Supplementary Material for

Rapid Variability of Seawater Chemistry Over the Past 130 Million Years

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Model Data and Code as zipped archives
1 Materials and Methods

Attempts to model the S-cycle date back to at least the 1970’s (29), and can be classified into three categories: 1) Models which use the turnover of pyrite as the main control on the marine $\delta^{34}$S ratio and ignore the effects of potential changes to the volcanic fluxes (see references in (30)); B) models which explicitly allow for variations in the volcanic fluxes (30); C) models which allow for variations of the seawater sulfate concentration and incorporate the feedbacks between sulfate concentration, organic matter remineralization, and pyrite burial flux. (11).

The burial flux of pyrite depends on the availability of organic matter (OM), the availability of reactive iron ($Fe_x$), and the availability of hydrogen sulfide. In the modern ocean, the capacity of marine sediments to form pyrite is limited by OM and, in select marine environments, reactive iron ($Fe_x$) availability (10, 31). Both variables scale with sedimentation rate. This implies that if we change the pyrite burial rate in response to increased $Fe_x$ availability, we also have to change the organic matter burial rate, which results in a positive coupling of the respective isotope signals (see (11) for an in depth discussion of this problem). No such positive coupling is observed for the $\delta^{34}$S excursions in the Early Cretaceous and Eocene. We therefore assume that there are no major global changes to the availability of $Fe_x$ and OM. Furthermore, we assume that pyrite weathering as well as the mantle degassing flux remain constant through time. This assumption is not meant to disregard changes to iron availability (31), the weathering and burial fluxes of pyrite, or changes to the hydrothermal flux. Clearly, all of these fluxes have changed through time. We impose this constraint rather to explore whether changes to the marine sulfate concentration are sufficient on their own to explain the observed $\delta^{34}$S-signature.

Using these assumptions, we can state the pyrite burial flux as a function of seawater-sulfate concentration. This relation was explored by (11) who used a reaction transport model to calculate the microbially mediated burial fluxes of $^{32}$SO$_4$ and $^{34}$SO$_4$ at discrete sulfate concentration values. The resulting data points can be approximated by a Monod type limiter function:

$$ FB_{py}(t) = a \frac{FB_{py}(t_0) \times [SO_4](t)}{b + [SO_4](t)} $$

where $FB_{py}$ denotes the pyrite burial flux in mol/yr, $[SO_4](t)$ the marine sulfate concentration in mM at a given time, and $FB_{py}(t_0)$ the pyrite
burial flux under steady state conditions. The coefficients $a$ and $b$ control
the overall range and steepness of the function respectively (see Fig. S1).
Previously published values for $a$ and $b$ were 1.0691 and 1.8685 respectively.
However, since we parametrize our model in such a way that it achieves
steady state under modern day conditions, the above parameters result in
a slight overestimation of the Cretaceous pyrite burial. We therefore adjust
this transfer function in such a way that our model is in steady state not
only in the modern ocean, but also for the Cretaceous ocean at the
beginning of our model run. We achieve this by using $a = 2.8$ and
$b = 1.0691$, which results in slightly lower pyrite burial rates (see Fig. S1).
We can thus formulate our model as

$$\frac{\partial [SO_4]}{\partial t} = FW_{Eva}(t) + FW_{Py}(t) + FW_V(t) - FB_{Py}([SO_4]) - FB_{Eva}(t)$$

(2)

Where $[SO_4]$ denotes the amount of $SO_4^{2-}$ in the ocean, $FW_{Eva}$, $FW_{Py}$
and $FW_V$ the input fluxes from the weathering of evaporites, pyrites, and
mantle degassing, $FB_{Eva}$ and $FB_{Py}$ the respective burial fluxes, and $t$
denotes time. Similar equations can be written for $^{32}S$ and $^{34}S$

$$\frac{\partial [^{32}SO_4]}{\partial t} = FW_{^{32}SO_4}(t) + FW_{Fe^{32}S_2}(t) + FW_{^{32}SO_4}(t)
- FB_{Fe^{32}S_2}([^{32}SO_4]) - FB_{^{32}SO_4}(t)$$

(3)

Where $[^{32}SO_4]$ denotes the mass the $^{32}S$ isotope in the marine sulfate pool,
$FW_{^{32}SO_4}$ the flux (i.e., mass/time) of the $^{32}S$ isotope from evaporite
weathering (and precipitation in the case of the FB prefix), $FW_{Fe^{32}S_2}(t)$
represents the flux of the $^{32}S$ isotope from pyrite weathering (and
precipitation in the case of the FB prefix), and $FW_{^{32}SO_4}(t)$ denotes the
flux of $^{32}S$ isotope from mantel degassing. We convert the total mass of
sulfur to the mass of $^{32}S$ with

$$^{32}S = \frac{S \times 1000}{r_0(\delta + 1000) + 1000}$$

(4)

where $\delta$ denotes $\delta^{34}S$ in the conventional delta formation, and $r_0$ the
absolute $^{34}S/^{32}S$ ratio of the respective international standard material,
and $S$ the mass of sulfur. We can now substitute Eq. (1) and Eq. (4) into
Eq. (3), and obtain

\[ \frac{\partial [^{32}SO_4]}{\partial t} = FW_{^{32}SO_4}(t) + FW_{Fe^{32}S_2}(t) + FW_{^{32}SO_4}(t) - a \frac{FB_{Fe^{32}S_2}(t_0) \times [^{32}SO_4](t)}{b + [^{32}SO_4](t)} \times 1000 - \frac{(\delta_{msr} + 1000)r_0 + 1000}{FB_{^{32}SO_4}(t)} \]

(5)

where the first line describes the sum of the $^{32}S$ input fluxes, the second line denotes the $^{32}S$ burial by pyrite as a function of seawater $^{32}S$ concentration, ($\delta_{msr}$) denotes the isotopic fractionation due to microbial sulfate reduction (MSR) between sulfate and sulfide, and the last line describes the removal of $^{32}S$ by evaporite precipitation; $t_0$ denotes the $^{32}S$ pyrite burial rate under steady state conditions. Note that in the above notation, changes to the isotopic composition of the fluxes are equivalent to changes of the flux ratios of $^{32}S$ and $^{34}S$. A similar equation can we written for $^{34}S$ if we replace Eq. (4) with

\[ ^{34}S = \frac{Sr_0(\delta + 1000)}{r_0(\delta + 1000) + 1000} \]

(6)

we convert these fluxes back into isotopic ratios using the conventional delta notation:

\[ \delta^{34}S = \frac{^{34}S}{r_0} \times 1000 \]

(7)

We scale all fluxes to achieve steady state under conditions which approximate modern day conditions, but we did not strive to match them exactly. Using an ocean volume of $1.38 \times 10^{18}$ m$^3$ (14), our model reaches steady state at a sulfate concentration of 28.186 mM, an evaporite burial flux of $1.1182 \times 10^{12}$ mol/year, a pyrite burial flux of $8.8235 \times 10^{12}$ mol/year, an volcanic flux of $0.5 \times 10^{12}$ mol/year, a pyrite weathering flux of $0.55 \times 10^{12}$ mol/year, and an evaporite weathering flux of $0.95 \times 10^{12}$ mol/year. Note that the global S-fluxes are generally not well known. Estimates for the pyrite burial flux e.g., vary from $0.48 \times 10^{12}$ mol/year to $1.3 \times 10^{12}$ mol/year (32–34). Our fluxes are thus well within the range of previously published flux estimates.

To achieve isotopic equilibrium, we assign the following isotopic ratios: Volcanic input 0 %o [VCDT], evaporite weathering 22 %o [VCDT], and pyrite weathering -17 %o [VCDT]. We prescribe the isotopic offset between ocean water and pyrite as $\delta_{msr} = -36$ %o, and assume that CaSO$_4$
precipitates in isotopic equilibrium with ocean water (i.e., the $\delta^{34}\text{S}$ of CaSO$_4$ is equal to the $\delta^{34}\text{S}$ of contemporaneous ocean water). Using these parameters, our steady state ocean attains a $\delta^{34}\text{S}$ ratio of 21.666 \%o [VCDT], which is close to the Cenozoic long term average(35). All model runs are started at 130 Ma with an initial sulfate concentration of 8 mM(11, 27). Note that during the Cretaceous weathering fluxes might have been lower than today (36), we therefore adjust the pyrite and evaporite weathering fluxes to 85\% percent of their modern value (see Fig. S2). Note that in order to fit the shape of the Eocene increase, we had to adjust the $\delta^{34}\text{S}$ ratio of the evaporitic weathering flux from 22 to 23\%o [VCDT] during the dissolution event. It is possible that this is a modeling artifact, however, it is noteworthy, that Latest Neoproterozoic/Early Cambrian evaporites(37) have elevated $\delta^{34}\text{S}$ ratios.

The actual marine $\delta^{34}\text{S}$ record contains signals of different magnitudes, which complicates comparison with our model data which are only a first order approximation. In order to dampen the contribution from lower order signals, we apply a moving average filter with a window width of 10 Myrs to both, the $\delta^{34}\text{S}$-data, and our model results.
2 Supplementary Figures
Figure S1: Limiter function used to describe the relation between pyrite burial and sulfate concentration(11). The parameter b refers to Eq. (1).
Figure S2: A) The model is forced by an evaporite precipitation event between 122 and 120 Ma and an evaporite dissolution event between 51 and 47 Ma. B) The dissolution event has a major impact on the $\delta^{34}$S ratio of the global S-weathering flux. The Cretaceous $\delta^{34}$S weathering flux ratio is slightly lower since we adjusted the pyrite and evaporite weathering flux proportionally to 85% of their modern value. See text for explanation.
3 Model Code and Data

The model code is available from Science online as a zip-archive (SM1220656.zip). This archive contains the following files:

- **COPYING**: The copyright statement. The code is released under the GNU GENERAL PUBLIC LICENSE, Version 2, June 1991. The full license text is also available at http://www.gnu.org/licenses/gpl-2.0.html. If you use our code, please acknowledge Wortmann & Paytan 2012.

- **sw_evolution_science.m**: The actual model code. The model is written using the public domain Matlab clone "Octave", which is available at http://www.gnu.org/software/octave/. It will run with version 3.6.1, but is likely to run with other versions too. The code is essentially Matlab compatible, but the compatibility has not been tested.

- **sw_functions.m**: A collection functions used by sw_evolution_science.m. The functions are Matlab compatible, but the structure of the function file is not.

- **adina.m**: Data from (16).

- **sw_evolution_long_pulse.csv**: Data file generated by sw_evolution_science.m, which contains all data used in this manuscript.

- **sw_evolution_long_pulse.eps**: Graphical output from sw_evolution_science.m in EPS format.

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References and Notes


13. Materials and methods are available as Supplementary materials on *Science* Online.


