

Biogeochemical cycles of carbon, sulfur, iron, and oxygen

Oxygen in our atmosphere is the most abundant electron acceptor involved with energy producing biogeochemical redox reactions (*i.e.*, $O_2 + 4e^- \leftrightarrow 2O^{2-}$). One would think that because iron is one of the most abundant elements on the Earth and it has two readily available redox states ($Fe^{3+} + e^- \leftrightarrow Fe^{2+}$) it too would be an important player (*i.e.*, ferric iron being an electron acceptor) affecting the amount of oxygen in the Earth's atmosphere. Iron is important, however also important is the redox reaction of sulfate to sulfide ($S^{6+} + 8e^- \leftrightarrow S^{2-}$). Iron and sulfur redox both involve reaction with diatomic oxygen molecules. For example, oxidation from Fe^{2+} to Fe^{3+} requires $1/4$ of an O_2 molecule, whereas oxidation from S^{2-} to S^{6+} takes 2 O_2 molecules. Redox of organic carbon and methane requires one to two O_2 molecules (e.g., C^0H_2O or C^4H_4 to $C^{4+}O_2$).

If we look at the occurrence of elements in the earth's crust, we see that O, C, Fe, and S are by far the most abundant redox sensitive elements. In biota, N and trace transition elements are important too, but we will ignore them for now because transition elements are not volumetrically large on the Earth's surface and most of the N is in the atmosphere as N_2 . Let's just first explore the coupling between Fe, O, and S.

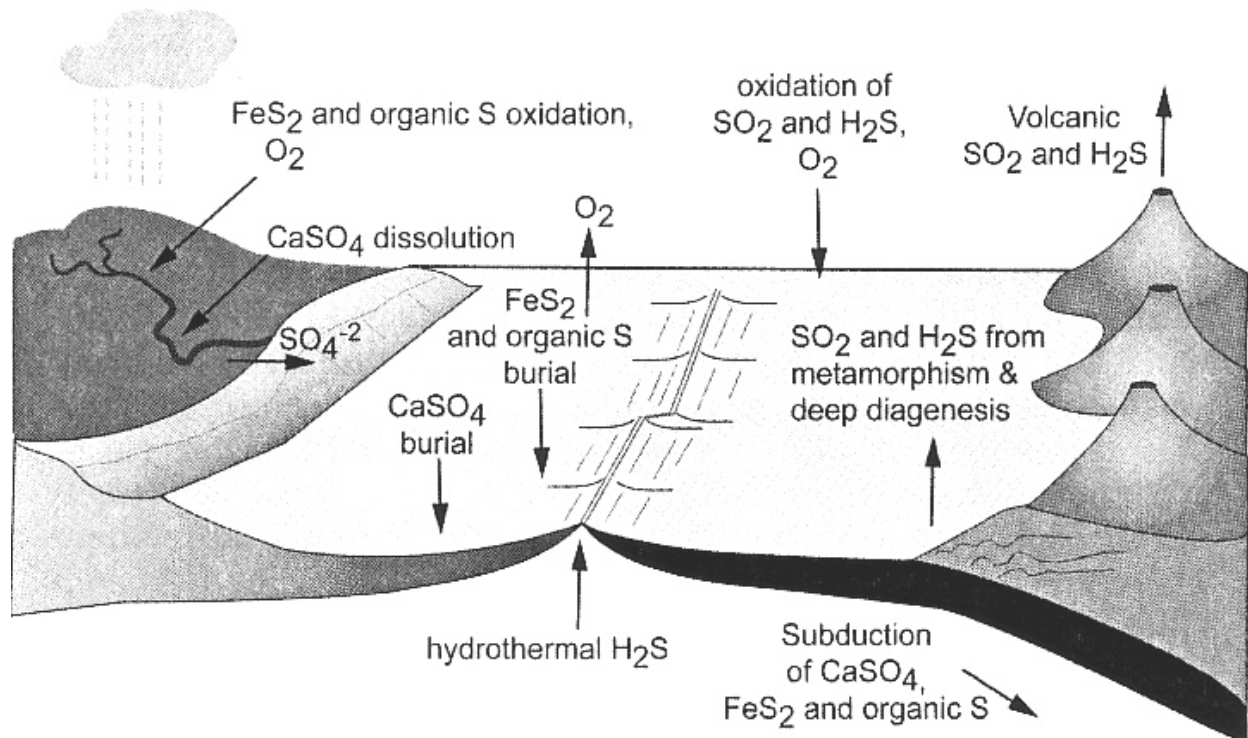
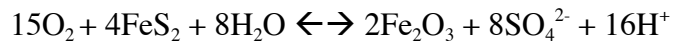


Figure 6.1. The long-term sulfur cycle. Downward pointing arrows associated with O_2 signify O_2 consumption; upward pointing arrows signify O_2 production.

For more details see the book by Robert Berner (2004) *The Phanerozoic Carbon Cycle: CO_2 and O_2* , Oxford University Press, 150 pp.

The major reactions involving the long-term sulfur cycle include the redox of iron, sulfur, and oxygen:



This reaction above can be thought of as the sum of several reactions (left \rightarrow right / left \leftarrow right) involving (1) plant photosynthesis/respiration or burial/weathering of organic matter, (2) bacterial sulfate reduction/sulfide oxidation, (3) sedimentary pyrite formation/pyrite reduction, and (4) the neutralization of acid and bicarbonate/dissociation of carbonic acid. The reactions for each are shown below.

- (1) $16\text{CO}_2 + 16\text{H}_2\text{O} \leftrightarrow 16\text{CH}_2\text{O} + 16\text{O}_2$
- (2) $16\text{CH}_2\text{O} + 8\text{SO}_4^{2-} \leftrightarrow 8\text{H}_2\text{S} + 16\text{HCO}_3^-$
- (3) $2\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{S} + \text{O}_2 \leftrightarrow 4\text{FeS}_2 + 8\text{H}_2\text{O}$
- (4) $16\text{H}^+ + 16\text{HCO}_3^- \leftrightarrow 16\text{CO}_2 + 16\text{H}_2\text{O}$

If we include the burial and weathering of carbonates:

Where:

Burial (left \rightarrow right)

Weathering (left \leftarrow right)

- (5) $16\text{Ca}^{2+} + 16\text{HCO}_3^- \xrightarrow{\text{Weathering}} 16\text{CaCO}_3 + 8\text{H}_2\text{O} \xrightarrow{\text{Burial}}$

Then we can combine the reactions of the carbon cycle and sulfur cycle to account for the burial and weathering of pyrite:

- (6) $2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2-} + 16\text{Ca}^{2+} + 16\text{H}^+ + 16\text{HCO}_3^- \leftrightarrow 16\text{CaCO}_3 + 15\text{O}_2 + 4\text{FeS}_2 + 16\text{H}_2\text{O}$

The balance of oxygen in the atmosphere over long periods of time can be expressed by the **balance between the burial** of organic matter (F_{bg}) and pyrite (F_{bp}) and the **weathering** of organic carbon (F_{wg}) and pyrite (F_{wp}).

This is expressed by the stoichiometry of the reactions, where $^{15}/_8$ is the ratio of oxygen to sulfate molecules,

$$\Delta\text{O}_2/\Delta t = F_{\text{bg}} - F_{\text{wg}} + (^{15}/_8) (F_{\text{bp}} - F_{\text{wp}})$$

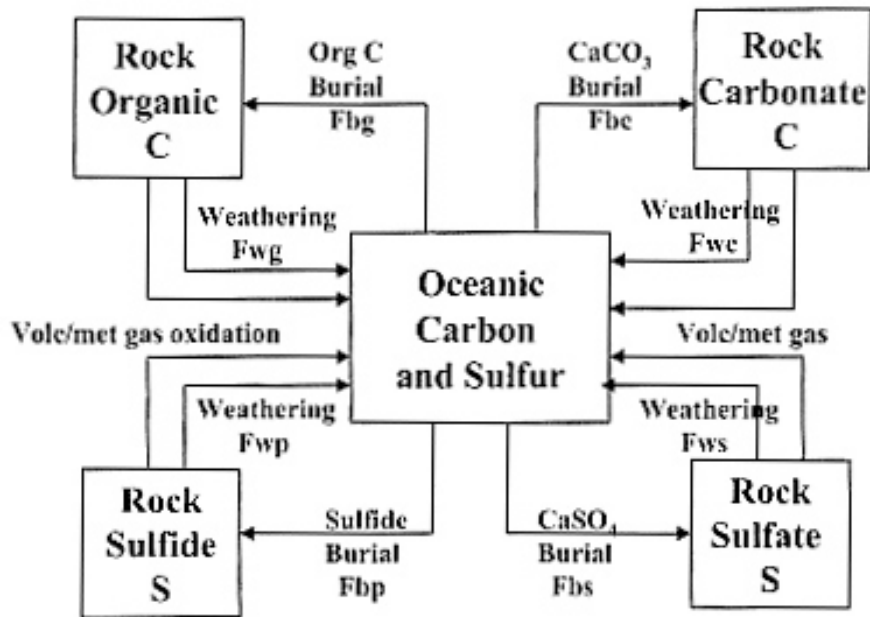


Figure 6.3. Isotope mass balance model for the carbon and sulfur cycles as they affect atmospheric oxygen.

where

M_s = mass of sulfur in the oceans (the total mass in the atmosphere, biosphere, and soils is by comparison negligible)

F_{wp} = sulfate flux from oxidative weathering of pyrite

F_{ws} = sulfate flux from weathering of Ca sulfates

F_{mp} = sulfur degassing flux for pyrite from volcanism, metamorphism, and diagenesis

F_{ms} = sulfur degassing flux for Ca sulfates from volcanism, metamorphism, and diagenesis

F_{bs} = burial flux of Ca sulfates in sediments

F_{bp} = burial flux of pyrite in sediments

$\delta = \left[\frac{^{34}\text{S}/^{32}\text{S}}{(^{34}\text{S}/^{32}\text{S})_{\text{std}}} - 1 \right] 1000$.

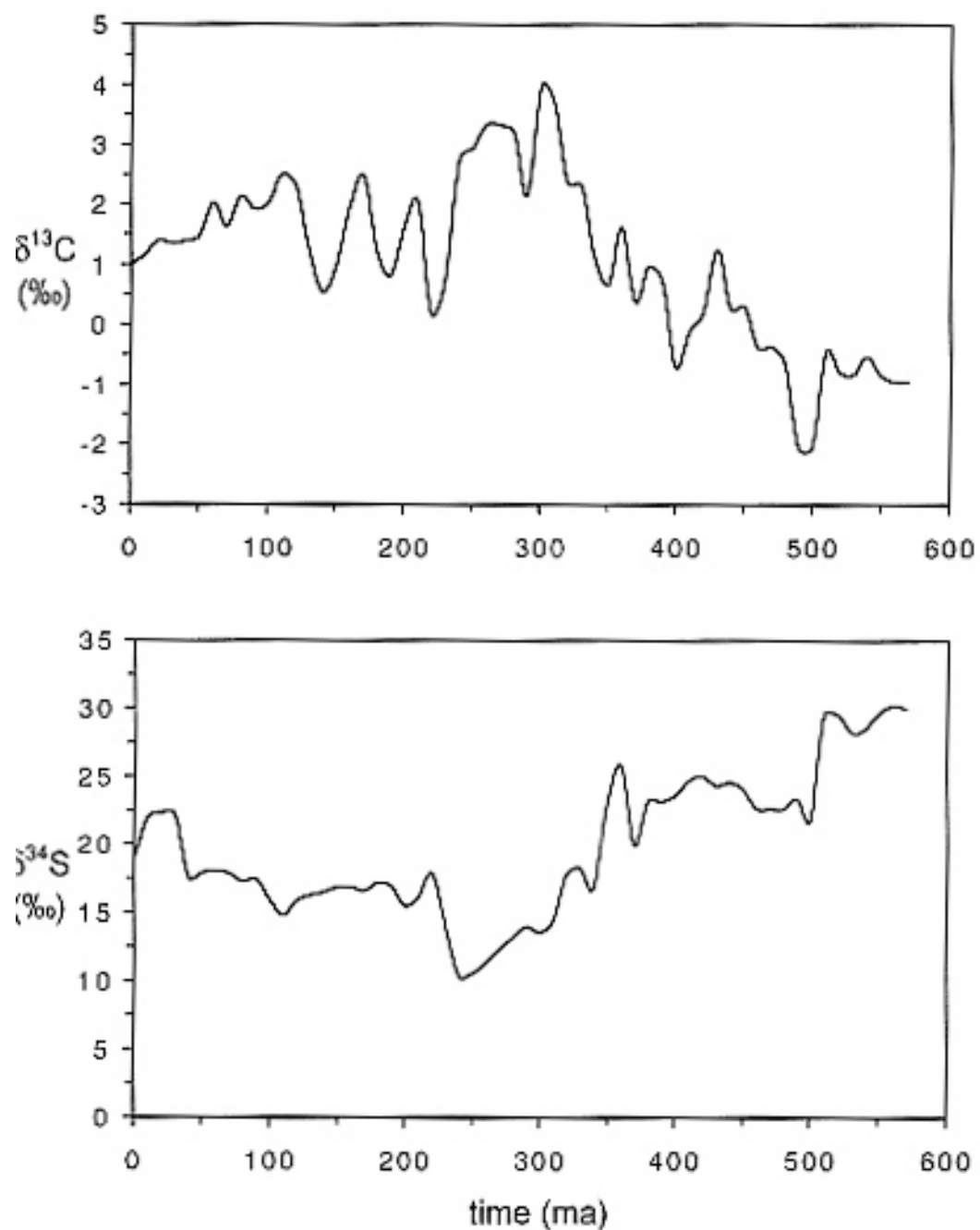


Fig. 1. The isotope records of Phanerozoic marine carbonates and evaporite gypsum (from Lindh, ms).

