

# Pulse of atmospheric oxygen during the late Cambrian

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A rise in atmospheric O<sub>2</sub> has been linked to the Cambrian explosion of life. For the plankton and animal radiation that began some 40 million yr later and continued through much of the Ordovician (Great Ordovician Biodiversification Event), the search for an environmental trigger(s) has remained elusive. Here we present a carbon and sulfur isotope mass balance model for the latest Cambrian time interval spanning the globally recognized Steptoean Positive Carbon Isotope Excursion (SPICE) that indicates a major increase in atmospheric O<sub>2</sub>. We estimate that this organic carbon and pyrite burial event added approximately  $19 \times 10^{18}$  moles of O<sub>2</sub> to the atmosphere (i.e., equal to change from an initial starting point for O<sub>2</sub> between 10–18% to a peak of 20–28% O<sub>2</sub>) beginning at approximately 500 million years. We further report on new paired carbon isotope results from carbonate and organic matter through the SPICE in North America, Australia, and China that reveal an approximately 2‰ increase in biological fractionation, also consistent with a major increase in atmospheric O<sub>2</sub>. The SPICE is followed by an increase in plankton diversity that may relate to changes in macro- and micronutrient abundances in increasingly oxic marine environments, representing a critical initial step in the trophic chain. Ecologically diverse plankton groups could provide new food sources for an animal biota expanding into progressively more ventilated marine habitats during the Ordovician, ultimately establishing complex ecosystems that are a hallmark of the Great Ordovician Biodiversification Event.

evolution | climate change | stable isotope | Paleozoic | dinoflagellate

Fluctuations in atmospheric oxygen (O<sub>2</sub>) and oceanic redox are thought to have played fundamental roles in driving biological evolution throughout geologic time (1, 2). Well-studied examples include the rise of animals at the end of the Precambrian eon (3) and the rise of modern phytoplankton groups in the early Mesozoic (4), both of which have been linked to increases in atmospheric O<sub>2</sub>. Rising oxygen levels may directly influence nutrient availability for phytoplankton or animal physiology, with subsequent biological feedbacks between the benthos and plankton leading to increased ecological complexity (5–7). Here we document a significant increase in atmospheric O<sub>2</sub> during the later Cambrian and examine the impact this may have had on biological evolution.

Beginning in the later parts of the Cambrian and continuing through much of the Ordovician, a series of complex, diachronous episodes of both plankton and animal diversification are collectively referred to as the Great Ordovician Biodiversification Event (GOBE), or Ordovician radiation (8–10). Although ecological interaction between free-floating (planktic) and bottom-dwelling (benthic) organisms has been recognized as major driver of biological evolution during this time period (11, 12), changes in the physical environment were likely an important stimulus. Specifically, previous authors have proposed that increased nutrient availability could fuel increases in primary productivity and food resources during the GOBE. However, potential mechanisms to drive enhanced productivity and associated trophic

changes remain poorly understood (12, 13). The unique evidence we present here for a later Cambrian (Furongian Series) rise in atmospheric O<sub>2</sub> may have altered oceanic redox and the concentrations of bioavailable nutrients in the surface oceans, ultimately promoting diversification in certain phytoplankton groups and potentially higher overall net primary production as well.

Late Cambrian changes in the oceanic trophic chain (“plankton revolution” of Servais et al.) (12) began in the aftermath of a major perturbation in the global carbon cycle that is recorded in the geologic record as a large positive  $\delta^{13}\text{C}_{\text{carb}}$  excursion [Steptoean Positive Carbon Isotope Excursion (SPICE) event] (14) (Fig. 1). The SPICE event has been documented worldwide and is characterized by a positive  $\delta^{13}\text{C}$  shift of approximately +4‰ in Upper Cambrian (Paibian Stage of Furongian Series) sections throughout North America and time-equivalent strata in China, Siberia, Baltica, Australia, and Kazakhstan (refs. 14–16, Fig. S1, and *SI Text*). Intercontinental correlation of the SPICE is based on the presence of cosmopolitan trilobite *Glyptagnostus reticulatus* below the  $\delta^{13}\text{C}$  peak and *Irvingella* above. The SPICE was also associated with an approximately +20‰ increase in the <sup>34</sup>S/<sup>32</sup>S ratio of seawater sulfate as measured in carbonate-associated sulfate ( $\delta^{34}\text{S}_{\text{CAS}}$ ) (Fig. 1) and likely represents an interval of enhanced organic carbon and pyrite sulfur beneath anoxic (euxinic) waters (17). The positive  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{34}\text{S}_{\text{CAS}}$  excursions, which lasted for several million years based on the best absolute age constraints for the Cambrian (14), should have been associated with significant net O<sub>2</sub> production. Here we show that a rise in atmospheric O<sub>2</sub> occurred during the SPICE using two different methods. First, we utilize a conventional carbon-sulfur isotope mass balance approach that is based on published  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{34}\text{S}_{\text{CAS}}$  measurements (18, 19). Second, we present unique paired analyses of carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ) and organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ) in three global sections through the SPICE to consider an O<sub>2</sub> proxy that is based on changes in biological fractionation of carbon isotopes (20, 21).

## Results and Discussion

**Carbon and Sulfur Isotope Mass Balance.** Calculations of atmospheric O<sub>2</sub> levels through geologic time can be made using global estimates of the burial and weathering rates of organic carbon and pyrite sulfur in sedimentary rocks (18, 19). The isotope mass balance approach utilizes secular trends in the stable isotope ratios of carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ) and sulfur ( $\delta^{34}\text{S}_{\text{CAS}}$ ) in marine minerals. Because photosynthesis and bacterial sulfate reduction discriminate in favor of the light isotopes of carbon (<sup>12</sup>C) and sulfur (<sup>32</sup>S),

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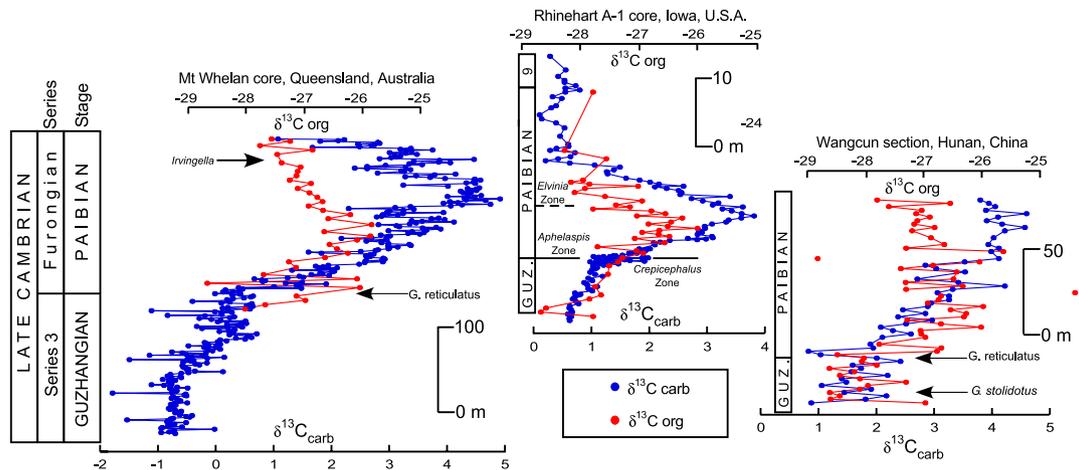
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**Fig. 2.** Plot of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  (‰ VPDB) through the Late Cambrian SPICE excursion. Cosmopolitan trilobite taxa allowing for global correlation are indicated with arrows (Australia, China), and North American trilobite zones that correlate are shown for Iowa (refs. 14 and 25; Figs. S1 and S2; Tables S2, S3, and S4; and S1 Text).

ever, part way through the rising limb of the  $\delta^{13}\text{C}_{\text{carb}}$  excursion, the  $\delta^{13}\text{C}_{\text{org}}$  values begin to decrease, yielding an increase in the isotopic difference between paired  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  ( $\Delta^{13}\text{C}$ ) data from  $\sim 28$  and  $29\text{‰}$  before the SPICE to a peak of  $31\text{‰}$  at the height of the excursion followed by a return to preexcursion values after the SPICE (Fig. 3).

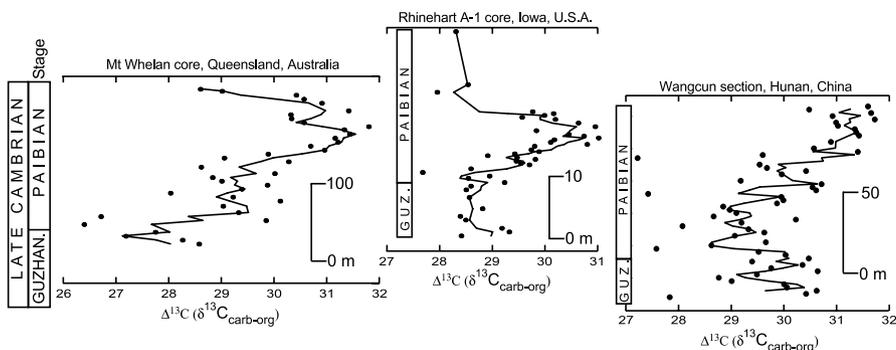
The dependence of biological carbon isotope fractionation on the partial pressure of atmospheric oxygen ( $p\text{O}_2$ ) has been demonstrated in laboratory experiments using vascular land plants, bryophytes, and marine phytoplankton (20, 21, 27). Increased isotopic discrimination for  $^{12}\text{C}$  is observed at increasing  $\text{O}_2$  levels because  $\text{CO}_2$  levels rise within the plant or plankton cell as photorespiration begins to outpace photosynthesis ( $\text{O}_2$  competes with  $\text{CO}_2$  for sites on the photosynthetic enzyme Rubisco).

We modified equation 4 in Beerling et al. (21) to calculate  $\text{O}_2$  from our measured  $\delta^{13}\text{C}_{\text{carb}}$  and  $^{13}\text{C}_{\text{org}}$  values:  $\Delta^{13}\text{C}_{\text{meas}} = \Delta^{13}\text{C}_{\text{initial}} + J \times [(M_{\text{O}_2}/38) - 1]$ . The term  $\Delta^{13}\text{C}_{\text{meas}}$  is the measured value for the difference between  $\delta^{13}\text{C}_{\text{carb}}$  and  $^{13}\text{C}_{\text{org}}$  and  $\Delta^{13}\text{C}_{\text{initial}}$  is an estimate of the Early Paleozoic baseline value (approximately  $29\text{‰}$ ) (19). We use a value of  $J = 5$  in our calculations, based on the best fit to both the experimental data for isotopic discrimination in modern marine phytoplankton and isotope mass balance model results (see ref. 20). The increase in fractionation of approximately  $+2\text{‰}$  observed during the SPICE (Fig. 3) translates to a  $p\text{O}_2$  increase from a starting point between  $14\text{--}18\%$  to a peak just over  $30\%$  (Fig. 4A). Use of an alternative value for  $J$  ( $J = 2.5$ ), representing a weaker dependence of fractionation on  $p\text{O}_2$ , leads to a much larger

increase in  $\text{O}_2$  ( $>40\%$ ) and unrealistic  $\text{O}_2$  volatility (including negative values) (Fig. 4B).

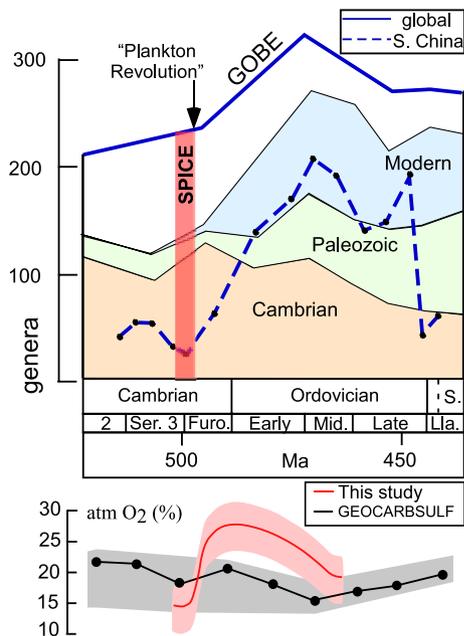
The modeled increase in  $\text{O}_2$  using isotope mass balance during the SPICE is generally a good fit with the estimate based on increased carbon isotope fractionation (Fig. 4A). However, there is an apparent mismatch at the end of the SPICE (approximately  $496$  Ma in Fig. 4A) during which isotopic fractionation indicates that  $p\text{O}_2$  returned to near pre-SPICE levels, whereas C and S isotope mass balance indicates that  $p\text{O}_2$  remained at peak levels. This return to lower  $\Delta^{13}\text{C}$  likely indicates the role that fluctuations in atmospheric  $p\text{CO}_2$  may also play in photosynthetic carbon isotope fractionation (20, 21, 23, 26–29). Indeed, the enhanced isotopic fractionation by phytoplankton that we interpret as a response to the SPICE  $\text{O}_2$  pulse occurred in spite of a decrease in atmospheric  $\text{CO}_2$  brought about by the organic carbon burial that promoted the rise in  $\text{O}_2$  (i.e., a decrease in  $\text{CO}_2$  acting alone should lead to a decrease in fractionation) (26). Experimental results showing that isotopic fractionation in plants may be most sensitive to  $p\text{O}_2$  at low  $p\text{CO}_2$  and respond to changes in atmospheric  $p\text{O}_2/p\text{CO}_2$  (refs. 21, 27) may reconcile our apparent mismatch between the isotope mass balance and fractionation approaches at the end of the SPICE.

To address the influence of changing  $p\text{O}_2/p\text{CO}_2$  on  $\Delta^{13}\text{C}$ , we modeled  $p\text{CO}_2$  during the SPICE using a modified  $\delta^{13}\text{C}$  mass balance model from Kump and Arthur (26). We ran the model with constant  $\Delta^{13}\text{C}$  to make no assumptions about how our measured  $\Delta^{13}\text{C}$  values (Fig. 3) influence calculation of  $p\text{CO}_2$  based on carbon sources and sinks. During the model run (see Figs. 1 and 4 for  $\text{O}_2$ ), the positive  $\delta^{13}\text{C}_{\text{carb}}$  excursion drives



**Fig. 3.** Plot of  $\Delta^{13}\text{C}$  ( $=\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) through the Late Cambrian based on data in Fig. 2. Line through raw data is three point running average.





**Fig. 6.** Cambrian–Silurian genus level diversity from the global compilation of Alroy (36) and regional South China compilation of Rong et al. (38). Labeled are the SPICE  $\delta^{13}\text{C}_{\text{carb}}$  excursion, onset of the plankton revolution (12), and the GOBE (8–10). Changes in  $\text{O}_2$  are based on isotope mass balance model, using smoothed trends in carbon and sulfur isotopes based on compilation in the supporting online materials from Gill et al. (17).  $\text{O}_2$  levels remain high after the SPICE organic carbon and pyrite sulfur burial event and fall through the early Ordovician, but still remain elevated above pre-SPICE levels (for comparison, GEOCARBSULF curve is modified after ref. 19).

On longer timescales, some important transitions in the plankton (12, 31, 32) and benthos (33) may have begun following the SPICE oxygenation event in the late Cambrian Furongian Series (Fig. 6).

A late Cambrian (Furongian) increase in plankton diversity is evident in the appearance of a significant number of new morphologies of organic-walled microfossils (acritarchs), including dinoflagellate-like taxa (9, 12). Although the attribution of acritarch taxa to the dinoflagellates or groups ancestral to the dinoflagellates (or any other group of eukaryotic phytoplankton) remains speculative, certain late Cambrian acritarchs share patterns of ecological and geographic distribution, organic wall chemistry, and morphologies that are comparable to those of modern dinoflagellates (7, 12). Furthermore, molecular biomarker evidence (e.g., dinosteranes) confirms that dinoflagellates were already present by the early Cambrian even if the morphological evidence is ambiguous (7, 34). Dinoflagellates, like the other modern phytoplankton that contain red algae plastids (i.e., membrane-bound organelles containing chlorophyll *c* as an accessory pigment), have higher quotas for trace elements that are relatively concentrated in oxygenated waters (e.g., cadmium and molybdenum) (4) compared to cyanobacteria and phytoplankton with green algae plastids. Thus, it is possible that the SPICE  $\text{O}_2$  pulse led to an increase in oxygenated coastal ocean settings and promoted diversification of dinoflagellate-like (i.e., red plastid group) taxa relative to the prasinophyte green algae (which were members of the green plastid group, and likely the dominant producers overall throughout much of the Paleozoic; 4, 5, 7).

The latest Cambrian (Furongian) changes in the plankton included not only increased diversity but also the independent development in diverse lineages of a feeding, planktotrophic larval stage, presumably in response to more abundant food resources and predation pressures from expanding epifaunal suspension feeders (11, 31, 32). Ultimately, the SPICE oxygenation

event and the beginnings of this plankton revolution (Fig. 6) may thus represent a critical initial step in the trophic chain (12) that allowed for animal groups to spread into increasingly oxygenated and ecologically diverse marine habitats during the GOBE, and become larger in size (35). Depending on the time resolution possible in recent global or regional marine animal diversity compilations (36–38), the GOBE could arguably be viewed as having been “rooted” in the latest Cambrian (Furongian) (Fig. 6). Still, because the details show that the GOBE was a multifaceted event comprised of a series of strongly diachronous biologic transitions operating on regional scales throughout the Early and Middle Ordovician (8–10, 39), no single factor would seem to suffice as an explanation. Indeed, two of the most widely recognized diversity pulses of the GOBE lag the SPICE by some approximately 25 and 35 million years (40–43) (i.e., at the Ibxian–Whiterockian boundary in North America, which is near the base of the global Dapingian Stage, and then a later event in the mid-Darriwilian).

Our isotope mass balance model indicates that atmospheric  $\text{O}_2$  likely remained elevated for tens of millions of years after the SPICE, although the levels dropped gradually due in part to the higher rate of organic matter weathering (and marine remineralization) relative to burial (Fig. 6). If an upper bound on the  $\text{H}_2\text{S}$  concentration of an anoxic (euxinic) ocean is 1 mM (44), then a maximum of approximately  $2.8 \times 10^{18}$  mol  $\text{O}_2$  was consumed as part of the negative feedback on the SPICE anoxic event, or about 15% of that produced by organic carbon and pyrite burial. The strong correspondence of the initial  $\delta^{13}\text{C}$  shifts in both carbonates and organic matter at the onset of the SPICE rules out the potentially large oxygen sink associated with a dissolved organic carbon (DOC)-rich “Rothman ocean” invoked to explain Neoproterozoic carbon isotope anomalies (45). Even as  $\text{O}_2$  levels began to drop in the early Ordovician, increasingly colder waters (42) would be capable of dissolving more atmospheric  $\text{O}_2$  and progressively ventilating an anoxic deep ocean (46–48). Pruss et al. (46) argued that the transition to more oxic oceans drove an increase in the carbonate saturation state of surface waters that enabled the radiation of heavily skeletonized invertebrates and algae in the early Ordovician. A progressively oxygenated deep ocean should also have led to the eventual end of the recurring “biomere” extinction events that likely inhibited animal biodiversification through the later Cambrian and into the earliest parts of the Ordovician (49). Biomere extinctions have been linked to the episodic spread of anoxia into shelf environments and high rates of organic matter burial (14, 17), and therefore the termination of the biomere pattern should coincide with a period of relative stability in  $\delta^{13}\text{C}_{\text{carb}}$  (50, 51) and lower organic carbon-to-phosphorus ratios in marine sediments (52). Regardless of the details, it seems likely that the late Cambrian SPICE  $\text{O}_2$  pulse played an important role in biological evolution that continued well into the Ordovician.

## Materials and Methods

Samples collected from all three sections were previously analyzed for  $\delta^{13}\text{C}_{\text{carb}}$ . For  $\delta^{13}\text{C}_{\text{org}}$  studies here, fresh rock surfaces were generated by a water-based diamond-blade saw and the resulting thin-section billets were polished, and placed into an ultrasonic bath containing ultrapure (deionized, 18 M $\Omega$ ) water to remove surficial organic contaminants. Micritic (fine-grained) components were microdrilled (approximately 1.5 g of powder) from the thin-section billets. Sample powders were accurately weighed and thoroughly acidified using approximately 6N HCl to remove carbonate minerals. Insoluble fractions were then repeatedly rinsed in ultrapure water and dried at 85 °C. Remaining residues were weighed and homogenized, and then loaded into tin capsules. Samples were combusted with a Costech Elemental Analyzer and the resulting  $\text{CO}_2$  gas analyzed for  $\delta^{13}\text{C}$  through a Finnigan Delta IV stable isotope ratio mass spectrometer under continuous flow using an open-split CONFLO III interface in the Stable Isotope Biogeochemistry Laboratory at The Ohio State University. Carbon isotope ratios presented here are reported in per mil notation relative to the Vienna Pee Dee Belemnite limestone standard [% Vienna Pee Dee Belemnite standard

(VPDB)]. Repeated measurements of the IAEA-CH7 standards were  $\pm 0.15\%$  for  $\delta^{13}\text{C}$  and  $\pm 1.0\%$  for  $\% \text{C}$  (1 standard deviation). Weight percent of TOC in samples is determined by comparison of voltages for the ion beam intensities of masses 44, 45, and  $46 \text{CO}_2^+$  between our samples and known wt. % carbon of the gravimetric standard Acetanilide.

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