



Geochemical evidence for widespread euxinia in the Later Cambrian ocean

The Harvard community has made this article openly available. <u>Please share</u> how this access benefits you. Your story matters

Citation	Gill, Benjamin C., Timothy W. Lyons, Seth A. Young, Lee R. Kump, Andrew H. Knoll, and Matthew R. Saltzman. 2011. "Geochemical Evidence for Widespread Euxinia in the Later Cambrian Ocean." Nature 469, no. 7328: 80–83.
Published Version	doi:10.1038/nature09700
Citable link	http://nrs.harvard.edu/urn-3:HUL.InstRepos:13041344
Terms of Use	This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Open Access Policy Articles, as set forth at http:// nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of- use#OAP

1	Sulphur isotope evidence for widespread euxinia in the Later Cambrian
2	ocean
3	Benjamin C. Gill ^{1*} , Timothy W. Lyons ¹ , Seth A. Young ² , Lee R. Kump ³ , Andrew H.
4	Knoll ⁴ , and Matthew R. Saltzman ⁵
5	
$ \begin{array}{r} 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ \end{array} $	 ¹Department of Earth Sciences, University of California, Riverside, 900 University Avenue, Riverside, CA, 92521, USA ²Department of Geological Sciences, Indiana University-Bloomington, 1001 East 10th Street Bloomington, IN 47405-1405, USA ³Department of Geosciences, Penn State University, 503 Deike Building, University Park, PA 16802, USA ⁴Department of Organismic and Evolutionary Biology, Harvard University, 26 Oxford Street, Cambridge, MA, 02138, USA. ⁵School of Earth Science, The Ohio State University, 275 Mendenhall Laboratory, 125 South Oval Mall, Columbus, Ohio 43210, USA *Corresponding Author, present address: Department of Earth and Planetary Sciences Harvard University, 20 Oxford Street, Cambridge, MA, 02138, USA.
18	Global-scale anoxia in the deep ocean is frequently invoked as a primary
19	driver of mass extinction, as well as a long-term inhibitor of evolutionary radiation
20	on the early Earth. In recent biogeochemical studies, it has been hypothesized that
21	oxygen deficiency was widespread in subsurface water masses of later Cambrian
22	oceans ^{1,2} , possibly influencing evolutionary events during this time ^{1,2,3} . Physical
23	evidence of widespread anoxia in Cambrian oceans has remained elusive, and thus
24	its potential relationship to the paleontological record remains largely unexplored.
25	Here, we present sulphur isotope records from six globally distributed stratigraphic
26	sections of later Cambrian marine rocks (ca. 499 million years old) that show a
27	positive excursion in phase with the well-known Steptoean Positive Carbon Isotope
28	Excursion (SPICE). Numerical box modeling of the paired carbon-sulphur isotope

Sulphur isotope evidence for widespread euxinia in the Later Cambrian

29 data indicates that these isotope shifts reflect transient increases in the burial of 30 organic carbon and pyrite sulphur in sediments deposited under ocean-scale anoxic 31 and sulphidic (euxinic) conditions. Independently, molybdenum abundances in a 32 coeval black shale point convincingly to ocean-scale anoxia. These results identify 33 the SPICE interval as the best characterized ocean anoxic event in the pre-Mesozoic 34 ocean and an extreme example of oxygen deficiency in the later Cambrian deep ocean. Thus, a redox structure similar to those in Proterozoic oceans^{4,5,6} may have 35 36 persisted or returned in the oceans of the early Phanerozoic Eon. Indeed, the 37 environmental challenges presented by widespread anoxia may have been a 38 prevalent if not dominant influence on animal evolution in Cambrian oceans. 39

40 Carbonate rocks of Cambrian age preserve large, rapid (of a few million years 41 duration or less) and globally correlated excursions in the marine carbon isotope record $(\delta^{13}C_{carb})$, which indicate perturbations in the global carbon cycle (Figure S1)^{7,8,9,10}. The 42 43 mechanisms that drove these events, however, are poorly known. What makes these 44 excursions particularly interesting to geobiologists is the observation that many coincide 45 with biological events recorded by fossils, suggesting causal links between biological and environmental history^{3,10}. The focus of our work is on the last large excursion of the 46 47 period, the Steptoean Positive Carbon Isotope Excursion, or SPICE.

48 The SPICE is recorded as a +4-6‰ shift in $\delta^{13}C_{carb}$ that occurs globally in later 49 Cambrian successions (at the beginning of the Furongian International Series and Paibian 50 International Stage, 499 Ma); it is thought to have lasted on the order of 2-4 million

51	years ^{10,11} . A well-documented extinction of trilobites coincides with the onset of the
52	SPICE on the paleocontinent of Laurentia ^{10,12} , and the isotopic excursion has also been
53	correlated to intervals of biological turnover on other paleocontinents ¹³ . The SPICE is
54	also coincident with global changes in sea level; its onset coincides with a transgressive
55	event, and its peak is concurrent with a lowstand recorded as the Sauk-II/III hiatus ^{10,11} .
56	We report sulphur isotope data from six globally distributed stratigraphic sections
57	across the SPICE, and each reveal parallel, positive carbon and sulphur isotope
58	excursions (Figures 1, 2 and 3). These sections represent diverse sedimentary
59	environments; thus, similarities among the trends despite differences in depositional
60	conditions speak to the global and primary nature of the geochemical signals (see
61	Supplementary Materials for details of individual stratigraphic sections and data
62	supporting the preservation of the geochemical signals).
63	The SPICE sulphur isotope excursion is one of the largest identified in the
64	geologic record and is the first to be correlated globally at this scale of resolution. This
65	excursion occurs in both carbonate-associated sulphate (CAS) and pyrite, which further
66	supports a primary marine signal, and its magnitude indicates a major perturbation in the
67	global sulphur cycle. There are, however, significant differences in the details of the
68	sulphate sulphur isotope trends among basins. In particular, the pre-event $\delta^{34}S_{CAS}$
69	baseline differs among the various locations (Figure 2). While some records show
70	relatively steady sulphur isotope values before the excursion (i.e., western and eastern
71	Laurentia), the Gondwanan data show a positive trend up section before the excursion
72	(Figure 2).

73	Despite overarching similarities, the absolute values and amplitudes of the
74	excursion also differ among the studied basins. The Gondwanan record is the most
75	extreme, with $\delta^{34}S_{CAS}$ values reaching almost +70‰ and an amplitude of +35‰ (Figure
76	2). On the other end of the spectrum, the record in eastern Laurentia shows a peak value
77	of +38‰ and amplitude of only +12‰ (Figure 2). These isotopic differences support the
78	idea that the sulphur reservoir in the later Cambrian ocean was spatially heterogeneous
79	and that sulphate concentrations were therefore $low^{14,15}$. We also observe that the sulfate
80	isotope excursion peaks stratigraphically slightly before the carbon isotope maximum
81	(see Supplementary Figure S2), which suggests that the sulphate reservoir was relatively
82	more sensitive to change than the marine pool of dissolved inorganic carbon (DIC). This
83	state of sulphate in later Cambrian seawater differs greatly from the modern reservoir,
84	which is relatively homogenous globally with a concentration of 28 mmol/kg (mM) and a
85	sulphur isotope composition of $+21\%$. This contrast with the modern ocean indicates
86	that the residence time of sulphate in the Cambrian ocean was much shorter.
87	The parallel behavior between the carbon and sulphur isotope excursions
88	(Figures 2 and 3) suggests that the SPICE records a transient increase in the amount of
89	carbon and sulphur buried as organic matter and pyrite (FeS ₂) in marine sediments. Such
90	parallel burial occurs in anoxic marine sediments and beneath euxinic water columns ¹⁶ —
91	that is, beneath water columns that are both anoxic and contain free hydrogen sulphide.
92	Organic matter fuels microbial sulphate reduction (MSR), and pyrite is formed when H ₂ S
93	produced from MSR reacts with iron minerals and is buried along with the residual
94	organic matter. Ultimately, the burial of both species results in the removal of carbon

95	and sulphur from the ocean. This coupling can result in positive isotope shifts for both
96	species in seawater: the carbon and sulphur leaving the ocean through burial are enriched
97	in ¹² C and ³² S via isotope fractionations accompanying photosynthetic and MSR
98	pathways, respectively, leaving the seawater correspondingly enriched in ¹³ C and ³⁴ S.
99	We tested this hypothesis by modeling the ocean inventories of carbon and
100	sulphur during the SPICE. Specifically, we constructed a simple box model that
101	simulates the cycling of each element in the ocean (see Supplementary Material for
102	details). The model shows that the isotope excursions can be replicated by transiently
103	increasing the amount of organic carbon buried by factors of 1.5 to 2.5 and pyrite sulphur
104	by factors of 2.5 to 4.5 for a duration of 0.5 to 1.5 million years (Figure 4: see
105	Supplementary Material for additional model details).
106	Importantly, our model puts quantitative constraints on the size of the marine
107	sulphate reservoir during the later Cambrian. An assumption of pre-SPICE sulphate
108	concentrations greater than 2.5 mM demands more than 8 million years for recovery of
109	$\delta^{34}S_{sulphate}$ (i.e., return to the pre-event baseline) following the SPICE (Figure S13), which
110	is unreasonable in light of the available constraints on the duration of the $SPICE^{11}$. Our
111	simulations suggest, therefore, that the concentration of seawater sulphate was very low
112	— at or below the low end of the 2-12 mM range suggested by previous work 14,15 .
113	Another important result from the model is that the predicted ratio of carbon-to-
114	sulphur (C/S) linked to this transient burial was very low: 1 to 4 moles C/mole S or 0.4-
115	1.5 g C/g S (Figure 4). In younger sediments, similar C/S ratios are only observed in
116	sediments deposited under euxinic conditions ¹⁶ . The scale of this Cambrian euxinia is

117 suggested by comparison to the Black Sea, the largest modern euxinic basin. Our

estimates for the transient burial flux of sulfur that caused the isotope excursion are equal

119 to 50-75 times that of the euxinic portion Black Sea^{17} , thus providing the first quantitative

120 evidence for global-scale euxinia in the Paleozoic ocean.

121 Our argument for increased euxinia becomes stronger when we consider that ΔS 122 may have decreased over the event (Figure 2). ΔS is the isotopic offset between coexisting CAS and pyrite ($\Delta \delta^{34} S_{CAS-pyrite}$) that results from MSR and related microbial 123 124 pathways that lead to pyrite formation. For the two sections that have sufficient pyrite for 125 isotopic analysis (eastern Laurentia and Gondwana), there is a strikingly systematic negative shift in ΔS parallel to the positive excursions in $\delta^{34}S_{CAS}$ and $\delta^{13}C_{carb}$ (Figure 2). 126 127 Importantly, a smaller ΔS , when applied to our model, requires greater pyrite burial to 128 explain the positive sulphur excursion. The further increase in pyrite burial results in an 129 even lower mean C/S ratio, strengthening the case for burial under euxinic conditions 130 (see Supplementary Figure S14 for sensitivity tests of Δ S). Our Cambrian sulphur 131 isotope data must record a decrease in seawater sulphate concentration associated with 132 voluminous euxinic pyrite burial during the SPICE under generally low levels of 133 sulphate. 134 Additional evidence for the expansion of euxinic conditions comes from the 135 coeval Alum Shale in Sweden, where a systematic decrease in molybdenum enrichment 136 coincides with the SPICE (Figure 3). Molybdenum is a transition metal, typically enriched in organic-rich sediments deposited under euxinic conditions^{18,19}. The 137 138 variability in molybdenum concentrations occurs despite iron proxy data that indicate

139 persistent euxinia over the interval of interest (Figure 3); the Alum basin appears to have 140 been locally euxinic before, during and after the SPICE. The suggestion then is that 141 another process drove the scale of enrichment. In short, the decline going into the SPICE 142 and increase coming out argue for a decrease in the global molybdenum inventory of seawater as the euxinic conditions expanded and then contracted on a global scale^{6,19,20} 143 144 — a scenario consistent with the predictions of the modeled C and S data. We envision 145 conditions during the SPICE to have been analogous to those during oceanic anoxic 146 events or OAEs of the Mesozoic, where the spread of euxinic conditions led to extensive 147 deposition of organic-rich, pyritic sediments in the deep ocean yielding concomitant isotopic shifts in dissolved inorganic carbon²¹ and seawater sulfate²². 148

The geochemical and stratigraphic framework of the SPICE provides new insight into the pronounced biological turnover associated with this event. Taken together with evidence for sea-level rise, the geochemical data suggest that shoaling of toxic anoxic deep waters onto the shelf led to the extinction of shelf fauna, a situation similar to that envisioned for end-Permian extinctions²³. Such a scenario was proposed previously to explain recurrent later Cambrian trilobite extinctions¹² but in acknowledged absence of independent constraints for such conditions.

Additional oscillations observed in the later Cambrian marine δ^{13} C record could reflect environmental perturbations similar to the SPICE. We suggest that anoxic water masses occurred widely in the subsurface of the later Cambrian ocean (i.e., below the wind-mixed surface layer), a view that finds qualitative support in the stratigraphic distribution of organic-rich, pyritic black shales, which peak in abundance in later

161	Cambr	ian successions ²⁴ . If correct, the high rates of biological turnover ²⁵ and repeated
162	trilobit	e extinctions ^{12,26} documented for later Cambrian fossils find at least partial
163	explan	ation in episodic expansion of oxygen-depleted waters. In larger terms, broad
164	pattern	s of Cambrian animal evolution may reflect persistent oxygen deficiency in
165	subsurface waters of Cambrian oceans, shedding new light on early evolution of the	
166	Phanerozoic biosphere in the wake of late Proterozoic oxygenation.	
167 168 169	Refere	ences
170	1	Hough, M. L. et al. A major sulphur isotope event at c. 510 Ma: a possible
171		anoxia-extinction-volcanism connection during the Early-Middle Cambrian
172	2	transition? <i>Terra Nova</i> 18 , 257-263 (2006).
173	2	Hurtgen, M. T., Pruss, S. B. & Knoll, A. H. Evaluating the relationship between
174		the carbon and sulfur cycles in the later Cambrian ocean: An example from the
175		Port au Port Group, western Newfoundland, Canada. <i>Earth Planet. Sci. Lett.</i> 281 ,
I/6	3	288-297 (2009).
1//		Znuravlev, A. & Wood, R. Anoxia as the cause of the mid-Early Cambrian (Determine) estimation exact C_{1} and 24 211 214 (1000)
1/8	4	(Botomian) extinction event. Geology 24, 311-314 (1996).
1/9		(1008)
180	5	Poulton S W Fralick P W & Canfield D F The transition to a sulphidic
182		α ocean ~1 84 billion years ago Nature 431 173-177 (2004)
183	6	Scott C et al. Tracing the stepwise oxygenation of the Proterozoic ocean Nature
184		452 456-459 (2008)
185	7	Brasier M D Corfield R M Derry L A Rozanov A Y & Zhuravley A Y
186		Multiple δ^{13} C excursions spanning the Cambrian explosion to the Botomian crisis
187		in Siberia <i>Geology</i> 22 , 455-458 (1994).
188	8	Saltzman, M. R., Runnegar, B. & Lohmann, K. C. Carbon isotope stratigraphy of
189		Upper Cambrian (Steptoean Stage) sequences of the eastern Great Basin: Record
190		of a global oceanographic event Geol. Soc. Am. Bull. 110, 285-297 (1998).
191	9	Montanez, I. P., Osleger, D. A., Banner, J. L., Mack, L. E. & Musgrove, M.
192		Evolution of the Sr and C isotope composition of Cambrian Oceans. GSA Today
193		10 , 1-7 (2000).
194	10	Saltzman, M. et al. A global carbon isotope excursion (SPICE) during the Late
195		Cambrian: relation to trilobite extinctions, organic-matter burial and sea level.
196		Palaeogeogr. Palaeoclimatol. Palaeoecol. 162, 211-223 (2000).

197	11	Saltzman, M. R. <i>et al.</i> The Late Cambrian SPICE (δ^{13} C) Event and the Sauk II-
198		SAUK III Regression: New Evidence from Laurentian Basins in Utah, Iowa and
199		Newfoundland. J. Sed. Res. 74, 366-377 (2004).
200	12	Palmer, A. The Biomere Problem: Evolution of an Idea. <i>Journal of Paleontology</i>
201		58 , 599-611 (1984).
202	13	Peng, S. <i>et al.</i> Global Standard Stratotype-section and Point of the Furongian
203		Series and Paibian Stage Cambrian. Lethaia 37 , 365-379 (2004).
204	14	Brennan S T Lowenstein T K & Horita J Seawater chemistry and the advent
205		of biocalcification <i>Geology</i> 32 473-476 (2004)
206	15	Gill B C Lyons T W & Saltzman M R Parallel high-resolution carbon and
200		sulfur isotone records of the evolving Paleozoic marine sulfur reservoir
208		Palaeogeogr Palaeoclimatol Palaeoecol 256 156-173 (2007)
200	16	Berner R Sedimentary pyrite formation: An undate <i>Geochim Cosmochim Acta</i>
20)		48 605-615 (1984)
210	17	Neretin I N Volkov I I Böttcher M F & Grinenko V A A sulfur hudget
211 212		for the Black Sea anoxic zone Deen-Sea Research Part 148 2569-2593 (2001)
212	18	Emerson S & Huested S Ocean anoxia and the concentrations of molybdenum
213		and vanadium in seawater Mar Cham 34 177-196 (1991)
214	19	Algeo T I & Lyons T W Mo_total organic carbon covariation in modern
215		anovic marine environments: Implications for analysis of paleoredox and
210		naleohydrographic conditions. <i>Paleoceanaranhy</i> 21 , 23 (2006)
217	20	Algeo T I Can marine anoxic events draw down the trace element inventory of
210		segurater? <i>Coology</i> 32 1057 1060 (2004)
219	21	Arthur M A Doon W E & Brott I M Goodhamical and alimatic affacts of
220		increased marine organic earbon buriel at the Conomanian/Turonian boundary
221		Nature 335 714 717 (1089)
222	22	Adams D. D. Hurtson M. T. & Sagaman P. P. Valaania triagaring of a
223		Adams, D. D., Hungell, W. T. & Sagellian, D. D. Volcanic unggening of a
224		(2010)
223	23	(2010). Wignall D. D. & Twitchett, D. I. Occanic Anavia and the End Dermian Mass
220		Extinction Science 272, 1155, 1159 (1006)
227	24	Extinction. Science 212, 1153-1156 (1990).
228		Berry, W. B. N. & Wilde, P. Progressive ventilation of the oceans; an explanation
229		for the distribution of the lower Paleozoic black shales. Am. J. Sci. 278, 257-275
230	25	(1978). Developed D. K. Knell A. H. & Weng, C. C. Origination and many
231		Bambach, R. K., Knoll, A. H. & Wang, S. C. Origination, extinction, and mass
232	26	depletions of marine diversity. <i>Paleobiology</i> 30 , 522-542 (2004).
233	20	Palmer, A. R. Biomere: A New Kind of Biostratigraphic Unit. <i>Journal of</i>
234	27	Paleontology 39 , 149-153 (1965).
235	2.8	Scotese, C. K., Atlas of Earth History (Arlington, Texas, 2001).
236	20	Aniberg, P. et al. Cambrian high-resolution biostratigraphy and carbon isotope
237		chemostratigraphy in Scania, Sweden: first record of the SPICE and DICE
238		excursions in Scandinavia. Lethaia, 13 (2008).

239 240	²⁹ Lyons, T. W. & Severmann, S. A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins. <i>Geochimica Cosmochimica Acta</i> 70 ,
241	5698-5722 (2006).
242	³⁰ Raiswell, R., Buckley, F., Berner, R. A. & Anderson, T. F. Degree of pyritization
243	of iron as a paleoenvironmental indicator of bottom-water oxygenation. J. Sed.
244	Res. 58, 812-819 (1988).
245	
246	Author contributions BCG, TWL, MRS, SY collected samples used in this study. BCG
247	did the chemical analyzes and collected mass spectrometer and ICP-MS data. BCG and
248	LRK built the geochemical box model. BCG wrote the manuscript, with contributions
249	from TWL, AHK and LRK. All the authors contributed to discussion and interpretations.
250	,
251	Acknowledgements NSF-EAR and NASA Astrobiology provided funding. Fieldwork
252	and sample collection were aided by S. Bates, L. Bongers, H. Dayton, S. Mason, P.
253	McGoldrick, J. Owens, C. Seeger, E. Starbuck. Sulphur isotope analyzes were aided by
254	S. Bates and W. Gilhooly. Discussions with G. Love, N. Hughes, D. Johnston, P. Cohen
255	and T Dahl improved the manuscript
256	······································
257	Figure captions
20 /	
258	
259	Figure 1. Paleo-reconstruction of the later Cambrian Earth ²⁷ showing locations where the
260	SPICE has been identified (filled circles). Locations investigated in this study: Western
261	Laurentia (WL) — Shingle Pass and Lawson Cove, Great Basin USA; Eastern Laurentia
262	(EL) — TE-1 Texas County Core, Missouri, USA; Gondwana (GD) — Mount Whelan
	· · · · · · · · · · · · · · · · · · ·
263	#1 and Mount Murray, Queensland, Australia; Baltica (BL) — Andrarum #3 core,
264	Sweden.
265	
266	Figure 2: Chemostratigraphies of the studied carbonate sections. Isotope data are plotted
267	by stratigraphic height in meters. International series and stages are based on published
268	biostratigraphy and most recent definitions of the subdivisions of the Cambrian (see

269 Supplementary Material). Carbon isotopes profiles from Single Pass and Lawsons Cove

sections and Mt. Whelan #1 core are from references 8 and 10, respectively. The CAS
sulphur isotope profile from Shingle Pass is from reference 15.

272

273 Figure 3: Chemostratigraphic data from the Alum Shale, Andrarum #3 Core, Sweden. 274 Molybdenum, molybdenum/total organic carbon (Mo/TOC), total iron and aluminum and 275 iron speciation data are plotted along side organic carbon and pyrite sulphur isotope data. 276 Carbon isotope profile is from reference 28. Since Mo covaries with the concentration of organic matter in sediments¹⁹, Mo concentrations have been normalized to TOC to 277 278 correct for variations in organic content. Shaded regions of the degree of pyritization 279 (DOP), Fe_{py}/Fe_{HR}, Fe_{HR}/Fe_T and Fe/Al plots display values that indicate anoxia and 280 euxinia: Fe_T/Al values above 0.5 and Fe_{HR}/Fe_T above 0.4 indicate deposition under anoxic water columns²⁹, and DOP and Fe_{pv}/Fe_{HR} values above 0.75 are conservatively 281 diagnostic of euxinic environments³⁰. Note that the decrease and minimum in Mo and 282 283 Mo/TOC correspond to the initiation and peak of the carbon and sulfur isotope 284 excursions, respectively.

285

Figure 4: Examples of the modeled carbon and sulfur isotope composition of the ocean during the SPICE. The sulfur isotope plot shows the effect of varying the magnitude of the transient increase in pyrite burial. In these simulations the burial of rates organic carbon and pyrite sulfur were increased for a half million years to create the isotope excursions. Organic carbon burial was doubled from 4.1*10¹⁸ to 8.2*10¹⁸ moles/Myrs and pyrite burial was increased from the steady state rate (0.98*10¹⁸ moles/Myrs) by the

- 292 factors listed in the legend. Values in parenthesis are the molar carbon to sulfur (C/S)
- 293 ratios of the transient burial fluxes introduced into the model. The starting marine sulfate
- concentration in these simulations was 1.5 mM.
- 295
- 296
- 297

Figure 1











