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Sulphur isotope evidence for widespread euxinia in the Later Cambrian ocean

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Global-scale anoxia in the deep ocean is frequently invoked as a primary driver of mass extinction, as well as a long-term inhibitor of evolutionary radiation on the early Earth. In recent biogeochemical studies, it has been hypothesized that oxygen deficiency was widespread in subsurface water masses of later Cambrian oceans[1,2], possibly influencing evolutionary events during this time[1,2,3]. Physical evidence of widespread anoxia in Cambrian oceans has remained elusive, and thus its potential relationship to the paleontological record remains largely unexplored. Here, we present sulphur isotope records from six globally distributed stratigraphic sections of later Cambrian marine rocks (ca. 499 million years old) that show a positive excursion in phase with the well-known Steptoean Positive Carbon Isotope Excursion (SPICE). Numerical box modeling of the paired carbon-sulphur isotope

data indicates that these isotope shifts reflect transient increases in the burial of organic carbon and pyrite sulphur in sediments deposited under ocean-scale anoxic and sulphidic (euxinic) conditions. Independently, molybdenum abundances in a coeval black shale point convincingly to ocean-scale anoxia. These results identify the SPICE interval as the best characterized ocean anoxic event in the pre-Mesozoic 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 persisted or returned in the oceans of the early Phanerozoic Eon. Indeed, the environmental challenges presented by widespread anoxia may have been a prevalent if not dominant influence on animal evolution in Cambrian oceans.

Carbonate rocks of Cambrian age preserve large, rapid (of a few million years 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 mechanisms that drove these events, however, are poorly known. What makes these excursions particularly interesting to geobiologists is the observation that many coincide 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 period, the Steptoean Positive Carbon Isotope Excursion, or SPICE.

The SPICE is recorded as a +4-6‰ shift in $\delta^{13}C_{carb}$ that occurs globally in later Cambrian successions (at the beginning of the Furongian International Series and Paibian International Stage, 499 Ma); it is thought to have lasted on the order of 2-4 million years[10,11]. A well-documented extinction of trilobites coincides with the onset of the SPICE on the paleocontinent of Laurentia[10,12], and the isotopic excursion has also been correlated to intervals of biological turnover on other paleocontinents[13]. The SPICE is also coincident with global changes in sea level; its onset coincides with a transgressive event, and its peak is concurrent with a lowstand recorded as the Sauk-II/III hiatus[10,11].

We report sulphur isotope data from six globally distributed stratigraphic sections across the SPICE, and each reveal parallel, positive carbon and sulphur isotope excursions (Figures 1, 2 and 3). These sections represent diverse sedimentary environments; thus, similarities among the trends despite differences in depositional conditions speak to the global and primary nature of the geochemical signals (see Supplementary Materials for details of individual stratigraphic sections and data supporting the preservation of the geochemical signals).

The SPICE sulphur isotope excursion is one of the largest identified in the geologic record and is the first to be correlated globally at this scale of resolution. This excursion occurs in both carbonate-associated sulphate (CAS) and pyrite, which further supports a primary marine signal, and its magnitude indicates a major perturbation in the global sulphur cycle. There are, however, significant differences in the details of the sulphate sulphur isotope trends among basins. In particular, the pre-event $\delta^{34}S_{CAS}$ baseline differs among the various locations (Figure 2). While some records show relatively steady sulphur isotope values before the excursion (i.e., western and eastern Laurentia), the Gondwanan data show a positive trend up section before the excursion (Figure 2).

Despite overarching similarities, the absolute values and amplitudes of the excursion also differ among the studied basins. The Gondwanan record is the most extreme, with $\delta^{34}S_{CAS}$ values reaching almost +70‰ and an amplitude of +35‰ (Figure 2). On the other end of the spectrum, the record in eastern Laurentia shows a peak value of +38‰ and amplitude of only +12‰ (Figure 2). These isotopic differences support the idea that the sulphur reservoir in the later Cambrian ocean was spatially heterogeneous and that sulphate concentrations were therefore low[14,15]. We also observe that the sulfate isotope excursion peaks stratigraphically slightly before the carbon isotope maximum (see Supplementary Figure S2), which suggests that the sulphate reservoir was relatively more sensitive to change than the marine pool of dissolved inorganic carbon (DIC). This state of sulphate in later Cambrian seawater differs greatly from the modern reservoir, which is relatively homogenous globally with a concentration of 28 mmol/kg (mM) and a sulphur isotope composition of +21‰. This contrast with the modern ocean indicates that the residence time of sulphate in the Cambrian ocean was much shorter.

The parallel behavior between the carbon and sulphur isotope excursions (Figures 2 and 3) suggests that the SPICE records a transient increase in the amount of carbon and sulphur buried as organic matter and pyrite (FeS_2) in marine sediments. Such parallel burial occurs in anoxic marine sediments and beneath euxinic water columns[16] — that is, beneath water columns that are both anoxic and contain free hydrogen sulphide. Organic matter fuels microbial sulphate reduction (MSR), and pyrite is formed when H_2S produced from MSR reacts with iron minerals and is buried along with the residual organic matter. Ultimately, the burial of both species results in the removal of carbon and sulphur from the ocean. This coupling can result in positive isotope shifts for both species in seawater: the carbon and sulphur leaving the ocean through burial are enriched in ^{12}C and ^{32}S via isotope fractionations accompanying photosynthetic and MSR pathways, respectively, leaving the seawater correspondingly enriched in ^{13}C and ^{34}S.

We tested this hypothesis by modeling the ocean inventories of carbon and sulphur during the SPICE. Specifically, we constructed a simple box model that simulates the cycling of each element in the ocean (see Supplementary Material for details). The model shows that the isotope excursions can be replicated by transiently increasing the amount of organic carbon buried by factors of 1.5 to 2.5 and pyrite sulphur by factors of 2.5 to 4.5 for a duration of 0.5 to 1.5 million years (Figure 4: see Supplementary Material for additional model details).

Importantly, our model puts quantitative constraints on the size of the marine sulphate reservoir during the later Cambrian. An assumption of pre-SPICE sulphate concentrations greater than 2.5 mM demands more than 8 million years for recovery of $\delta^{34}S_{sulphate}$ (i.e., return to the pre-event baseline) following the SPICE (Figure S13), which is unreasonable in light of the available constraints on the duration of the SPICE[11]. Our simulations suggest, therefore, that the concentration of seawater sulphate was very low — at or below the low end of the 2-12 mM range suggested by previous work[14,15].

Another important result from the model is that the predicted ratio of carbon-to-sulphur (C/S) linked to this transient burial was very low: 1 to 4 moles C/mole S or 0.4-1.5 g C/g S (Figure 4). In younger sediments, similar C/S ratios are only observed in sediments deposited under euxinic conditions[16]. The scale of this Cambrian euxinia is 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 to 50-75 times that of the euxinic portion Black Sea[17], thus providing the first quantitative evidence for global-scale euxinia in the Paleozoic ocean.

Our argument for increased euxinia becomes stronger when we consider that ΔS may have decreased over the event (Figure 2). ΔS is the isotopic offset between coexisting CAS and pyrite ($\Delta\delta^{34}S_{CAS\text{-}pyrite}$) that results from MSR and related microbial pathways that lead to pyrite formation. For the two sections that have sufficient pyrite for 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). Importantly, a smaller ΔS, when applied to our model, requires greater pyrite burial to explain the positive sulphur excursion. The further increase in pyrite burial results in an even lower mean C/S ratio, strengthening the case for burial under euxinic conditions (see Supplementary Figure S14 for sensitivity tests of ΔS). Our Cambrian sulphur isotope data must record a decrease in seawater sulphate concentration associated with voluminous euxinic pyrite burial during the SPICE under generally low levels of sulphate.

Additional evidence for the expansion of euxinic conditions comes from the coeval Alum Shale in Sweden, where a systematic decrease in molybdenum enrichment coincides with the SPICE (Figure 3). Molybdenum is a transition metal, typically enriched in organic-rich sediments deposited under euxinic conditions[18,19]. The variability in molybdenum concentrations occurs despite iron proxy data that indicate persistent euxinia over the interval of interest (Figure 3); the Alum basin appears to have been locally euxinic before, during and after the SPICE. The suggestion then is that another process drove the scale of enrichment. In short, the decline going into the SPICE 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] — a scenario consistent with the predictions of the modeled C and S data. We envision conditions during the SPICE to have been analogous to those during oceanic anoxic events or OAEs of the Mesozoic, where the spread of euxinic conditions led to extensive deposition of organic-rich, pyritic sediments in the deep ocean yielding concomitant isotopic shifts in dissolved inorganic carbon[21] and seawater sulfate[22].

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 extinctions[23]. Such a scenario was proposed previously to explain recurrent later Cambrian trilobite extinctions[12] but in acknowledged absence of independent constraints for such conditions.

Additional oscillations observed in the later Cambrian marine $\delta^{13}C$ 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

Cambrian successions[24]. If correct, the high rates of biological turnover[25] and repeated trilobite extinctions[12,26] documented for later Cambrian fossils find at least partial explanation in episodic expansion of oxygen-depleted waters. In larger terms, broad patterns of Cambrian animal evolution may reflect persistent oxygen deficiency in subsurface waters of Cambrian oceans, shedding new light on early evolution of the Phanerozoic biosphere in the wake of late Proterozoic oxygenation.

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Author contributions BCG, TWL, MRS, SY collected samples used in this study. BCG did the chemical analyzes and collected mass spectrometer and ICP-MS data. BCG and LRK built the geochemical box model. BCG wrote the manuscript, with contributions from TWL, AHK and LRK. All the authors contributed to discussion and interpretations.

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Figure captions

Figure 1. Paleo-reconstruction of the later Cambrian Earth[27] showing locations where the SPICE has been identified (filled circles). Locations investigated in this study: Western Laurentia (WL) — Shingle Pass and Lawson Cove, Great Basin USA; Eastern Laurentia (EL) — TE-1 Texas County Core, Missouri, USA; Gondwana (GD) — Mount Whelan #1 and Mount Murray, Queensland, Australia; Baltica (BL) — Andrarum #3 core, Sweden.

Figure 2: Chemostratigraphies of the studied carbonate sections. Isotope data are plotted by stratigraphic height in meters. International series and stages are based on published biostratigraphy and most recent definitions of the subdivisions of the Cambrian (see Supplementary Material). Carbon isotopes profiles from Single Pass and Lawsons Cove

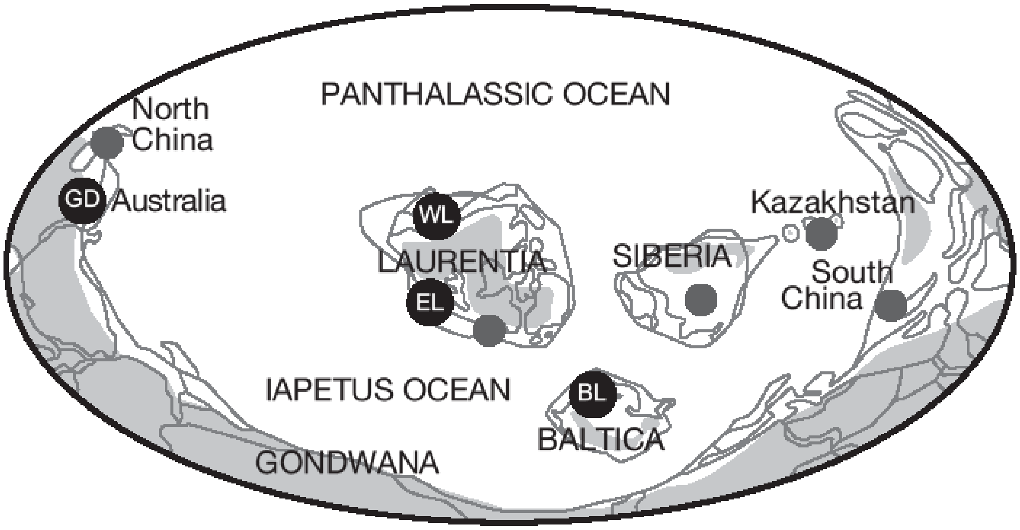
sections and Mt. Whelan #1 core are from references 8 and 10, respectively. The CAS sulphur isotope profile from Shingle Pass is from reference 15.

Figure 3: Chemostratigraphic data from the Alum Shale, Andrarum #3 Core, Sweden. Molybdenum, molybdenum/total organic carbon (Mo/TOC), total iron and aluminum and iron speciation data are plotted along side organic carbon and pyrite sulphur isotope data. Carbon isotope profile is from reference 28. Since Mo covaries with the concentration of organic matter in sediments[19], Mo concentrations have been normalized to TOC to correct for variations in organic content. Shaded regions of the degree of pyritization (DOP), Fe_{py}/Fe_{HR}, Fe_{HR}/Fe_T and Fe/Al plots display values that indicate anoxia and euxinia: Fe_T/Al values above 0.5 and Fe_{HR}/Fe_T above 0.4 indicate deposition under anoxic water columns[29], and DOP and Fe_{py}/Fe_{HR} values above 0.75 are conservatively diagnostic of euxinic environments[30]. Note that the decrease and minimum in Mo and Mo/TOC correspond to the initiation and peak of the carbon and sulfur isotope excursions, respectively.

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 $4.1*10^{18}$ to $8.2*10^{18}$ moles/Myrs and pyrite burial was increased from the steady state rate ($0.98*10^{18}$ moles/Myrs) by the

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

Figure 1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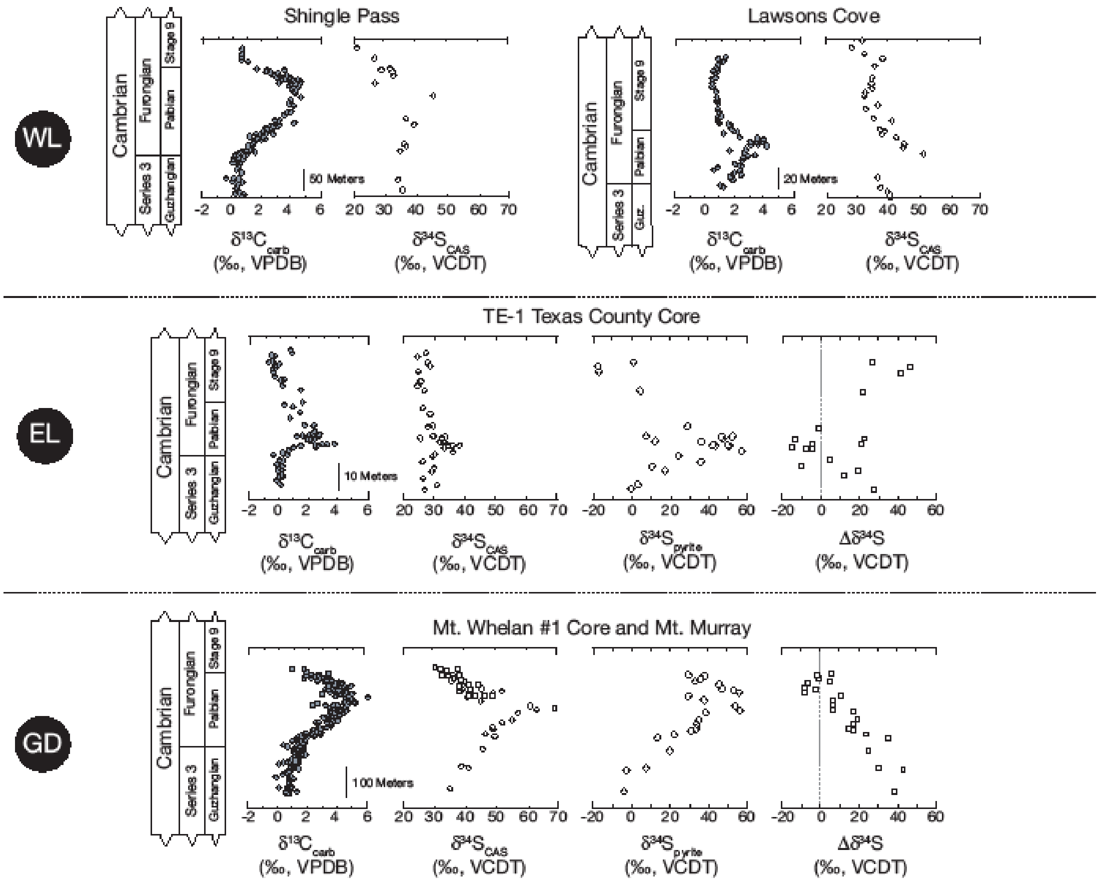
North China
GD
Australia
WL
LAURENTIA
EL
SIBERIA
Kazakhstan
South China
IAPETUS OCEAN
BL
BALTICA
GONDWANA

Figure 2


WL
Shingle Pass
Lawsons Cove
EL
TE-1 Texas County Core
GD
Mt. Whelan #1 Core and Mt. Murray
Cambrian
Series 3
Furongian
Guzhangian
Guz.
Paibian
Stage 9
50 Meters
20 Meters
10 Meters
100 Meters
$\delta^{13}C_{carb}$ (‰, VPDB)
$\delta^{34}S_{CAS}$ (‰, VCDT)
$\delta^{34}S_{pyrite}$ (‰, VCDT)
$\Delta\delta^{34}S$ (‰, VCDT)
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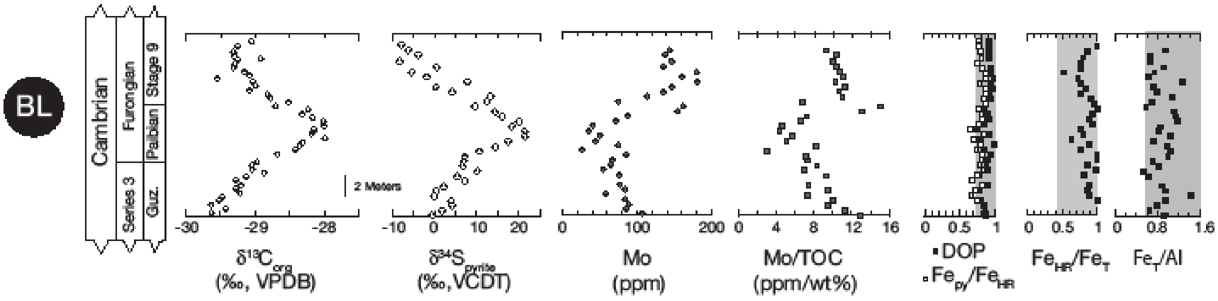
20 30 40 50 60 70
-20 0 20 40 60

Figure 3


BL
Cambrian
Furongian
Stage 9
Paibian
Series 3
Guz.
2 Meters
-30
-29
-28
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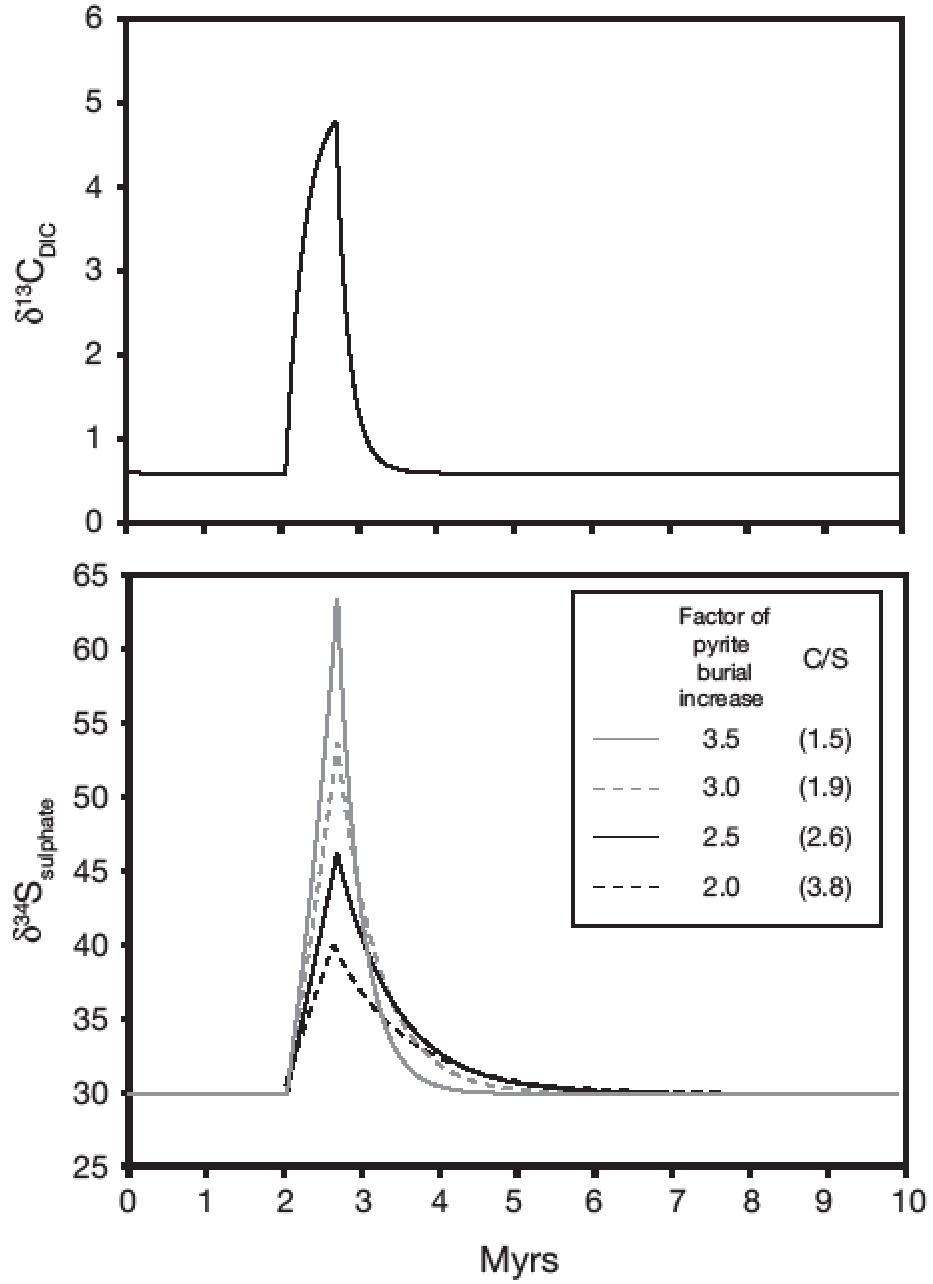
-10
0
10
20
$\delta^{34}S_{pyrite}$ (‰, VCDT)
0
100
200
Mo (ppm)
0
4
8
12
16
Mo/TOC (ppm/wt%)
0
0.5
1
■ DOP
□ Fe_{py}/Fe_{HR}
0
0.5
1
Fe_{HR}/Fe_T
0
0.8
1.6
Fe_T/Al

Figure 4



$\delta^{13}C_{DIC}$
0
1
2
3
4
5
6
$\delta^{34}S_{sulphate}$
25
30
35
40
45
50
55
60
65
Factor of pyrite burial increase
C/S
3.5
(1.5)
3.0
(1.9)
2.5
(2.6)
2.0
(3.8)
0
1
2
3
4
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7
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Myrs