fluxes leave the inorganic C and S pools in the remainder of the ocean relatively enriched in heavy isotopes - meaning that positive $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursions might be expected to be connected to a net increase in oxygen. However, over shorter timescales, ocean anoxia is associated with increased preservation of marine organic carbon, and sometimes with increasingly prevalent anoxic/sulfidic (euxinic) conditions. More than 10 positive $\delta^{13}\text{C}$ excursions in the Phanerozoic Era of greater than 4‰ magnitude are understood to be periods of enhanced organic carbon burial (Saltzman and Thomas, 2012). Several of these events are also recognized as periods when anoxic and sulfidic (euxinic) conditions expanded in the ocean (Gill et al., 2011; Jenkyns, 2010; Meyer and Kump, 2008; Monteiro et al., 2012).

The long-term production of organic carbon is ultimately limited over long timescales, by the phosphate concentration of the oceans (Redfield, 1958). Various phosphate removal fluxes are redox-sensitive, giving rise to a positive feedback between anoxia, phosphorous availability and global primary production (blue boxes in Fig. 1). Ocean anoxia promotes marine P recycling by preventing oxygen-dependent Fe-oxyhydroxide P burial (Colman and Holland, 2000). This enhances the availability of phosphorus in the water column, increasing (P-limited) production. Over the relatively short ($\sim 10^4$ y) timescales relevant to phosphate dynamics, this increase in production fuels more anoxia in a net positive feedback. Over longer timescales ($\sim 10^6$ y) the increase in production, which translates into a higher organic carbon burial flux, ultimately gives rise to a counteracting negative feedback mechanism, where enhanced organic carbon burial into sediments represents a source of O₂

to the atmosphere, thereby reducing anoxia in a net negative feedback (Lenton and Watson, 2000; Van Cappellen and Ingall, 1994), thought (for example) to have been relevant to Cretaceous oceanic anoxic events (Handoh and Lenton, 2003). Importantly, the existence of this feedback process predicts that the termination of expanded anoxia should correspond (within the residence time of the P cycle) with the end of elevated organic carbon burial and the peak of (or slightly after) the positive $\delta^{13}\text{C}$ excursion within the residence time of the marine C cycle ($\sim 10^5$ y).

The central idea behind this work is that carbon and sulfur isotopes track organic carbon and pyrite export to sediments, respectively, but are not in themselves a unique proxy for ocean anoxia, whereas U isotopes more specifically track ocean anoxia/euxinia (Table 1). Therefore, by comparing the two signals against each other we gain information about the link between these burial fluxes and direct changes in ocean redox.

We compare stratigraphic data and models for the C, S and U isotope evolution of seawater during the Steptoean Positive Carbon Isotope Excursion (SPICE) (~ 500 – 496 Ma), a well-documented positive 4 – 6 ‰ $\delta^{13}\text{C}$ excursion recognized worldwide (Kouchinsky et al., 2008; Saltzman et al., 2004, 2000, 1998). The SPICE event is thought to represent a 2 – 4 Myr interval when anoxic and sulfidic water masses expanded over the shallow ocean, contemporaneous with enhanced burial of organic carbon (Gill et al., 2011; Saltzman et al., 2011), as well as pyrite and molybdenum (Gill et al., 2011). Modelling of S isotopes during the event implies that global pyrite burial was 50 – 75 times that seen in the modern Black Sea (Gill et al., 2011). Assuming euxinic sediments accumulated at similar area-specific rates as the modern Black Sea, this would imply that euxinia expanded over 15 – 23×10^6 km² of the sea floor. This area is more than 10 -fold greater than the extensive euxinic/dysoxic epicontinental sea that covered most of Scandinavia from the Middle–Late Cambrian into the Ordovician ($\sim 1 \times 10^6$ km²) (Buchardt et al., 1997; Gill et al., 2011; Nielsen and Schovsbo, 2011). Thus, it leaves the interesting possibility that euxinia might have expanded worldwide on continental shelves during the SPICE event. Such an expansion in euxinia would have impacted the geochemistry of many redox-sensitive element cycles, including uranium.

2. Uranium isotope geochemistry

Uranium behaves conservatively in modern oceans and thus has a long oceanic residence time ($t_U = 440 \pm 120$ ky) relative to ocean mixing time scales (~ 1 – 2 ky) (Dunk et al., 2002; Sarmiento and Gruber, 2006). Previous work suggests that the U isotope record constitutes a primary signal of global ocean chemistry, consistent with model predictions presented in this work (Brennecke et al., 2011a; Montoya-Pino et al., 2010; Weyer et al., 2008). The isotope signature in seawater reflects changes in the apportioning of the global uranium burial flux between ^{238}U -depleted oxic and ^{238}U -enriched anoxic settings, thus, the relative proportions of oxic and anoxic U removal.

Uranium isotope variations result mainly from the nuclear volume effects (Schauble, 2007). The largest isotope fractionations occur during uranium reduction between U(VI) and U(IV) species, although non-redox reactions can also induce isotope fractionation (Bopp et al.,

2009, 2010; Brennecke et al., 2011b; Stirling et al., 2007). The U isotope fractionation is expressed in terms of $\delta^{238}\text{U}$ in per mil deviation from a universal reference material (see Fig. 2 and Table S6 for details). Fig. 2 shows marine U sinks and their relative contribution to the total U removal fluxes, which include euxinic sediments (~20%), oxic high productivity settings with sulfidic sediments (~26%), biogenic carbonates (~23%), deltaic sediments in the coastal zone (~19%), and basaltic alteration (~10%) during hydrothermal circulation and seafloor weathering (Dunk et al., 2002).

Most U burial in the ocean is associated with isotope fractionation and this contributes to a ^{238}U deficit in marine waters ($-0.44 \pm 0.03\text{‰}$, $n = 12$) relative to oceanic input ($\sim -0.22\text{‰}$, $n = 1$) and crustal rocks (volcanic rocks, $-0.42 \pm 0.04\text{‰}$, $n = 21$; granitic rocks $-0.30 \pm 0.03\text{‰}$, $n = 27$) (Stirling et al., 2007, 2005; Telus et al., 2012; Weyer et al., 2008). Importantly, the most reducing environments generally induce the largest net U isotope fractionation (Fig. 2). Therefore, the $\delta^{238}\text{U}$ of seawater is a proxy for how much sediment is buried in anoxic settings versus oxic settings in the oceans, with a more negative signal in ambient seawater implying increased fractionation associated with anoxic burial settings. All sediments accumulating authigenic U tap this global reservoir and, therefore, potentially preserve the history of seawater U isotope chemistry through time.

Uranium exists as a uranyl-tricarbonate anion $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ in seawater (Langmuir, 1978). In this hexavalent form, U is soluble and appears highly unreactive, although it is directly incorporated into aragonite (with neither redox change nor coordination change) during transfer from solution to solid (Reeder et al., 2000), or significant isotopic fractionation (Romaniello et al., 2013; Stirling et al., 2007; Weyer et al., 2008).

Authigenic U accumulation also occurs in carbonates within anoxic and sulfidic pore fluids, but these sediments display enrichments of isotopically heavy U, $0.31 \pm 0.05\text{‰}$ higher than seawater (Romaniello et al., 2013). In general, two burial pathways for carbonate-associated uranium (CAU) can be envisioned (our data likely records both). “Primary CAU” is uranium from seawater that is incorporated into carbonate minerals as it precipitates on the seafloor. “Secondary CAU” is uranium that precipitates within the pore fluids, where alkalinity is produced from diagenetic reactions and where sediments go anoxic with depth.

The magnitude of U isotope fractionation expressed in carbonate sediments not only depend on the relative proportions of primary and secondary U, but also on the chemical reactions involved in secondary CAU removal, as well as the depth below sediment-water interface (L) where removal occurs. The chemical removal pathway(s) for secondary CAU in reducing carbonates are not known. U reduction occurs in the Fe reducing zone of the sediments (Scholz et al., 2011). However, the availability of sulfide and/or sulfate reducers are expected to play a role both because sulfide lowers the reduction potential and it accelerates U removal rates (Hua and Deng, 2008; Hua et al., 2006; Klinkhammer and Palmer, 1991; Morford et al., 2009; Shaw et al., 1994), and isotopically heavy U(IV) may be associated with organic phases, substitute into the calcite crystal lattice (Romaniello et al., 2013; Sturchio, 1998), and/or form complexes with phosphate at $\text{pH} < 7.5$ typical of sulfate reducing sediments (Bargar et al., 2013; Goldberg et al., 2012; Hua et al., 2006; Langmuir,

1978; Romaniello et al., 2013). These uncertainties cloud estimates of the intrinsic isotope fractionation factor(s) (ϵ_{int}) between reactant(s) and product(s) in the formation of secondary CAU. Nevertheless, any diffusion-limited, intra-sedimentary U removal process will leave a smaller net isotopic offset in the sediments (ϵ_{eff}) as a function of depth (L) to the zone of U removal; i.e. O_2 penetration depth and/or depth from sulfidic zone (Brandes and Devol, 1997; Clark and Johnson, 2008; Kitchen et al., 2012). In the Bahamas, for example, secondary CAU removal occurs at the sediment-water interface ($L = 0$), so the net isotope offset would be half the intrinsic isotope fractionation between reactant and product, $\epsilon_{\text{eff}} \approx \epsilon_{\text{int}}/2$. Thus, the ϵ_{eff} offset of $>+0.31\text{‰}$ in secondary CAU is tentatively ascribed to reductive U removal near the sediment-water interface with an intrinsic fractionation twice this magnitude, $>\sim 0.6\text{‰}$. These spatial uncertainties introduce potential errors associated with inferring $\delta^{238}\text{U}$ of ancient seawater from marine carbonate sediments. For the models presented in this study, we first assume constant isotope fractionations for each sink and later relax this assumption (Table 1; Table S3). It is important to note that the application of U isotope data for reconstructing the dynamics of global ocean anoxia in the past does not rely on the absolute magnitude of this offset, only on the assumption that it is roughly constant relative to the evolving isotopic composition of seawater (e.g. $L \approx \text{constant}$).

The C and S isotope systematics are less dependent on water column redox chemistry and the proportion of euxinic sediment burial than is U. This is clear from a comparison of the modern marine sinks for carbon, sulfur and uranium (Table 1), which reflects the fact that a large portion of U burial occurs under euxinic waters today (even though these areas account for less than 1% of the seafloor), whereas most reduced C and S burial occurs in shallow oxygenated settings where the main controlling factor is sedimentation rate (i.e. river deltas; Table 1). The importance of the oxygenation state of the environment on the net isotope fractionation expressed in sediments appears to be greater for U and S than for C:

$\delta^{13}\text{C}_{\text{seawater}} - \delta^{13}\text{C}_{\text{Organic,oxic}} \sim 30\text{‰}$ vs. $\delta^{13}\text{C}_{\text{seawater}} - \delta^{13}\text{C}_{\text{Organic_euxinic}} \sim 23\text{‰}$ (Fry et al., 1991; Hayes et al., 1993) (note that oxic sites typically induce greater fractionation for C). For S, the isotope offsets of pyrite-S in euxinic sediments from overlying seawater is (as for U), on average about twice the magnitude of sedimentary pyrite formed in oxic settings; $\delta^{34}\text{S}_{\text{seawater}} - \delta^{34}\text{S}_{\text{pyrite,oxic}} \sim 21\text{‰} - (-15\text{‰}) \sim 35\text{‰}$ vs. $\delta^{34}\text{S}_{\text{seawater}} - \delta^{34}\text{S}_{\text{pyrite,euxinic}} \sim 21\text{‰} - (-37\text{‰}) = 58\text{‰}$ (Canfield et al., 2010; Habicht and Canfield, 2001; Lyons, 1997; Strauss, 1997).

Taken together, the stronger redox control on U burial rates and net isotope fractionation expressed in sediments implies that seawater U isotope composition is a more precise record of the extent of anoxia than are the sulfur and carbon isotope compositions of seawater. Because the isotope systems behave differently in this way, we can potentially extract complementary information on both pO_2 sourcing and the expansion of anoxic settings.

3. Samples and methods

3.1. Geological settings

Samples were taken from the Mt Whelan #1 drill core through the Georgina Limestone Formation, Queensland, Australia. The Georgina limestone was deposited in a tropical setting on the outer shelf of Gondwana in relatively-deep water (below wave base), marine

settings during the Guzhangian–Paibian stages of the Cambrian Period (Green and Balfe, 1980). The drill core represents a 300 m stratigraphic section of mostly mid-grey, clayey micrite (microcrystalline calcite). Regular primary lamination is preserved in the sediments with a general lack of current-produced structures. Together with the abundance of pyrite (up to 5.7 wt%), significant organic carbon contents (up to 0.5 wt%), in situ ammonium feldspars and lack of bioturbation, we infer that the pore fluids were likely anoxic and sulfidic during deposition (Gill et al., 2011; Green and Balfe, 1980; Saltzman et al., 2011). We envision that uranium was incorporated as U(VI)-carbonate into a primary carbonate mineral precipitate and also by secondary carbonate precipitation within the anoxic and sulfidic pore fluids (e.g. U(IV) in the calcite lattice). Thus, diagenetic processes may have caused isotope offset between sediments and overlying seawater. Indeed, we stress that there are notable differences between the Cambrian rocks and modern analogue settings studied to date, including water depth, dominant carbonate mineralogy (low-magnesium calcite, not aragonite), and diagenetic histories.

The absolute time span of the SPICE interval is uncertain. Interpolation using U–Pb dates from ash beds and the assumption of equal durations for the 10 trilobite biozones in between suggest that the positive $\delta^{13}\text{C}$ excursion represents roughly 2–4 Myrs (Saltzman et al., 2004). This corresponds to an average sedimentation rate (after compaction) for our section in the Georgina basin of 50 m/Myr, or a mass accumulation rate of 70 g calcite $\text{m}^{-2} \text{yr}^{-1}$ (assuming an average clay content of 50 wt%). This is a rather high sedimentation rate for clay-rich carbonate sediments deposited below wave base, but is comparable to the mass accumulation rate of Late Holocene carbonate shelves: 20–100 $\text{gm}^{-2} \text{yr}^{-1}$ (Milliman, 1993). Thus, it is reasonable that both the rising limb and falling limb of the SPICE excursion lasted $\sim 10^6$ yr and likely longer than $\sim 10^5$ yr.

3.2. Methods

We adopt a soft leaching procedure to extract mainly carbonate associated U from the Whelan samples and, (if present) U associated with diagenetically reactive phosphate phases (authigenic carbonate fluorapatite and ferric oxyhydroxide-associated P) (Ruttenberg, 1992), but not any detrital or organic-bound U.

Drill core samples were cut in ~ 15 –25 g pieces and secondary veins, if present, were removed using a water-cooled saw. The rock surface was first leached in 2 M HCl to remove surface contaminants and then crushed in a shatter box to a fine powder suitable for analysis of carbonate-associated uranium. Approximately 1 g of the fine powder was weighed out in acid-cleaned Teflon beakers and leached using a mild leaching procedure: ultra-clean H_2O was added to a powder, and then small volumes of 1 M cold hydrochloric acid were added to preferentially dissolve the carbonate. The acid concentration of the mixture never exceeded 0.5 M to avoid dissolution of Fe-oxides and clay particles. This mixture was ultrasonicated and then centrifuged to separate the liquid from the solids. Following the removal of the supernatant, the residue was washed twice with ultra-clean H_2O , shaken, centrifuged before the supernatant was again transferred to the leachate to ensure maximum transfer of the carbonate-associated uranium.

All samples were spiked prior to chemical purification using the IRMM-3636 ^{233}U – ^{236}U double spike (Condon et al., 2010) and left for >48 hours on a hotplate first in nitric acid and subsequently in hydrochloric acid. This was done to allow spike-sample equilibration and ensure all U compounds were in the same chemical form prior to ion chromatographic separation. Chemical purification of U and its isotopic analysis were conducted following the procedures outlined in Connelly et al. (2012). In detail, ~400 ng U was purified from matrix elements using a four-step chromatographic procedure consisting of two U-TEVA columns (both 2 mL resin volume) followed by two anion columns (1 mL and 0.12 mL resin volumes). As a last step prior to mass spectrometry, samples were treated with 20 μL of concentrated HNO_3 on a hot plate. U isotope measurements were performed by High Resolution Multi-Collector Inductively Coupled Plasma Mass Spectrometry (HR-MCICPMS) using a Thermo Fisher Scientific Neptune Plus at the Natural History Museum of Denmark, University of Copenhagen. Sample analyses were bracketed by the spiked CRM-145 standard with each sample analyzed five times. The accuracy and external reproducibility of our measurements were assessed through repeated analysis of U solutions, multiple digestions of international rock standards as well as replicate analysis of samples. Based on these experiments, we estimate the external reproducibility and accuracy of our $^{238}\text{U}/^{235}\text{U}$ data to be 0.03‰ (2 sd). For example, BCR-2 is found at $\delta^{238}\text{U} = 0.271 \pm 0.017\text{‰}$ consistent with previous measurements at $0.29 \pm 0.07\text{‰}$ (Table 2; Weyer et al., 2008). A test of the importance of adding the spike prior to digestion and U purification was performed analyzing a bulk rock digestion twice (with HF + HNO_3 in Teflon bomb, following the procedure by Connelly et al., 2012) where one sample was spiked prior to digestion and chemical purification and the other spiked after purification. Identical $^{238}\text{U}/^{235}\text{U}$ values were obtained for these two approaches (Table 2). Given that 40–70% of the U in the sample resides in the residual clay fraction, we verified that the U in the clay fraction did not contribute significantly to the CAU pool by measuring the composition of several residues from the leaching procedure. The residual solids were spiked, digested in a high-temperature dissolution bomb with HF + HNO_3 , and the U was purified and analysed in the same fashion as that from the carbonate fraction. Three of five clay residues display indistinguishable $\delta^{238}\text{U}$ values within the range of granitic rocks consistent with a lithogenic (unreactive) U component in the clay (Table 2), while two samples (WH1-11, WH1-16) from the uppermost part of the section display lower $\delta^{238}\text{U}$, at -0.7 and -0.4‰ , and rather low U/Th (Table S1), likely due to different source rock or formation pathway. In all cases, we saw no systematic isotope correlation between clay-bound U and carbonate associated uranium. Instead, the clay residues display U isotope compositions decoupled from the systematic U isotope excursion recorded in the carbonate fraction.

4. Results and discussion

The C and S isotope data from the Mt. Whelan drill core show positive excursions over 200 m of stratigraphy similar to those observed for comparable rock sections on several other paleocontinents including Laurentia, Baltica, China and Siberia (Fig. 3) (Ahlberg et al., 2009; Gill et al., 2011; Kouchinsky et al., 2008; Saltzman et al., 2011). During this time period, the S isotope offset between carbonate-associated sulfate and pyrite systematically

declines to zero, indicative of a global, quantitative depletion of the oceanic sulfate reservoir towards the end of the SPICE event (Gill et al., 2011).

The new U isotope data from the SPICE carbonates shows a smooth negative U isotope excursion temporally coincident with the rising limb of the carbon isotope excursion (Fig. 3). This confirms that the event also affected the marine U cycle in a manner expected for globally enhanced euxinic U burial. The $\delta^{238}\text{U}$ profile decreases from -0.21‰ to -0.39‰ and then returns to its initial level at approximately the peak of the C-isotope excursion during the SPICE.

The pre-SPICE $\delta^{238}\text{U}$ value (-0.21‰) is difficult to define, but appears slightly lower than equivalent modern anoxic carbonate cements with average $\delta^{238}\text{U} = -0.13 \pm 0.04\text{‰}$ (2SE) (Romaniello et al., 2013). A low $\delta^{238}\text{U}$ baseline value before the event is qualitatively consistent with a slightly larger euxinic removal pathway for U compared to today. This interpretation assumes that: 1) isotope fractionation between overlying seawater and sediment is constant and similar to today, 2) the $\delta^{238}\text{U}$ of oceanic input to the Cambrian ocean was similar to today, and 3) that a $\delta^{238}\text{U}$ baseline value before the isotope excursion is representative of the marine U cycle in steady state. With these assumptions, the low $\delta^{238}\text{U}$ baseline is in good agreement with Mo drawdown and a rapid positive S isotope excursion suggestive of widespread euxinic conditions in the Cambrian, already before the SPICE event (Gill et al., 2011). Alternatively, the low baseline in the Whelan section may result from a lower $\delta^{238}\text{U}$ value in riverine discharge than today (e.g. modern rivers at Danube river value of -0.22‰ , and Cambrian rivers closer to the composition of crustal rocks, -0.39‰ to -0.30‰).

Regardless of the baseline value, before the SPICE event, seawater became relatively depleted in ^{238}U , leading to the observed -0.18‰ excursion in the sedimentary succession. The magnitude of this excursion is greater than observed during the Oceanic Anoxic Event 2 (OAE 2) in the Cretaceous and smaller than that seen during the End-Permian extinction event at -0.13‰ and -0.28‰ , respectively (Brennecke et al., 2011a; Montoya-Pino et al., 2010).

The congruence between the different isotope excursions (negative $\delta^{238}\text{U}$, positive $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$) suggests that the U isotope profile is recording changes in global seawater chemistry. Additionally, there is no systematic change in carbonate mineralogy in the section that could explain the entire negative $\delta^{238}\text{U}$ excursion as a secondary phenomenon local to the Georgina Basin (details in the supplementary information, Fig. S1). That said, local features are observed in the $\delta^{238}\text{U}$ profile. One of the lightest natural isotope compositions ever measured is found midsection, $\delta^{238}\text{U} = -0.71\text{‰}$ (WH1-39), resembling a $>0.4\text{‰}$ outlier from neighboring samples (>6 standard deviations). This sample has significantly higher U/Th ratio than the rest of the studied samples, suggesting it formed via a distinct pathway, e.g. precipitation as primary CAU with a $\delta^{238}\text{U}$ value closer to contemporaneous seawater or, perhaps, a $\delta^{238}\text{U}$ value even lower than seawater if residual U from secondary CAU formation was incorporated into the carbonate at this horizon (Table S1, Fig. S1). Therefore, we consider this point an outlier, and do not model it in our analysis.

Rapid fluctuations are observed in the $\delta^{238}\text{U}$ profile above the smooth negative U isotope excursion. The fluctuations indicate that isotope fractionation changes within the basin, during the removal pathway from seawater to sediment, and is therefore not representative of secular variations in global seawater chemistry. Two rapid negative shifts of similar constant magnitude (between -0.28‰ and -0.22‰) are comparable to the offset from modern seawater occurring in modern sulfidic carbonate sediments (Romaniello et al., 2013). The beginning of the rapid fluctuations coincides with a significant drop in the contents of carbonate-associated uranium (Fig S1; Table S1), suggesting these samples have not just been diluted with isotopically unfractionated primary CAU.

On the basis of these fluctuations, we infer that the local redox setting is changing after the smooth negative $\delta^{238}\text{U}$ excursion. U burial first commenced relatively fast in sulfate reducing sediments (at low pH, high HS^- levels) and subsequently continued at a slower rate in sulfide-free sediments at a higher oxidation potential (and higher pH), perhaps even under oxic conditions. Independent support for this scenario occurs in the Mt Whelan S isotope profiles, where the change to (fluctuating) lower $\delta^{34}\text{S}$ values coincides with the disappearance of S isotope fractionation signal ($\delta^{34}\text{S} = 0$, Fig. 3), implying pyrite formation in a sulfate depleted environment ($<0.2 \text{ mM SO}_4^{2-}$, Habicht et al., 2002).

4.1. Models for seawater C, S and U abundance and isotope evolution

The dynamic relationship between global ocean anoxia (its effect on global marine P availability) and atmospheric oxygenation can be revealed if we can define the timing and duration of the expansion of O_2 sources (promoting increased organic carbon and pyrite burial) relative to the anoxic SPICE event (promoting reduced U burial). The onset of the U isotope excursion at the beginning of the positive $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursions suggests anoxia and euxinia developed at the very beginning of the event, yet its short duration suggests euxinia waned prior to the decline in organic carbon and pyrite burial.

There is a fundamental challenge in inferring absolute burial fluxes of redox-sensitive species from the isotope evolution of seawater. A stratigraphic, and thus temporal, displacement between C–S and U isotope peaks is not necessarily equivalent to a temporal offset between reduced C–S and U burial fluxes. Several factors could have influenced the isotope trajectories including 1) oceanic inventories, 2) responses of burial fluxes to changing inventories, and 3) isotope fractionation factors. In order to test these various scenarios, we established a simple mass balance model to simulate the dynamic evolution of the oceanic inventories (M) and isotopic compositions (δ) in response to a period of non-steady state behavior:

$$dM/dt = J_{\text{in}} - \sum J_k \quad (1)$$

$$d(\delta \cdot M)/dt = \delta_{\text{in}} J_{\text{in}} - \sum (\delta_{\text{SW}} - \Delta_k) J_k \quad (2)$$

Each element cycle responds to changes in the source (J_{in}) and sink fluxes (J_k) listed in Table 1. These sinks are subdivided into different areas, each with constant C/S/U ratios and isotope offsets (Δ_k) relative to seawater composition (δ_{SW}). In this way, an expanding sink

corresponds to an areal expansion of this setting, affecting all three cycles simultaneously (Table 1 and Supplementary information). We first assume that the global sinks carry constant isotope offsets from seawater, and that these offsets do not change over the course of the burial event, and then we explore inventory-dependent isotope fractionation factors afterwards.

The SPICE burial episode was modelled as a perturbation to the Cambrian ocean state, applying enhanced burial fluxes in euxinic settings for 1–3 Myrs (equations in supplementary information). Initially the C, S and U sources and sinks were balanced at modern-day values (Table 1, Table S2). Inventories and fluxes were then adjusted to plausible steady state Cambrian conditions (typically 10-fold greater euxinic areas) and the C/S ratio was lowered in all reducing sinks relative to modern values (from 2.8 to 1.0 by mass) consistent with early Paleozoic values and greater burial in euxinic settings (Table S4; Berner and Raiswell, 1983). As today, the reductive U removal process should have operated in estuarine settings, oxygen minimum zones and euxinic settings. To maintain realistic export rates from the ocean, burial fluxes (J) were assumed to scale with oceanic inventories (M) as $J \sim M^a$ (each element cycle is allowed to respond differently, i.e. a_C , a_S , a_U).

Various distinctive burial scenarios were modelled in an attempt to simultaneously fit all isotope trajectories across the SPICE event (Table S2). We defined twelve criteria related to the magnitude, timing and shape of the observed isotope excursions (plus three steady state criteria based on their baseline values): (1–2) The $\delta^{238}\text{U}$ excursion peaks before $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ peak and (3) the $\delta^{34}\text{S}$ excursion peaks before $\delta^{13}\text{C}$. (4–5) The $\delta^{238}\text{U}$ excursion terminates near the peak of the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursions. (6–8) The amplitudes of the isotope excursions were +4‰, +20‰ and −0.18‰ for $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ and $\delta^{238}\text{U}$, respectively. (9–10) The characteristic decay time scales of the isotope profiles $t = \text{offset}/(d\delta/dt)$ were $t_C/t_U = 1$, $t_S/t_U = 1$ (see supplementary information). And, (11–12) the magnitude of S isotope offset between sulfate and pyrite in the Georgina Basin, $^{34}\text{S}_{\text{local}}$, declined from −35‰ at the onset to 0‰ at the termination of the $\delta^{238}\text{U}$ excursion.

Criteria 11–12 constrain the sulfate level in the Georgina Basin sediments, where pyrite precipitated, as lower than in surface seawater. Nevertheless, we suggest the systematic ^{34}S decline correlates with the rate at which sulfate is drawn down from seawater. To explore the effect of sulfate decline in the context of the other isotope profiles, we assume that sulfate available for sulfate reduction is a constant ratio,

$R_{\text{SW}/\text{sed}} = [\text{SO}_4^{2-}]_{\text{seawater}} / [\text{SO}_4^{2-}]_{\text{sediment}}$, of the sulfate concentrations in the open ocean. Muted S isotope fractionation occurs at sedimentary sulfate levels below 1 mM (Canfield et al., 2010) and no S isotope fractionation is expressed below 0.2 mM (Habicht et al., 2002). We adopt either a linear or a logarithmic relationship (Eqs. (S6) and (S7)); for example,

$$\Delta_{\text{local}}^{34} = 50 \cdot \log \left(\left[\text{SO}_4^{2-} \text{ (mM)} \right]_{\text{seawater}} / R_{\text{SW}/\text{sed}} \right) + 35\% \quad (3)$$

Eq. (3) describes the isotope offset recorded locally in the Georgina Basin, and not the offset of the global reducing S sinks.

Modern euxinic settings are small sinks for organic C (C_{org} , 1%) and pyrite S (S_{py} , 3%) compared to U (~20%) (Table 1). Extrapolating this to the SPICE event implies that expanding euxinia would have a relatively large effect on the U isotope budget relative to that on seawater C and S isotope budgets (Fig. 4). To make a substantial impact on the $\delta^{13}C$ and $\delta^{34}S$ compositions of seawater, the average sediment buried (anywhere) during the SPICE anomaly would have had significantly higher C_{org}/U and S_{py}/U ratios than occur in modern euxinic sediments ($C_{org}/U = 0.7\text{--}2.0$ wt%/ppm, McManus et al., 2006). For comparison, the contemporaneous euxinic Alum shale likely originated with $C_{org}/U = 0.9\text{--}1.3$ wt%/ppm before organic C was lost during thermal maturation, i.e. today $C_{org}/U = 0.2\text{--}0.3$ wt%/ppm (Schovsbo, 2002), vitrinite reflectance is $R\% = 2.50$ (Burchardt et al., 1986) suggesting ~4.5 times higher C_{org}/U during deposition relative to today (Raiswell and Berner, 1987). Thus, the model requirement for higher C_{org}/U in average marine sediments at the time suggests that the majority of organic carbon and pyrite sulfur burial occurred elsewhere in the Cambrian ocean, i.e. not spatially associated with U removal. Therefore, the predominant C_{org} and S_{py} sink in shallow settings (deltas) was also amplified in our model to simultaneously fit the three isotope curves (Fig. 4).

4.2. Two distinct burial stages within the SPICE event

The model runs show that the U isotope excursion tightly tracks the expansion of the euxinic sink (Figs. 4–6). The marine C and S inventories were larger and responded more slowly than U, producing extended excursions and some degree of displacement between isotope peaks (Fig. 5). This is represented in a generic way by the relationship between the perturbed (additional) flux in reducing settings (J') and the corresponding isotope excursion (δ') relative to steady state that can be derived for each element (see supplementary information):

$$\delta' = 1/J_{input} \left[\Delta_{perturbed, sink} J' - M \frac{d(\delta')}{dt} \right] \quad (4)$$

The second term determines the magnitude of the displacement between δ' and J' . Importantly, even a one-stage burial scenario (all three J 's co-vary) causes isotope peak displacement if the reservoir size is large relative to the flux causing the perturbation in the equations for C and S relative to that of U.

All simple one-stage burial scenarios with various sizes of inventories have a side effect – the characteristic decay time scale extends when larger C and S inventories compared to U are used to generate significant peak displacements. For example, if a single burial event was responsible for the pattern, we would expect the substantially larger C and S reservoirs to translate into a significantly longer decay time after the perturbation. Crucially, this contradicts the observed data, since the characteristic decay time scales derived from the $\delta^{13}C$ and $\delta^{34}S$ profiles are similar or only slightly higher than for U (see derivation and discussion in the supplementary information). The similar decay timescales observed in all three isotope profiles suggest that the more rapid loss of the $\delta^{238}U$ signal is not merely an artifact of this reservoir effect – but is rather a direct geochemical signal representing the early waning of euxinia.

The characteristic decay time depends on exactly how burial fluxes scale with inventory ($dM/dt \sim -J_{\text{anox}} \sim -M^a$). A weaker flux-inventory response for C and S both imply a rapid change of the isotope signal when the burial episode ends (producing steeper decay profile) and shift the C and S peaks back in time closer to the U peak. Thus, any attempt to produce a large reservoir effect with steep C and S decay profiles (matching U), will simultaneously decrease the C–U and S–U isotope peak displacements. The core conclusion of the modelling exercise is therefore that the combination of significant isotope peak displacement, and similar C–S decay time scales relative to U, suggests two distinct burial stages occurred within the SPICE event.

This conclusion is further substantiated by the muted S isotope fractionations (near zero ^{34}S) recorded in the Georgina section after the U isotope excursion. Muted S isotope fractionations would not be observed if a single C–S–U burial event had terminated, and oceans were refilling with sulfate, as oceanic S inputs exceeded S outputs.

A two-stage model can fit all data (Fig. 6). For example, significant C–U and S–U isotope peak displacements would occur if extensive burial of C and S continued in deltas after the anoxic burial episode. The rapid C–S decay profiles would appear if there was a weaker response between C_{org} burial – and S_{py} burial to declining DIC and sulfate inventory relative to the equivalent response of the U reservoir ($a_C < a_U$ and $a_S < a_U$; Figs. S2–S3). Finally, the C isotope excursion would peak after the S isotope curve and produce the C–S isotope peak displacement if the marine DIC pool was relatively large and the sulfate inventory relatively small, as might be expected in a burial event leading to a sulfate crisis. Thus, we suggest that the SPICE event was not a simple one-stage anoxic event, but actually associated with a two-stage scenario involving changing seawater chemistry.

4.3. Alternative scenarios for the second stage of the SPICE event

We elaborate on three possible scenarios that fit both the isotope peak displacement and the similarity in decay time: (1) expanded anoxia continuing in a quantitatively U-depleted ocean, (2) ocean oxygenation occurred after the initial euxinia that caused the $\delta^{238}\text{U}$ excursion, but extensive organic carbon/pyrite burial continued, and (3) anoxic and non-euxinic conditions with low sulfate suppressing U removal (rather than U depletion).

1) Quantitative uranium drawdown—We first consider the consequences of exhausting of the marine U reservoir after ~1 million years of U burial in expanded anoxic marine zones. This would not lead to a global $\delta^{238}\text{U}$ decline, but might have produced a heterogeneous U distribution in the ocean with $\delta^{238}\text{U}$ in the Georgina Basin offset from global average. Evidence contradicts this scenario however; U removal rates (as evidence by U and U/Th enrichments) were never low during this period in the euxinic Alum Basin and the enrichments appears decoupled from the U isotope excursion (Fig. 7). The dramatic increase of the U levels in the oceans after the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursion also rules out quantitative U drawdown. In rejecting this scenario we can discount (for example), simple one-stage scenarios with enhanced burial in oxic high primary productivity zone settings (e.g. OMZ's) since this would also cause massive marine U depletion in concert with the U isotope excursion (Fig. S2).

2) Ocean oxygenation with extensive organic carbon/pyrite burial—The oxygenated scenario represents the case where ocean anoxia retreated at the peak of the $\delta^{13}\text{C}$ excursion, (presumably when atmospheric pO_2 had increased enough to oxygenate the increasingly P-rich oceans). Subsequent more efficient P removal in more oxygenated oceans would then have tended to remove P, raising the question of what supported the continued organic carbon and pyrite burial. An external nutrient supply (i.e. enhanced continental weathering) is one possibility if overall high rates of primary production were indeed sustained after this episode of expanded anoxia. Our model result, showing a simultaneous expansion of the deltaic sink, is directly consistent with enhanced erosion sourcing more sediment to the oceans during the SPICE episode. This could also imply an increase in chemical weathering and nutrient supply to the ocean (Fig. 1), and/or an increased supply of micro-sites for organic carbon preservation on the surface of clay particles (Hedges and Keil, 1995).

If oxygenation is the cause of the relaxation of the uranium isotopic signal ($\delta^{238}\text{U}$ return to baseline value; end of first stage), then the end of the second stage when seawater $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ returned to their baseline values is linked to a decline in chemical weathering and/or continental erosion. We argue that this premise should be tested with independent weathering proxies for oceanic nutrient input from land.

3) Anoxic, non-euxinic second stage—In the third scenario, organic carbon and pyrite burial were sustained via P regeneration from expanded anoxic zones similar to models for Cretaceous anoxic events (Handoh and Lenton, 2003), but with an important distinction that during the second stage, low oceanic sulfate would have limited sulfide availability and decreased U removal and/or perhaps U isotope fractionation in anoxic marine zones (Fig. S4). This implies a model for the Cambrian ocean that fundamentally differs from the redox composition of the modern ocean and more closely resembles a temporary reversion to ferruginous ocean conditions outlined for the Proterozoic ocean (Canfield et al., 2008; Planavsky et al., 2011; Poulton and Canfield, 2011).

If a shift from widespread euxinia to ferruginous ocean conditions occurred during the second stage, then the anoxic settings might have continued to support P recycling (and increasing seawater $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$). This requires that efficient P recycling from anoxic zones continues to operate under ferruginous anoxic waters, which is arguably problematic in light of evidence that P scavenging by mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ minerals such as ‘green rust’ is extremely efficient in anoxic, non-sulfidic “ferruginous” settings (Zegeye et al., 2012).

Moreover, the scenario of a euxinic to ferruginous transition only fits the data if the U isotope composition in seawater tracks euxinic ocean conditions and not anoxia in general (something that seems probable, but is not yet certain). It implies that U burial rates in anoxic settings (and/or concomitant isotope fractionation) decrease in the absence of hydrogen sulfide and/or sulfate reducers. Consistently with this, evidence from modern environments shows that the availability of sulfide and/or sulfate reducers increase the reduction potential and may accelerate U removal rates in sediments (Hua and Deng, 2008; Hua et al., 2006; Klinkhammer and Palmer, 1991; Morford et al., 2009; Shaw et al., 1994). Also, isotope fractionations will be muted if the zone of U removal is pushed further into the

sediment. Still, the role of sulfide on removal rates and isotopic signature necessitate further laboratory and field studies.

In reality, the SPICE episode may represent a mix of these end member scenarios. We envision that enhanced weathering and nutrient discharge to the ocean may have paced the event, while the anoxia-dependent nutrient feedback increased P recycling during at least the first stage. High organic carbon and pyrite sulfur burial during the second stage of the SPICE episode could reflect a combination of ongoing P recycling from organic matter in anoxic, ferruginous zones, enhanced P supply from land, and/or increased supply of mineral micro-sites suitable for preserving organic carbon. Although the C–S–U isotope comparison cannot definitively elucidate whether anoxia exerted an overriding control on global primary production and atmospheric pO₂ levels through the SPICE event, it can constrain plausible geochemical conditions at the time that are consistent with this hypothesis.

5. Implications for understanding the paleontological record

The U isotope data and the combined carbon–sulfur–uranium model show two interesting correlations to the paleontological record. First, the peak of the $\delta^{238}\text{U}$ excursion coincides with modelled peak euxinia that occurs at the rising limb of the $\delta^{13}\text{C}$ excursion. This means, peak euxinia occurs close to the trilobite extinction horizon, suggesting a causal relationship between environmental crisis and trilobite evolution.

Secondly, enhanced marine nutrient availability during the SPICE event would have fuelled phytoplankton populations in diverse marine habitats and, perhaps, enhanced phytoplankton diversity and the diversity of heterotrophic organisms grazing on them. Although this scenario arguably played an important role in the Great Ordovician Biodiversification event (GOBE), there is a significant time delay that needs to be addressed between the SPICE event and phytoplankton diversification in the Middle Ordovician, 30–40 million years later (Servais et al., 2008).

A massive, prolonged increase in atmospheric pO₂ after the SPICE event has been suggested as trigger for GOBE. This is claimed to have expanded animal-habitats in partly anoxic oceans and, perhaps, changed micronutrient levels (e.g. Cd, Mo) in favour of more modern-type phytoplankton taxa (Saltzman et al., 2011). The $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ excursions have been used to calculate a rise of atmospheric pO₂ from 10 to 20 atm% up to 10–30 My after the event. However, the initial pO₂ level associated with this calculation is chosen at a rather high level (Berner, 2009), and could just as well be only 2 atm% (Bergman et al., 2004; Dahl et al., 2010). Further, the predicted magnitude of pO₂ increase depends entirely on unconstrained parameter values; specifically the organic carbon fraction of total C weathering, f_{in} , ranging from 0.10 to 0.34 (Derry, 2013). In contrast, the model presented in this study (with no feedbacks) can reproduce the isotope excursions with only <0.1 atm% pO₂ increase from enhanced organic carbon and pyrite burial (details in SI), calling in to question any link with subsequent animal evolution.

More broadly, determining the links between environmental and biological evolution necessitates that we establish biogeochemical models that simultaneously predict nutrient availability, atmospheric pO₂ and ocean anoxia at this time. In these efforts, U isotopes can

provide important constraints on the temporal details of evolving anoxia/euxinia and concomitant marine nutrient recycling and show how this important event may have been more biogeochemically subtle than previously thought.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

A systems diagram showing the factors involved in the regulation of oceanic anoxia in the C, P and O₂ cycles. The positive feedback between anoxia and P availability is shown in blue boxes (Van Cappellen and Ingall, 1996). Triggers for ocean anoxia are highlighted and discussed for the Cambrian SPICE event in Section 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2.

Simplified view of the sources and sinks in the modern oceanic U cycle. Type settings and examples are listed in Table 1. The area of each square box is proportional to the magnitude of that flux, where dashed lines indicate uncertainties (after Dunk et al., 2002).

The $^{238}\text{U}/^{235}\text{U}$ ratio is traditionally reported in the $\delta^{238}\text{U}$ notation ratios as parts per 1000 relative to the international reference standard CRM-145. All currently available literature data from terrestrial samples and the reference standards to which they are normalized are summarized in Table S6. The U isotope composition of each reservoir is shown as average

$\delta^{238}\text{U}$ values ($\pm 2\text{SE}$) used to constrain the models presented in Section 4. Modern seawater displays $\delta^{238}\text{U} = -0.44 \pm 0.03\text{‰}$ (2SE , $n = 12$) (Stirling et al., 2007; Weyer et al., 2008). Danube river displays $\delta^{238}\text{U} = -0.22 \pm 0.02\text{‰}$, $n = 1$, which is higher than volcanic rocks ($\delta^{238}\text{U} = -0.42 \pm 0.04\text{‰}$, $n = 21$) and granitic crustal rocks at $-0.30 \pm 0.03\text{‰}$ ($n = 27$) (Stirling et al., 2007, 2005; Telus et al., 2012; Weyer et al., 2008). Uranium removal in more reducing marine environments also induces the largest net U isotope fractionation. Modern euxinic sediments with $\delta^{238}\text{U} = 0.04 \pm 0.05\text{‰}$ are strongly fractionated with a $+0.50\text{‰}$ offset relative to seawater (Montoya-Pino et al., 2010; Weyer et al., 2008). Reducing organic-rich siliciclastic sediments beneath the upwelling zone offshore of Peru display authigenic U enrichments with $\delta^{238}\text{U} = -0.28 \pm 0.07\text{‰}$ producing a range of isotopic offsets from modern seawater from $+0.04\text{‰}$ to $+0.29\text{‰}$ (Weyer et al., 2008). Similarly, authigenic U accumulation in anoxic and sulfidic pore fluids of carbonates from Bahamas display enrichments of isotopically heavy U within reducing pore fluids. The bulk carbonates display $\delta^{238}\text{U} = -0.13 \pm 0.04\text{‰}$ (2SE , $n = 23$, four sites) corresponding to a $+0.31 \pm 0.05\text{‰}$ offset relative to overlying seawater (Romaniello et al., 2013). In fully oxygenated settings, modern aragonitic corals, molluscs, calcifying green algae, and ooids display no isotope fractionation relative to seawater, $\delta^{238}\text{U} = -0.43 \pm 0.04\text{‰}$ (Romaniello et al., 2013; Stirling et al., 2007; Weyer et al., 2008). U removal associated with hydrothermal circulation through the basaltic ocean crust accounts for $\sim 10\%$ of total oceanic U removal (Dunk et al., 2002). However, the isotope fractionation associated with U incorporation into altered basalts from percolating seawater has not been studied. However, the relative importance of basalts on overall oceanic U removal appears to be small. Thus, basaltic U removal should contribute little to the U isotope composition of seawater.

Fig. 3. Chemostratigraphy of the ~500 Ma SPICE event recorded in Whelan no. 1 drill core, Queensland, Australia, showing the $\delta^{13}\text{C}$ of carbonates and organic matter, $\delta^{34}\text{S}$ of carbonate associates sulfate (CAS) and pyrite (PY), $\delta^{238}\text{U}$ of carbonate and sulfur isotope fractionation $\Delta^{34}\text{S} = \delta^{34}_{\text{CAS}} - \delta^{34}_{\text{PY}}$.

Fig. 4.

The modelled evolution of $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\delta^{238}\text{U}$, and ^{34}S in the Late Cambrian ocean as a consequence of a 1 My long period with up to 6-fold higher burial rate (relative to pre-event conditions) in anoxic settings (blue), 2-fold burial in deltaic sediments (red), and the combination of both (black). The timing of the forcing functions (dashed curve) is plotted to show the relative response time. Sulfate levels are assumed to be 1/3 of open ocean concentration inside Mt. Whelan sediments, where pyrite precipitates. Other model details are summarised in Table S4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5.

The modelled evolution of $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, and $\delta^{34}\text{S}$ in the Late Cambrian ocean are shown with various oceanic inventories. This illustrates the ‘reservoir effect’ and how it both influences the magnitude, the relative timing of the isotope peaks, and the rate of decay. The timing of the forcing functions (dashed curve) is plotted to show the relative response time. Note that a larger inventory both delays the peak and causes a slower decay of the isotopic offset after the event. The ratio between sulfate in Whelan sediments and the open ocean is chosen to show plausible local $\delta^{34}\text{S}$ trends, while average global S isotope fractionation is still fixed (35‰). Other model details are listed in Table S4.

Fig. 6.

The modelled evolution of $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\delta^{238}\text{U}$ and ^{34}S in the Late Cambrian ocean for a two-stage scenario that fits all constraints, including the amplitudes of the excursions, the relative timing of the peaks, and characteristic decay time (shape of isotope curves). This model assumes a large DIC pool ($16 \times$ modern), small sulfate pool ($0.1 \times$ modern) and slow response between C and S burial fluxes and inventories. Model details are listed in Table S4.

Fig. 7.

Comparison of data from the Whelan drill core to the euxinic Alum shale formation (Andrarum-3 drill core, Sweden). The correlation is based on assuming synchronous $\delta^{13}\text{C}$ isotope change in seawater controls variation of organic matter in the Alum shale (grey circles) and in the Whelan carbonates (pink). Geochemical data ($\delta^{34}\text{S}$, TOC, DOP, Fe/Al, U and U/Th) from the Alum shale (Gill et al., 2011) is shown together with the Phanerozoic average U content in anoxic shales (dashed line; Partin et al., 2013). The estimated sea level drop during the SPICE event is at most a few tens of meters (Saltzman et al., 2004). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Modern marine budgets for carbon, sulfur and uranium. Reducing and oxidizing sinks are shown in red and blue, respectively. Carbon and sulfur isotope fractionation occurs in all reducing environments with relatively small difference in magnitude. Fast-depositing sediments control reduced C and S burial, whereas reduced U burial principally is maintained in anoxic settings. The S burial rates in deltaic sediments may be overestimated by a factor 2-3, due to higher C/S in sediments from the Amazon delta (Aller and Blair, 1996). Nevertheless, the impact of the anoxic sink is significantly larger on the U cycle than on the C and S cycles. (For interpretation of the references to color in this table legend, the reader is referred to the web version of this article.)

Modern ocean budget		Ox. state	Dominant phase	C			S			U			
Residence time in modern ocean [ky]				100 ky	2000 ky	500 ky	20000 ky	500 ky	20000 ky	500 ky			
Source													
Sink setting	Examples	Oxidised	HCO ₃ ⁻ , SO ₄ ²⁻ , UO ₂ (CO ₃) ₂ ⁻	C sink [%F _{Source}]			S sink [%F _{Source}]			U sink [%F _{Source}]			
				2.6 × 10 ¹³ mol/y	1.8 × 10 ¹² mol/y	5.6 × 10 ⁷ mol/y	1.8 × 10 ¹² mol/y	5.6 × 10 ⁷ mol/y	1.8 × 10 ¹² mol/y	5.6 × 10 ⁷ mol/y			
Total oceanic input	rivers, ground water, aeolian	Oxidised		19	54	19							
Deltaic sediments	Amazon Shelf	Reduced	org C, FeS ₂ org U ^{IV}										
High productivity, anoxic	Walvis Bay, Black Sea	Reduced	org C, FeS ₂ org U ^{IV}	1.1	3.3	20						0.50	
High productivity areas, oxic waters	California Borderlands Peru margin	Reduced	org C, FeS ₂ org U ^{IV}	0.2	0.3	26						0.19	
Low productivity areas	Pelagic sediments 788 seafloor	Reduced	org C	0.9	0	0						-	
Carbonates, – with anoxic pore fluids	Banks + embayments Carbonate shelves Slopes and deep sea	Oxidised C, S Reduced U Reduced C	(carbonate C, CAS org C, U(VI))	20 ^b 1 ^a	1.1 ^b	5						0.27	
Carbonates, – formed oxic	Coral reefs, Halimeda bioherms, + slopes imported	Oxidized	(Ca/Mg/CO ₃ , CAS, uranylcarbonate)	58 ^b	2 ^b	18						0.0	
Evaporites (Oxidised S)	Spain	Oxidized	anhydrite, gypsum	0	40	0						-	
Basaltic alteration (U)	Mid-ocean ridge	Oxidized	U ^{VI} ?	0	0	10						(?)	
Ferromanganese crusts	Abyssal ocean	Oxidized	Mn-oxide bound U ^{VI}	0	0	2						-0.17	
Reference				R1	R1	R2						R3	

R1: Berner (1982).

R2: Dunk et al. (2002).

R3: Romaniello (2013), (Weyer et al., 2008).

^a Reduced carbon in anoxic carbonates accounts for additional 1% F_{out} (R1).

^b The relative proportion of C, S and U in oxic-formed carbonates (coral reefs, halimeda bioherms, and slopes imported) versus anoxic-formed carbonates (banks, embayments, shelves, slopes and deep sea) is 74:26, 68:32 and 77:23, respectively, using the carbonate budget from Dunk et al. (2002) and assuming a carbonate-associated sulfate (CAS) content of 1000 ppm (median value of Key Largo limestone, Gill et al., 2008). The relative proportion of reducing and oxidizing C (f_{org} = 0.14) and S sinks (f_{py} = 0.17) are taken from Berner (1982), because these values settle the marine C and S isotope budgets in a steady state near modern value. However, the total marine C input and export (i.e. 2.6×10^{13} mol/y, Gill et al., 2011) is lower than stated in Berner (1982), due to an overestimate of the global carbonate accumulation rate (Berner uses 62×10^{12} molCyr⁻¹ = 740 MtCyr⁻¹), whereas more recent values are 32×10^{12} molCyr⁻¹ (Milliman, 1993) and 24×10^{12} molCyr⁻¹ (Dunk et al., 2002; reducing burial into slopes and deep sea from 15×10^{12} to 7×10^{12} mol C yr⁻¹). The ocean would settle to a steady state with $\delta^{13}\text{C} > 1$ and $J_{\text{org}} = 0.32 \cdot \Sigma J_{\text{out}}$, if the low carbonate fluxes were adopted without changing the organic C export rates.

^{238}U isotope fractionation is given in terms of $\delta^{238}\text{U}_{\text{Seawater}} - \delta^{238}\text{U}_{\text{Sink}}$.

Table 2

Uranium isotope data obtained from the Mt. Whelan #1 drill core, Queensland, Australia. The standard error is calculated from the standard deviation of the n replicate analyses.

Sample name	Depth [m]	U in leach [ppm]	$\delta^{38/235}\text{U}_{\text{CRM145}}$	2SE	n
Carbonate fraction (mild HCl leach)					
WH1-4	31.4	0.13	-0.346	0.018	5
WH1-9	45.8	0.66	-0.423	0.034	5
WH1-11	52.0	0.69	-0.206	0.024	5
WH1-11 rep		0.50			
WH1-16	68.25	0.54	-0.482	0.029	5
WH1-16 rep	1.84				
WH1-20	81.5	1.12	-0.208	0.023	5
WH1-24	93.0	0.99	-0.235	0.027	5
WH1-29	108.7	0.68	-0.234	0.021	5
WH1-33	120.0	0.92	-0.314	0.024	5
WH1-35	126.3	2.73	-0.276	0.024	5
WH1-39	138.5	0.49	-0.758	0.028	5
WH1-39 replicate digest	138.5	1.15	-0.753	0.036	5
WH1-41B (clay-rich)	144.53	2.17	-0.323	0.048	5
WH1-42	148.2	0.79	-0.315	0.029	4
WH1-42 rep		0.71			
WH1-42 rep2		1.54			
WH1-47a	163.1	0.72	-0.390	0.025	4
WH1-55	188.3	0.86	-0.336	0.023	5
WH1-64	216.3	1.12	-0.272	0.025	5
WH1-70	235.5	1.01	-0.353	0.023	5
WH1-74	246.81	1.97	-0.198	0.019	5
WH1-86	283.42	2.77	-0.278	0.019	5
WH1-98	320.77	2.28	-0.300	0.038	5
WH1-98rep	1.90				
Clay fraction (residual)	U in residue [ppm]				
WH1-9_clay	45.8	2.085	-0.327	0.030	5
WH1-11_clay	52.0	1.680	-0.685	0.060	5
WH1-16_clay	68.25	0.456	-0.402	0.020	3
WH1-24_clay	93	0.802	-0.319	0.053	5
WH1-47a_clay	163.065	1.364	-0.301	0.043	6
Bulk rock (total digest)	Bulk U [ppm]				
WH1-20 (spiked after purification)	81.5	3.33	-0.288	0.016	4
WH1-29 (spiked before purification)	108.7	2.65	-0.251	0.024	5
WH1-29 (spiked after purification)	108.7	2.65	-0.281	0.036	5
International reference standard					
BCR-2			-0.290	0.050	5
BCR-2, replicate digest			-0.271	0.017	5