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## Reorganisation of Earth's biogeochemical cycles briefly oxygenated the oceans 520 Myr ago

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### Abstract

The Phanerozoic radiation of bilaterian animals has been linked to oxygenation of Earth's oceans, due to the oxygen demand of the evolving animal ecosystems. However, how early animals may have regulated Earth's surface oxygen budget via self-stabilising feedbacks is poorly understood. Here, we report parallel positive uranium, carbon, and sulphur isotope excursions from carbonate successions in Siberia that document a brief global oxygenation episode 521–520 Myr ago, at the onset of diversification of larger arthropods known from the fossil record. Our data and model indicate that an abrupt increase in the sinking rate of marine organic matter expanded the oxygenated zone in the oceans and that reducing conditions returned  $1.3 \pm 0.8$  Myr after the onset of this transient oxygenation episode, necessitating a strong negative feedback to the increasing levels of oxygen. We speculate that larger zooplankton could have sourced both oxygen and food to the seafloor, fueling bioturbation over wider areas and, thereby, stabilising O<sub>2</sub>-rich habitats in the oceans. Thus, this reorganisation exemplifies how animal ecosystems might have influenced oxygen availability in Earth's surface environment soon after their establishment.

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### Letter

In contrast to many geochemical proxies that evaluate local ancient marine redox including iron speciation and trace metal (Mo, U, V) enrichments, the uranium isotope composition ( $\delta^{238}\text{U}$ , the per mille deviation of the  $^{238}\text{U}/^{235}\text{U}$  ratio relative to CRM 145 standard) of seawater can be used to evaluate ocean oxygenation at

a globally integrated scale. This is possible due to the long residence time and uniform  $\delta^{238}\text{U}$  of uranium in the modern ocean and predicted for the Cambrian ocean (Weyer *et al.*, 2008; Dahl *et al.*, 2014; Tissot and Dauphas, 2015). The  $\delta^{238}\text{U}$  proxy has been utilised to track past global ocean redox during three known oceanic anoxic events (Montoya-Pino *et al.*, 2010; Brennecke *et al.*, 2011; Dahl *et al.*, 2014; Elrick *et al.*, 2016; Lau *et al.*, 2016), where anoxic water masses expanded over larger areas of the seafloor and caused negative  $\delta^{238}\text{U}$  excursions. Here, we use uranium isotopes to identify a transient global oxygenation episode during the radiation of animals in the Cambrian.

Our new  $\delta^{238}\text{U}$  data of carbonate-associated uranium comes from limestones collected from the Siberian Platform across the provisional Cambrian Stage 2–3 boundary (~521 to 520 million years ago) (Fig. 1), when animals that shed their exoskeleton (ecdysozoa) began to diversify (Malooof *et al.*, 2010; Kouchinsky *et al.*, 2012). A perturbation in the marine carbon cycle is expressed at this time as a large positive carbon isotope excursion recognised globally and in all studied sections; geological maps and stratigraphic sections are shown in Figures S-1 and S-2 (Malooof *et al.*, 2010). This excursion serves as an important stratigraphic marker, although little is known about the biogeochemical significance of the event. The end-Stage 2 samples carry low  $\delta^{238}\text{U}$  values of  $-0.65$  ‰, increasing stratigraphically to a value of  $-0.45$  ‰ that approaches the modern oxygenated oceans,  $-0.39 \pm 0.01$  ‰ (Tissot and Dauphas, 2015), before again returning in two steps to  $-0.7$  ‰. This positive  $\delta^{238}\text{U}$  excursion of  $+0.25$  ‰ coincides with the positive carbon isotope excursion, suggesting that they are both linked to the changes in global seawater chemistry. The samples display no systematic correlation between the  $\delta^{238}\text{U}$  excursion and indicators of dolomitisation (Mg/Ca, dolomite), pore water redox conditions (total organic carbon content), diagenetic alteration (Mn/Sr,  $\delta^{18}\text{O}$ ) detrital input (Al/Ca, clay content) and primary carbonate mineralogy (Sr/Ca; see Supplementary Information S2) that might produce such a positive  $\delta^{238}\text{U}$  excursion, offset from contemporaneous seawater. That said, our samples consist of (abiotic) micrite with (biotic) shells made of secondary calcite (Fig. S-3). The difference between abiotic and biotic precipitation of calcite  $\delta^{238}\text{U}$  is predicted to induce a  $-0.1$  ‰ offset from seawater (Chen *et al.*, 2016). As we cannot determine the ratio of U derived from abiotic to biotic sources, we conclude that at this level of confidence, an overall positive  $\delta^{238}\text{U}$  trend is observed in the stratigraphy that we ascribe to secular changes of open marine  $\delta^{238}\text{U}$  in early Cambrian seawater. We note that our data set is limited to only one section and predict the same trend can be observed in other marine deposits with authigenic U enrichments.

The positive excursion of seawater  $\delta^{238}\text{U}$  represents a global oxygenation period in the oceans that dramatically decreased the fraction ( $f_U$ ) of total U burial occurring in anoxic marine settings. A simple isotope mass balance calculation constrains  $f_U$  from the  $\delta^{238}\text{U}$  of seawater ( $\delta_{\text{SW}}$ ) (see derivation in Supplementary Information S4). This calculation assumes an isotopically constant U input from rivers and a constant isotope fractionation between seawater and the U sinks. The modern ocean is at steady state with  $\delta^{238}\text{U}$  at  $-0.39 \pm 0.01$  ‰ and estimates

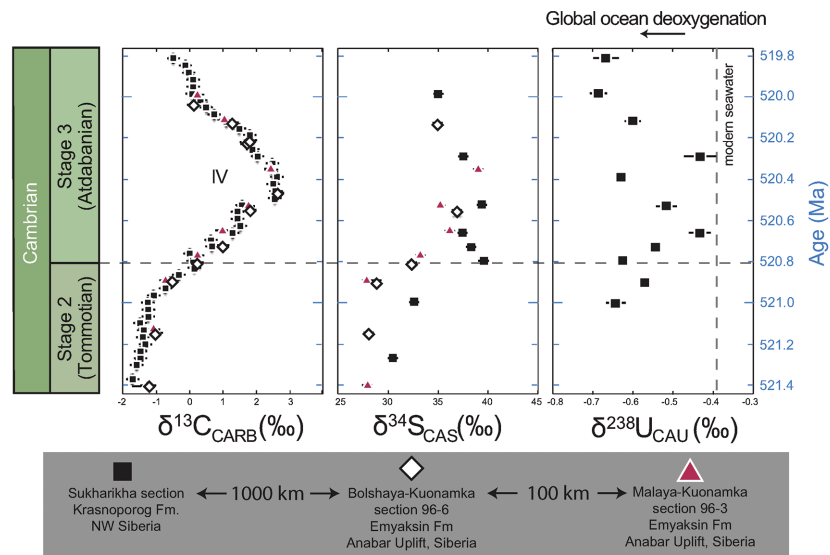
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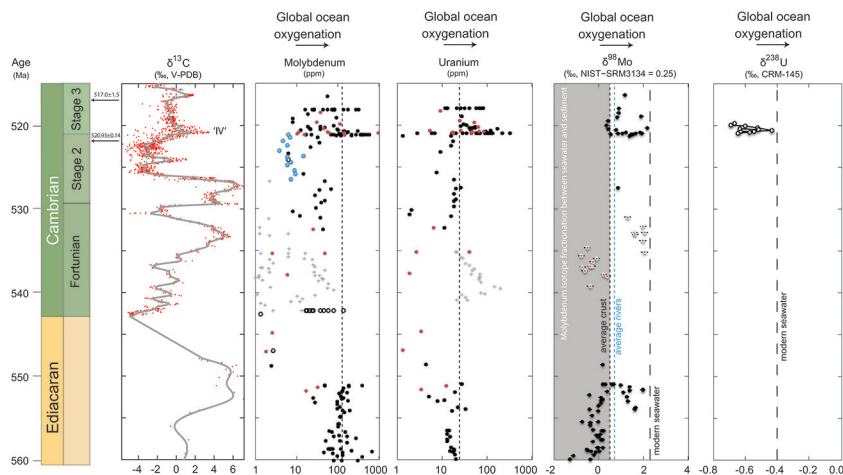
**Figure 1** Isotope data from three carbonate successions straddling the Cambrian Stage 2–3 boundary (Cambrian Stage 2–3) in Siberia. Carbon isotope data from carbonate ( $\delta^{13}\text{C}_{\text{CARB}}$ ) is taken from Kouchinsky *et al.* (2007). Sulphur and uranium isotope data are from carbonate-associated sulphate ( $\delta^{34}\text{S}_{\text{CAS}}$ ) and uranium ( $\delta^{238}\text{U}_{\text{CAU}}$ ), respectively. Age assignments derived from correlations to the carbon isotope stratigraphy and the age model of Maloof *et al.* (2010).

for the average oceanic input range from  $-0.30$  ‰ to  $-0.27$  ‰ (Tissot and Dauphas, 2015; Noordmann *et al.*, 2016). If the anoxic proportion of global U burial ( $f_U$ ) today is 12–25 % (Morford and Emerson, 1999; Dunk *et al.*, 2002; Noordmann *et al.*, 2016), and anoxic settings impart a  $+0.5 \pm 0.1$  ‰ net isotope offset from overlying seawater, this implies that the average isotope fractionation between seawater and all other oxic U sinks ( $\Delta_{\text{OTHER}}$ ) is  $-0.02 \pm 0.05$  ‰. Given this formulation, we calculate that  $68 \pm 18$  % of marine U burial before the Stage 2–3 event occurred in anoxic parts of the oceans when  $\delta^{238}\text{U}$  of seawater was  $-0.65$  ‰. This scenario compares to the ocean state during the anoxic expansion associated with the end-Permian extinction (Brenneka *et al.*, 2011). Further, the anoxic U burial fraction declined to  $29 \pm 12$  % at the peak of the event and then afterward returned to a more reducing ocean state with  $78 \pm 20$  % anoxic U burial (Fig. S-2). The stated uncertainties for  $f_U$  in the Cambrian are propagated errors from  $\Delta_{\text{OTHER}}$ ,  $\Delta_{\text{ANOX}}$ , and  $\delta_{\text{IN}}$  reflecting a range of plausible parameterisations of the marine U cycle (see sensitivity analysis in Supplementary Information S4 for details). These data consistently require the Cambrian Stage 2–3 event to have occurred when the oceans were far more reducing than today, culminating at an oxygenation state similar to the modern ocean.

Existing palaeoredox studies also point to ocean oxygenation during the Early Cambrian (Fig. 2). Specifically, the molybdenum isotope ( $\delta^{98}\text{Mo}$ ) record from shales and phosphorites show several fluctuations recorded in  $\sim 560$  to  $520$  Myr old stratigraphic sections in China (Wille *et al.*, 2008; Wen *et al.*, 2011; Xu *et al.*, 2012; Chen *et al.*, 2015; Kendall *et al.*, 2015; Wen *et al.*, 2015). The last positive  $\delta^{98}\text{Mo}$  excursion is broadly correlated to the first appearance of trilobites in China, strong Mo enrichments and with the oxygenation event reported here (Dahl *et al.*, 2010; Xu *et al.*, 2012; Chen *et al.*, 2015; Wen *et al.*, 2015; Jin *et al.*, 2016). The coincident positive  $\delta^{98}\text{Mo}$  and  $\delta^{238}\text{U}$  excursions point to a widespread oxygenation episode in the earliest Cambrian Stage 3 oceans where  $\text{O}_2$ -rich waters expanded and affected the Mo and U isotope composition of seawater as the overall burial fluxes of Mo and U into anoxic and euxinic settings decreased. We can predict the  $\delta^{98}\text{Mo}$  trajectory of seawater from the oceanic  $\delta^{238}\text{U}$  trajectory, if we assume the anoxic burial proportions of total Mo and U burial ( $f_{\text{Mo}}$ ,  $f_U$ ) are correlated. We adopt a power law relationship  $f_{\text{Mo}} = f_U^\alpha$  that satisfies  $f_{\text{Mo}} = f_U = 1$  during extreme anoxia and  $f_{\text{Mo}} = f_U = 0$  for extreme oxa. Using the modern ocean state as a calibration point, we find that  $\alpha = 1.34 \pm 0.38$  (see Supplementary Information for details). Based on this relationship, average seawater  $\delta^{98}\text{Mo}$  should have increased from 1.40 ‰ in the Cambrian Stage 2 to a peak at 2.0 ‰ before returning to 1.10 ‰ during the  $\delta^{238}\text{U}$  excursion. This prediction is in good agreement with the maximum values observed in the  $\delta^{98}\text{Mo}$  record during this time interval (Lehmann *et al.*, 2007; Chen *et al.*, 2015; Wen *et al.*, 2015) (Fig. 2). Collectively, the Mo and U isotopes indicate a transient, rather than a persistent change in ocean oxygenation at the beginning of Stage 3. This implies that earlier positive  $\delta^{98}\text{Mo}$  excursions ( $\sim 2$  ‰) in Terreneuvian phosphorite deposits (Wen *et al.*, 2011), and perhaps in the latest Ediacaran (Kendall *et al.*, 2015), represent episodic events rather than persistent ocean oxygenation. Similarly, detailed studies of the bottom water redox conditions in the Nanhua Basin, South China, suggest that oxygenated waters also invaded shallower part of the basin later in the Stage 3 (Jin *et al.* 2016). As such, the oxygenation history of the early Cambrian ocean appears more dynamic than previously thought (*e.g.*, Dahl *et al.*, 2010; Sperling *et al.*, 2013; Chen *et al.*, 2015).

The oxygenation event coincides with global changes in the marine carbon and sulphur cycles. We also report sulphur isotope data from carbonate-associated sulphate ( $\delta^{34}\text{S}_{\text{CAS}}$ ) from three distinct stratigraphic sections in Siberia that show a similar systematic positive  $\delta^{34}\text{S}_{\text{CAS}}$  isotope excursion coinciding with the  $\delta^{238}\text{U}$  and  $\delta^{13}\text{C}$  excursions (Fig. 1). The simultaneous excursions across the Cambrian Stage 2–3 boundary suggest the C, S and U cycles responded to the same global biogeochemical event. Similar parallel positive carbon and sulphur isotope excursions during the late Cambrian SPICE event (Gill *et al.*, 2011; Dahl *et al.*, 2014) and the Botoman Sinsk event were interpreted to represent a period of enhanced organic carbon and pyrite burial (Zhuravlev and Wood, 1996). While these events are linked to expanding ocean anoxia and animal extinctions, the positive  $\delta^{238}\text{U}$  excursion reported here reveals a distinct driver for the environmental change.

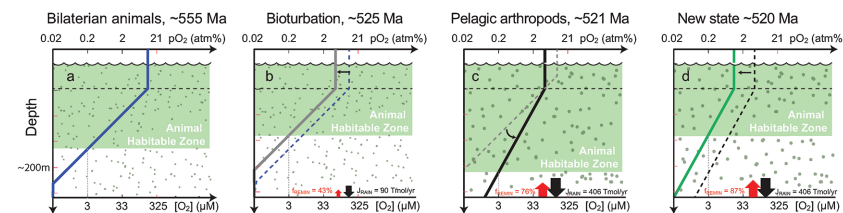




**Figure 2** Summary of the redox proxy and carbon isotope data from latest Ediacaran to Early Cambrian (560–515 Myr). Redox proxy data includes the sedimentary contents and stable isotope compositions of molybdenum and uranium: Euxinic shales (black circles), Ferruginous shales (red circles), oxic shales (blue circles), shales from unknown redox environments (gray crosses), phosphorites (white diamonds), and carbonates (white circles). The grey field on the molybdenum isotope plot indicates values that are definitively fractionated from seawater, although values greater than these may be so as well. References for the data are listed in the Supplementary Information Extended Data, Table S-22.

The Cambrian Stage 2–3 event coincides with the onset of the first major diversification of arthropods, which predates by a few million years the first appearance of macrozooplankton and suspension-feeding anomalocarids (Hou, 2004; Stein *et al.*, 2009; Vinther *et al.*, 2014). Therefore, we consider that this oxygenation episode reflects the first invasion of larger zooplankton in the pelagic zone that triggered an increase in the sinking rate and compaction of organic matter. Today, the export of organic matter from the photic zone (<200 m depth) — a process referred to as the biological pump — occurs as sinking molts, faecal matter, carcasses, and skeletons (Alldredge *et al.*, 1993; Hedges and Keil, 1995). The sinking velocity of a particle in the ocean is a quadratic function of its size. Therefore, a small increase in the mean size of particulate organic matter would have caused the rates of water column remineralisation to decrease, so that less O<sub>2</sub> was consumed in the water column and a more gentle O<sub>2</sub> gradient was established below the photic zone (Fig. 3, Meyer *et al.*, 2016). Consequently, more organic matter would have been exported to the seafloor resulting in enhanced rates of organic carbon and pyrite burial.

To quantify the potential consequences of faster sinking rates on organic carbon export ( $J_{RAIN}$ ) onto the seafloor, we utilise the  $\delta^{13}C$  and  $\delta^{34}S$  data and a simple biogeochemical model for the coupled marine C and S cycles. Organic carbon export fuels both organic carbon burial ( $J_{ORG} = J_{RAIN} - J_{REMIN}$ ) and



**Figure 3** Conceptual model for the episodic expansion of the oxygenation zone in the oceans. The emergence of bilateral animals (a–b) increased sediment mixing *via* bioturbation causing atmospheric pO<sub>2</sub> to decline. The oxygenation zone contracts until (c) a rapid increase in the sinking rate of organic matter changes O<sub>2</sub> consumption rates in the upper water column. (d) This accelerates organic carbon export to the sediments and delivers more food and O<sub>2</sub> to the benthos over wider areas of the seafloor. Enhanced bioturbation promotes atmospheric pO<sub>2</sub> decline, and re-stabilises the ocean in a more reducing state. Arrows and numbers illustrate organic export fluxes in one scenario (details in Table S-11). For simplicity, the organic C export increases in one step with the emergence of larger faecal pellets. Quantitative estimates for organic carbon export and remineralisation are derived from the coupled C and S isotope modelling (see Supplementary Information S5).

remineralisation in sediments ( $J_{REMIN}$ ). In this model, pyrite burial is proportional to the remineralisation flux ( $J_{PY} = \alpha \cdot J_{REMIN}$ ) because microbial sulphate reduction accounts for the major part of organic remineralisation in sediments and a fraction of its byproduct, sulphide, reacts with available Fe compounds to form pyrite (see Supplementary Information for model details). With this formulation ( $\alpha$  constant), we find that a 3–6 fold increase in the organic carbon rain rate is sufficient to increase  $\delta^{13}C$  (0 to 3 ‰) and  $\delta^{34}S$  (28 to 40 ‰) simultaneously. This can be achieved with only a 1.7–2.5 fold increase in the mean of the size distribution of sinking organic matter particulates, assuming similar density and shape for the particulates before and after the invasion of larger zooplankton. We consider this as a minimum estimate, if a greater portion of larger faecal pellets do not aggregate (Butterfield, 1997). However, it shows that even a modest size increase potentially influences the global biogeochemical cycles.

The evolutionary history of animals over the Neoproterozoic–Cambrian transition suggests a stepwise increase in their overall size and their digestive tracts, which would have enhanced the biological pump (Logan *et al.*, 1995; Butterfield, 2009; Lenton *et al.*, 2014). Biomarker evidence suggests a fundamental shift in the preservation state of marine organic matter with abundant faecal matter in sedimentary rocks younger than ~517 Ma compared to similar rocks older than ~565 Ma (Logan *et al.*, 1995). Although the abundance of pelagic animal fauna through the Cambrian Stage 2–3 interval is not known, it is apparent that the maximum size of pelagic heterotrophic organisms and their digestive tracts increased by three orders of magnitude from the Ediacaran into the Cambrian. Heterotrophic consumers such as micro- and mesozooplankton (20–200 µm) evolved in the latest Ediacaran (635–542 Ma) (Perrier *et al.*, 2015). The fossil record indicates that animals of probable chaetognath affinity (‘protoconodonts’) a few millimetres in size or larger swam in the early Fortunian ocean (>535 Ma),





and that large macrozooplankton (*i.e.* bivalved arthropod *Isoxys*) up to 45 mm had appeared in the earliest Stage 3 (~520 Ma) (Ivantsov, 1990; Hou, 2004; Stein *et al.*, 2009). However, it says nothing about when various types of zooplankton became ecologically important. Rather, we suggest that a stepwise increase in the size of zooplankton is a plausible trigger for the reorganisation of Earth's marine biogeochemical cycles and, consequently, the earliest Cambrian Stage 3 oxygenation episode. By implication, earlier steps in animal evolution may have also led to oxygenation events preserved in the geochemical record during the Ediacaran–Cambrian transition (see below).

Given that the geochemical evidence suggests that the Cambrian Stage 2–3 oxygenation episode was brief, a stabilising feedback must have acted to counterbalance marine oxygenation. Current models for the evolving biogeochemical cycles in the Cambrian have not included such a rapid feedback mechanism (Bergman *et al.*, 2004; Berner, 2006). Evidence from bioturbation indices (Mangano and Buatois, 2014) and Earth system modelling (Canfield and Farquhar, 2009; Boyle *et al.*, 2014) suggest that the Cambrian Stage 3 oxygenation episode occurred during an apparent atmospheric  $pO_2$  decline resulting from increased mixing of marine sediments by animals. Since the early Cambrian Stage 2 (~530 Ma), animals had evolved the ability to burrow deeper into sediments acting to lower marine P availability, organic productivity, organic carbon burial, and hence the main source of atmospheric  $pO_2$  (Boyle *et al.*, 2014). The emerging larger pelagic fauna accelerated this feedback mechanism, since the enhanced biological pump would have both increased the food supply and food quality for benthic heterotrophic organisms and led to more fully oxygenated conditions in the water column below the photic zone, thereby opening new ecospace for sediment-mixing animals over wider areas of the continental shelves. Subsequently, this focusing of organic matter at the seafloor increased overall rate of bioturbation, organic carbon remineralisation and oxygen consumption over larger areas of the seafloor and, ultimately, a decline in atmospheric  $pO_2$  that again limited the size of the oxygenated zones in the oceans (Fig. 3). It is notable that for this sequence of feedbacks to respond over the time scale of the Cambrian Stage 2–3 oxygenation episode ( $1.3 \pm 0.8$  Myr (Maloof *et al.*, 2010), see calculation in the Supplementary Information), atmospheric  $O_2$  inventory must have been significantly smaller than today in order to produce an excursion of the right duration. We derive an order of magnitude estimate for the atmospheric  $pO_2$  level at the Cambrian Stage 2–3 boundary of between  $4 \pm 2$  and  $7 \pm 4$  atm % from the duration of the falling limb isotope excursions, assuming the global burial rate of marine organic carbon was the same as today. We also assume that anoxia returns as atmospheric  $pO_2$  levels decline due to less organic carbon burial over the course of  $\sim 1/4$  to  $\sim 1/2$  the duration of the full  $\delta^{13}C$  excursion ( $\sim 325 \pm 200$  and  $\sim 650 \pm 400$  kyr). This atmospheric  $pO_2$  estimate scales linearly with global organic carbon burial flux, and requires that the acceleration of the biological pump (by faecal pellets) and the subsequent migration of the sediment-dwelling taxa are essentially instantaneous ( $\ll 100$  kyr). This atmospheric  $pO_2$  level is well above the metabolic need for some animals (Pasteur limit  $\sim 0.2$  atm %) (Mills and Canfield, 2014), but not

sufficiently high to oxygenate the deep oceans permanently (Lyons *et al.*, 2014) and it conforms with the idea that animal ecosystems could have become self-limiting in terms of determining the size of the habitable ecospace in the oceans (Sperling *et al.*, 2013; Boyle *et al.*, 2014).

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## Author Contributions

AK collected the samples. TWD conceived the idea, designed the study, interpreted the data and created the models. TWD, JNC, BCG, SFM and MB analysed the samples and wrote the manuscript with significant contributions from all co-authors.

## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1724](http://www.geochemicalperspectivesletters.org/article1724)

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