Review: Rise of **oxygen**, Part I

- Photosynthesis active for >3.5 Ga (from $^{13}C/^{12}C$)
  - highly competitive due to substrate availability
  - dramatic change for life on earth due to oxygen toxicity
- Evidence for O_2 from **B**anded **I**ron **F**ormations (BIF)
  - $4\ Fe^{2+} + O_2 + 2\ H^+$ à $4\ Fe^{3+}$ ($\downarrow$) $+ 2\ OH^-$
- Rise of O_2 in atmosphere ~2.3 Ga ago (why then?)
  - BIFs diminish, continental "Red Beads" appear
  - Sulfate metabolism appears ($^{34}S/^{32}S$ evidence)

- Modern O_2 in atmosphere not balanced by organic carbon in atmosphere-ocean systems (only ~1%)
  - Most O_2 seems to be stored in Fe_2O_3 and SO_4^{2-}

is questionable

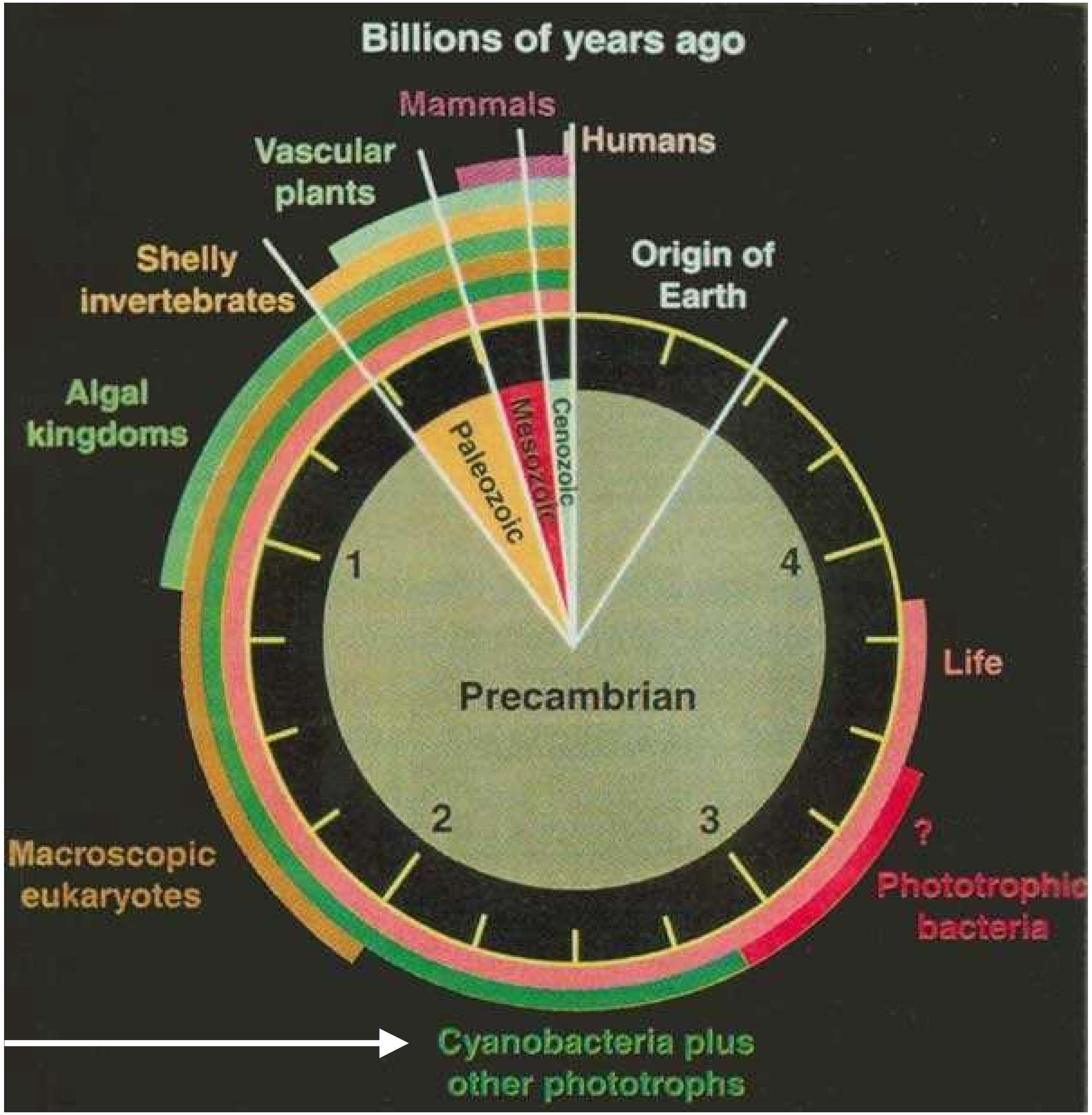


Table 1 Modern oxygen fluxes in the Earth system

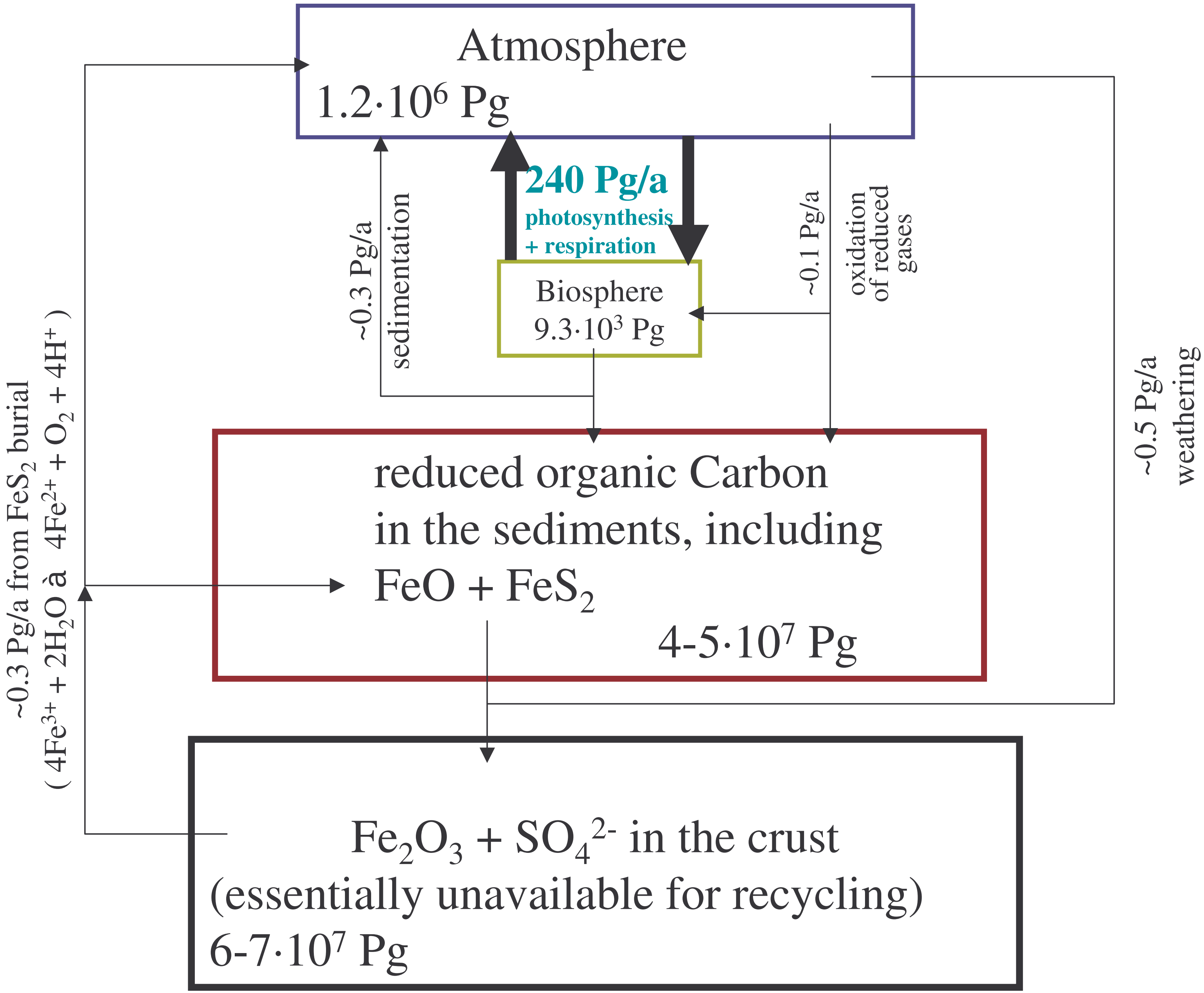
Oxygen fluxes	*Magnitude (10^{12} mol $O_2\ y^{-1}$)*	*Effect*
Organic carbon burial flux[a]	10 ± 3	Production
Pyrite (FeS_2) burial flux[a]	7.8 ± 3.6	Production
Sulfate burial flux[a]	$-(0.3 \pm 0.1)$	Loss
Reduced iron burial flux[a]	0.9 ± 0.4	Production
Continental oxidative weathering flux[a]	$-(15.5 \pm 6.7)$	Loss
Flux of reduced volcanic and metamorphic gases[a]	$-(3 \pm 1)$	Loss
Net O_2 photosynthetic flux to the atmosphere (assuming that burial fluxes and oxidative losses are balanced by negative feedbacks)	~ 0	Net change
Effective oxygen gain from hydrogen escape to space	0.02	Absolute gain for whole Earth

[a]Derived from data in Holland (1978).

Table 2 Reduced and oxidized reservoirs in Earth's continental crust. The Earth's exterior contains Fe_2O_3 and SO_4^{2-} that arose via oxidation, and free atmospheric O_2. Oxidized species are expressed in terms of the moles of O_2 required for their production; e.g., each mole of Fe^{3+} needed $\frac{1}{4}$ mole O_2 to be produced from Fe^{2+} via $FeO + \frac{1}{4}O_2 = \frac{1}{2}Fe_2O_3$. Reduced species are expressed in terms of O_2 moles required for their consumption; e.g., each mole of reduced carbon can be consumed by one mole of O_2

Species and reservoir	*Magnitude (10^{21} mol O_2 equivalent)*	*Size (R) comparisons[a]*
Oxidized species		
O_2 in the atmosphere and ocean	0.0378	$0.07\ R_{AOS}$
Fe_2O_3, SO_4^{2-}, and O_2 in the atmosphere–ocean–sedimentary (AOS) system	0.55	R_{AOS}
Total Fe^{3+} in the continental crust[b]	1.7–2.6	$(3.1 - 4.7)R_{AOS}$
Total oxygen locked up in the continental crust	2.0–2.9	$(1.5 - 2.2)R_{redC}$
Reduced species		
Reduced carbon in the AOS system	0.56	
Reduced carbon in felsic instrusives, gneisses, schists and felsic granulites	<0.78	
Total reduced carbon in the continental crust, R_{redC}	<1.3	R_{redC}

[a]AOS, atmosphere–ocean–sedimentary system; redC, reduced carbon in the centimental crupt.
[b]Most crustal oxidized iron, Fe^{3+}, resides not in sedimentary rocks but in continental basalt. Fe^{3+} derives from metamorphic or hydrothermal oxidation processes within the crust.



The modern O_2 cycle; amounts are in O_2 or O_2-equivalents

How did Earth "oxidize"?

- O_2 production should be balanced by consumption
  - for O_2 to rise, production must out-compete consumption
- no evidence for increased production from burial
  - O_2 sink(s) must have diminished

- $CO_2 + H_2O \leftrightarrow CH_2O$ (burial) $+ O_2$ (ocean)
- CH_2O (methanogenesis) à CH_4 ($\uparrow$) $+ CO_2$ (ocean)
- $CH_4 + h\upsilon$ (atmosphere) à 4 H + C à CO_2 ($\downarrow$)

- Net: Water + "biosphere" + light à O_2 + hydrogen (loss)
- à homework assignment

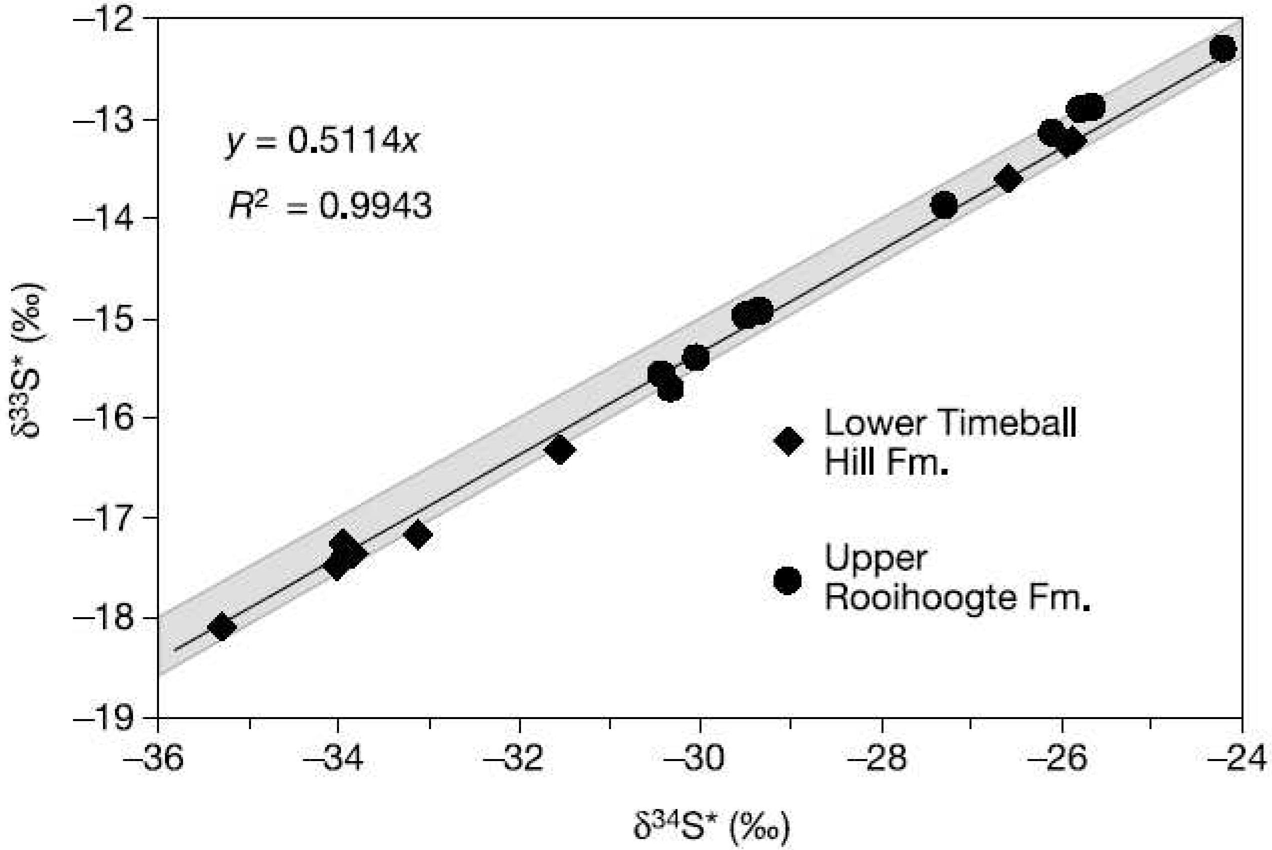


Figure 4 Plot of $\delta^{33}S^*$ versus $\delta^{34}S^*$ values in pyrite of the Rooihoogte and Timeball Hill formations. The grey area defines the field of isotopic data that can be produced by mass-dependent fractionation processes along the fractionation arrays with slopes ranging between 0.500 and 0.516 (ref. 35). Note that the $\delta^{33}S^*/\delta^{34}S^*$ ratio in the analysed samples lies on (or close to) the line of slope 0.5114.

Bekker *et al*., Nature 427, 2004