History of Earth Systems:

The biogeochemical cycling of Fe though time

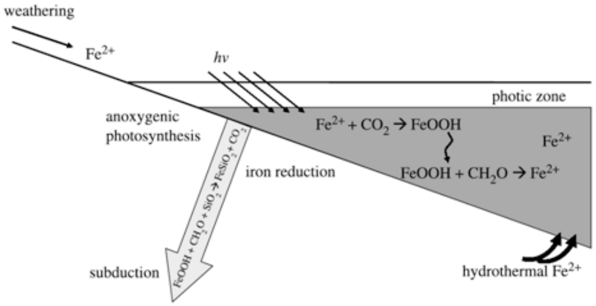
Silke Severmann

Ocean chemistry through time: what's changed (the most)?

Early ocean (Archean to Neoproterozoic)	Modern ocean (today)
pH = 8.0	pH = 8.0
T = 55°C	T = 25°C
HCO_3^- (CO^2) high	HCO_3^- (CO^2) high
SO_4^{2-} low	**SO_4^{2-} high (28mM)**
H_2S low during Archean ... but increasing in Neoproterozoic (?)	H_2S low (except for some isolated basins)
$Ca^{2+} \geq$ 10mM	Ca^{2+} 10mM
Fe^{2+} high (0.04-1mM Fe^{2+})	**Fe^{2+} low (0.1-10 nM Fe^{2+})**
Mo^{6+}, U^{6+} low	Mo^{6+} = 102 nM, U^{6+} =14 nM ("high")
Redox potential >0.0 to <0.4 V	Redox potential 0.80 V at surface (O_2)

Early Anaerobic metabolism

Canfield et al. (2006) Phil. Trans. R. Soc. B361, 1819-1836



Fe based ecosystems:

- Fe flux probably much higher and dominantly hydrothermal
- Fe^{2+} potentially a primary electron donor in early ocean (anaerobic phototrophic iron oxidation)
- Re-reduction of Fe by iron reducing bacteria, as well a geological recycling (subduction, metamorphism) of electron donors
- Could have generated1.7-5.0 x10^{14} mol C yr^{-1} (present day primary production rate is 4 x10^{15} mol C yr^{-1})

Biological transformation of iron: dissimilatory pathways

Anoxygenic ferrous iron oxidation by phototrophic bacteria

Widdel et al., Nature 362, 834 (1993)

$7 H_2O + 4 Fe^{2+} + CO_2 \rightarrow 4 FeOOH + CH_2O + 8 H^+$

Couple to nitrate reduction:

$10 FeCO_3 + 2 NO_3^- + 24 H_2O \rightarrow 10 Fe(OH)_3 + N_2 + 10 HCO_3^-$

Dissimilatory ferric iron reduction by chemolithotrophic bacteria

Lovley & Phillips, Nature 51, 683 (1988)

$CH_2O + 4 FeOOH + 7 H_2CO_3 \rightarrow 4 Fe^{2+} + 8 HCO_3^- + 6 H_2O$

Assimilatory iron utilization

For example, nitrate reduction by marine phototrophs is catalyzed by two iron containing enzymes:

$2 H^+ + NO_3^- + 2 e^- \xrightarrow[\text{reductase}]{\text{nitrate}} NO_2^- + 2 H_2O$ $8 H^+ + NO_2^- + 6 e^- \xrightarrow[\text{reductase}]{\text{nitrite}} NH_4^+ + 2 H_2O$

... and nitrogen fixation is catalyzed by an iron-sulfur containing enzyme (“The Fe hypothesis”):

$$N_2 + 8 H^+ \xrightarrow{\text{nitrogenase}} 2 NH_3 + H_2$$

Pyrite formation as an energy source for early life?

Wächtershäuser, System. Appl. Microbiol. 10, 207 (1988)
Drobner et al., Nature 346, 742 (1990).

Conversion of pyrrhotite to pyrite under strictly anaerobic conditions generates hydrogen, which could has served as fuel for early life:

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

Further, it provides a “functional evolutionary connection [...] between the hydrogen-producing system FeS-H_2S and the hydrogen-producing iron -sulphur centres of hydrogenase and nitrogenase.”

Passive (inorganic) pathways of iron mineral formation

Iron oxide precipitation:

$4 Fe^{2+} + 3 O_2 \rightarrow 2 Fe_2O_3$	Ferric oxide
$2 FeOOH + Fe^{2+} \rightarrow Fe_3O_4$	Magnetite (mixed valency!)

Iron carbonate precipitation:

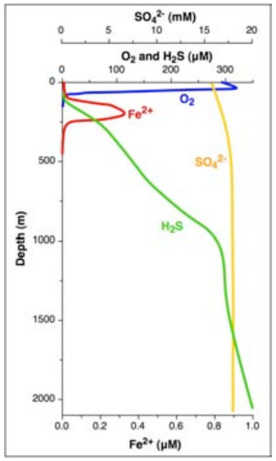
$Fe^{2+} + HCO_3^- + OH^- \rightarrow FeCO_3 + H_2O$	Siderite (ferrous)

Pyrite formation:

$Fe^{2+} + HS^- \rightarrow FeS + H^+$	“Iron monosulfide”
$FeS + S_n^{2-} \rightarrow FeS_2 + S_{n-1}^{2-}$	Pyrite

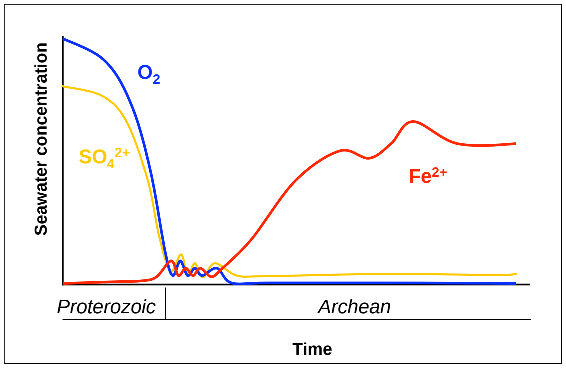
Iron solubility in seawater

Typical water column profile of the euxinic Black Sea (euxinic = sulfide is present in the water column)



Iron solubility is low in oxygenated as well as in sulfidic water
→ this leaves only a very narrow geochemical window for high dissolved iron concentrations!

Co-evolution of oceanic iron and sulfate through time



Disclaimer:
“Artists impression” - Details of this graph are subject to intense debate!

Banded Iron Formations (BIFs)

http://www.angelfire.com/rock3/michael/Interrocksmin.html

Alternating layers (mm to cm scale) of chert and Fe-bearing minerals, such as hematite, magnetite, siderite, pyrite.

http://www.eps.harvard.edu/people/faculty/hoffman/snowball_paper.html

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Iron mining in South Africa

http://web.uct.ac.za/depts/geolsci/dlr/hons1999/

At an average consumption of 150 kg/person/yr global iron resources from BIFs could last another 100,000 yrs.

When?

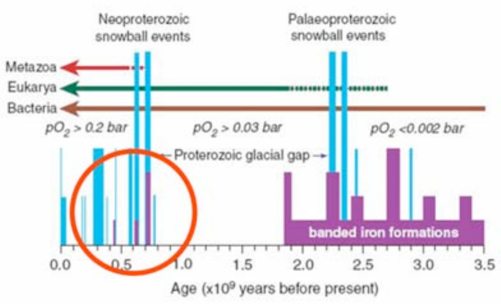


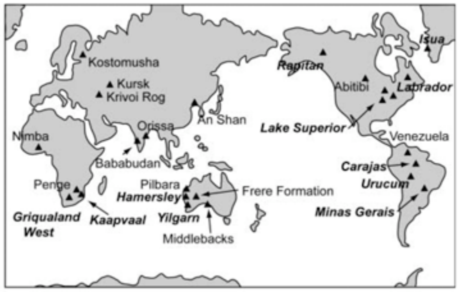
Fig. 12 Frequency of occurrence of iron formations (purple) (modified from Isley and Abbott, 1999), major glacial periods (blue) (Crowell, 1999), constraints on atmospheric oxygen levels (Rye and Holland, 1998), and steps in the history of life. Note the two eras of snowball events separated by a 1.5 billion year gap when evidence is lacking for glaciation at any latitude.

Oldest BIFs 3.75 Ga old from Nuvvuaqittuq supracrustal belt (NSB) in Northern Canada

Peak abundance between 2.7 and 2.5 Ga (“Great Oxidation Event” at 2.4 Ga)

Reoccurrence at 750 Ma after a long absence; last BIFs at 540 Ma, overlapping with 2nd major step in oxygenation.

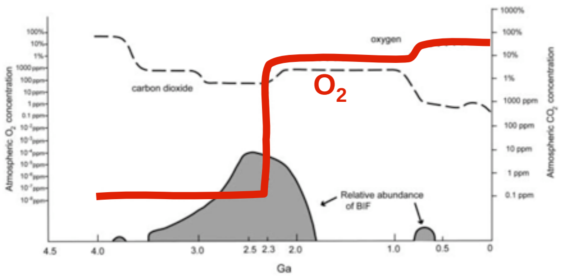
Where?



Precambrian BIFs
(from *Klein 2005*, modified after *Trendall 2002*)

Note: A very limited Archean rock record...

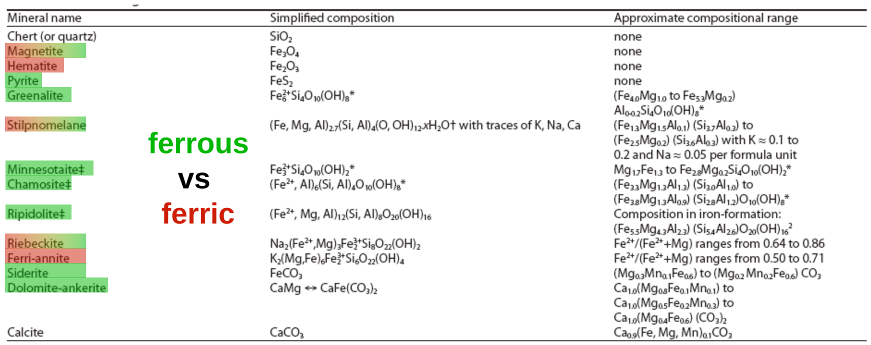
How?



The traditional view:

- BIFs are the manifestation of the evolution of oxygen producing photosynthesis - the dawn of the cyanobacteria.
- Accumulation of oxygen in the atmosphere and oceans causes precipitation of ferrous iron as Fe-oxide minerals.
- BIF deposition ceased when new steady state was reached (dcreasing hydrothermal Fe flux, increased weathering of ferric iron minerals).

What?



Mineral name	Simplified composition	Approximate compositional range
Chert (or quartz)	SiO_2	none
Magnetite	Fe_3O_4	none
Hematite	Fe_2O_3	none
Pyrite	FeS_2	none
Greenalite	$Fe^{2+}_6Si_4O_{10}(OH)_8$*	$(Fe_{4.0}Mg_{1.0}$ to $Fe_{5.3}Mg_{0.2})$ $Al_{0-0.2}Si_4O_{10}(OH)_8$*
Stilpnomelane	$(Fe, Mg, Al)_{2.7}(Si, Al)_4(O, OH)_{12}xH_2O$† with traces of K, Na, Ca	$(Fe_{1.3}Mg_{1.5}Al_{0.1})$ $(Si_{3.7}Al_{0.3})$ to $(Fe_{2.5}Mg_{0.2})$ $(Si_{3.6}Al_{0.3})$ with K ≈ 0.1 to 0.2 and Na ≈ 0.05 per formula unit
Minnesotaite‡	$Fe^{2+}_3Si_4O_{10}(OH)_2$*	$Mg_{1.7}Fe_{1.3}$ to $Fe_{2.8}Mg_{0.2}Si_4O_{10}(OH)_2$*
Chamosite‡	$(Fe^{2+}, Al)_6(Si, Al)_4O_{10}(OH)_8$*	$(Fe_{3.3}Mg_{1.3}Al_{1.3})$ $(Si_{3.0}Al_{1.0})$ to $(Fe_{3.8}Mg_{1.3}Al_{0.9})$ $(Si_{2.8}Al_{1.2})O_{10}(OH)_8$*
Ripidolite‡	$(Fe^{2+}, Mg, Al)_{12}(Si, Al)_8O_{20}(OH)_{16}$	Composition in iron-formation: $(Fe_{5.5}Mg_{4.3}Al_{2.3})$ $(Si_{5.4}Al_{2.6})O_{20}(OH)_{16}{}^2$
Riebeckite	$Na_2(Fe^{2+},Mg)_3Fe^{3+}_2Si_8O_{22}(OH)_2$	$Fe^{2+}/(Fe^{2+}+Mg)$ ranges from 0.64 to 0.86
Ferri-annite	$K_2(Mg,Fe)_6Fe^{3+}_2Si_6O_{22}(OH)_4$	$Fe^{2+}/(Fe^{2+}+Mg)$ ranges from 0.50 to 0.71
Siderite	$FeCO_3$	$(Mg_{0.3}Mn_{0.1}Fe_{0.6})$ to $(Mg_{0.2}Mn_{0.2}Fe_{0.6})$ CO_3
Dolomite-ankerite	CaMg ↔ $CaFe(CO_3)_2$	$Ca_{1.0}(Mg_{0.8}Fe_{0.1}Mn_{0.1})$ to $Ca_{1.0}(Mg_{0.5}Fe_{0.2}Mn_{0.3})$ to $Ca_{1.0}(Mg_{0.4}Fe_{0.6})$ $(CO_3)_2$
Calcite	$CaCO_3$	$Ca_{0.9}(Fe, Mg, Mn)_{0.1}CO_3$

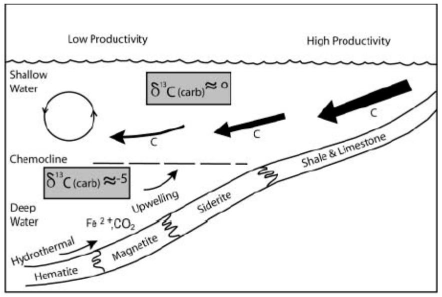
ferrous
vs
ferric

If BIFs formed through oxidation, why are many of the minerals ferrous?

- reaction between Fe-oxide and ferrous Fe?
- diagenetic or metamorphic overprinting??
- precipitation of ferrous minerals in an anoxic (euxinic) ocean???

Siderite-BIF formation in a stratified ocean

e.g. Transvaal Supergroup, Archean-Early Proterozoic

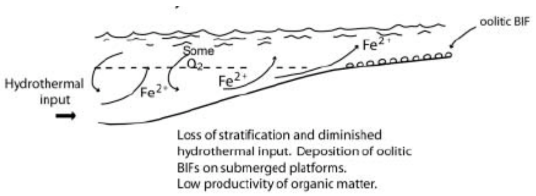


- High productivity (cyanobacteria?) on the shelf, shallow water facies characterized by limestone-dolomite-shale lithologies
- Organic carbon supply to deeper water initiates siderite precipitation below the chemocline with distinctly light carbon isotope composition relative to shallow carbonates.
- Further off-shore, where organic carbon supply is low (and some oxygen is available) magnetite and hematite-rich iron formations precipitate.

C. Klein, American Mineralogist ***90****, 1473 (2005)*

Oolitic and granular iron-formations in a mixed ocean

e.g. Lake Superior, Early to Middle Proterozoic

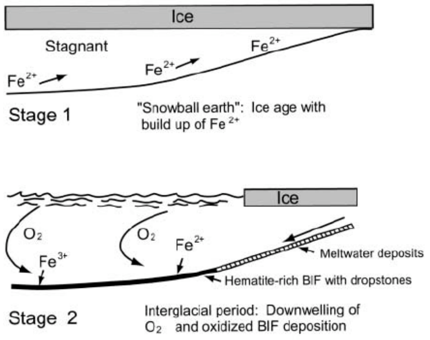


- Reduced hyrothermal input causes a declining chemical density stratification (evidenced by REE).
- Enhanced mixing facilitates iron transport into the surface oxygenated ocean.
- Most consistent with the “traditional view”.

C. Klein, American Mineralogist ***90****, 1473 (2005)*

Neoproterozoic iron-formations in a stagnant ocean

e.g. Raptian, "Snowball Earth"

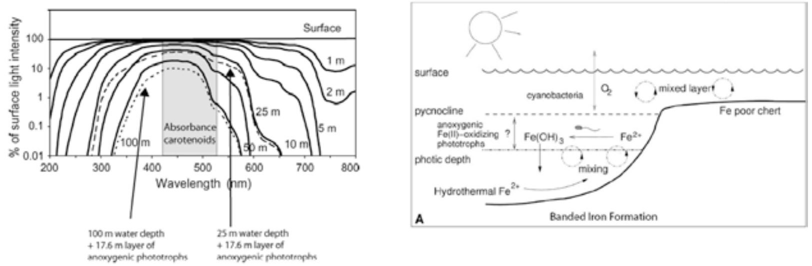


- Iron formations are intimately associated with glaciomarine deposits (diamictites), often containing drop-stones.
- Ice cover allowed for build-up of dissolved iron (hydrothermal) during glacial and rapid deposition during interglacial transgression.

*C. Klein, American Mineralogist **90**, 1473 (2005)*

Is oxygen really necessary?
The role of microbes in BIF formation

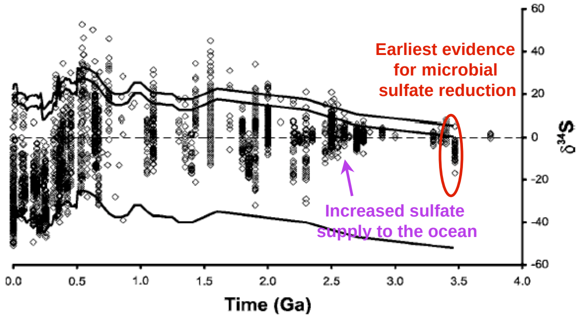
Kappler, Pasquero, Konhauser, and Newman, Geology 33, 865 (2005)



- Phototrophic bacteria catalyze iron oxidation under anoxic conditions.
- Even in the presence of cyanobacteria, light levels at few hundred meters depth are sufficient for anoxygenic phototrophs to survive.
- <u>Problems with biological models</u>: hard to prove, no microfossils preserved, no biomarkers, no organic carbon, isotopic record (especially Fe) ambiguous.
- BTW: Fe^{2+} can also be oxidized photochemically in the absence of O_2 *[Cairns-Smith, Nature 276, 807 (1978)].*

Iron drawdown in a euxinic ocean
"The Canfield Ocean"

*Canfield, Nature **396**, 450 (1998)*



Earliest evidence for microbial sulfate reduction

Increased sulfate supply to the ocean

- Challenge to prevailing paradigm that oxygenation of ocean caused disappearance of BIFs.
- Instead Canfield suggested that deep ocean remained oxygen-free, iron was instead scavenged by sulfide (Pyrite precipitation in euxinic water column).
- Increased atmospheric oxygen caused enhanced continental weathering and supply of sulfate to the ocean. Sulfate was reduced by microbes, causing rcationation of S isotopes.

How can isotopes help? ...some basics

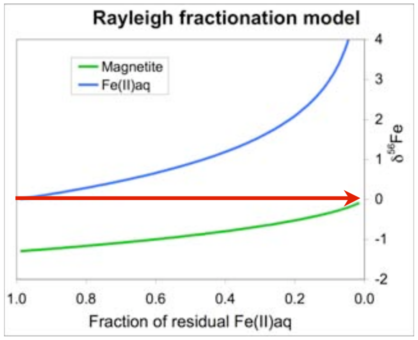
Isotope fractionation versus mass balance:

Microbial sulfate reduction and dissimilatory iron reduction both cause fractionations of their respective isotopes:

$\delta^{34}S_{sulfide} - \delta^{34}S_{sulfate} = \Delta^{34}S_{sulfide–sulfate}$ is -15 to -50 ‰ for natural populations

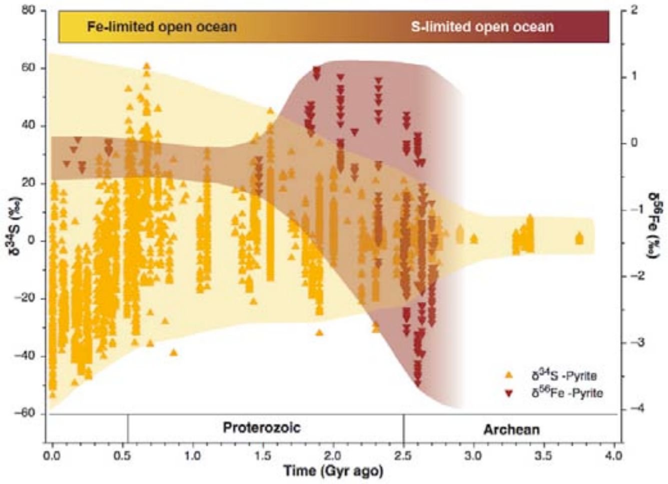
$\delta^{56}Fe_{Fe2+} - \delta^{56}Fe_{Fe\text{-}oxide} = \Delta^{56}Fe_{Fe2+–Fe\text{-}oxide}$ is -1.3 to -2.5 ‰ for natural populations

but...



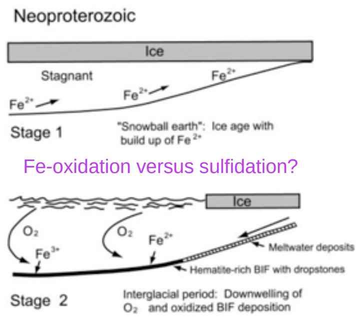
What goes in must come out if all is consumed: "Reservoir effect"

Sulfur and iron isotopes through time

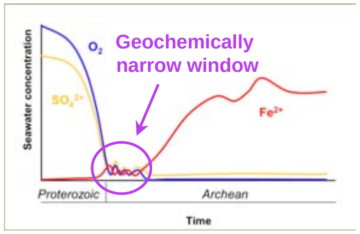


The complimentary chemistry of iron and sulfur is reflected in the long term isotope record.

Let’s revisit Neoproterozoic BIFs (Snowball Earth)



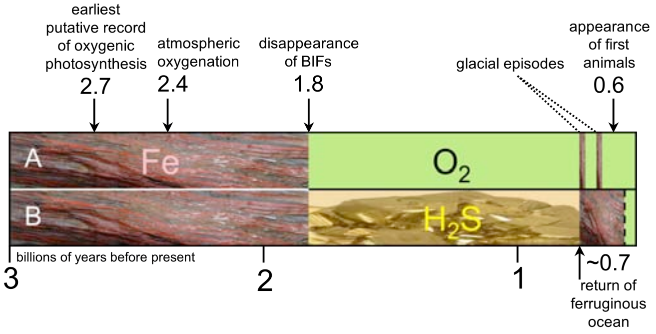
Fe-oxidation versus sulfidation?



Geochemically narrow window

When was the deep ocean oxygenated?

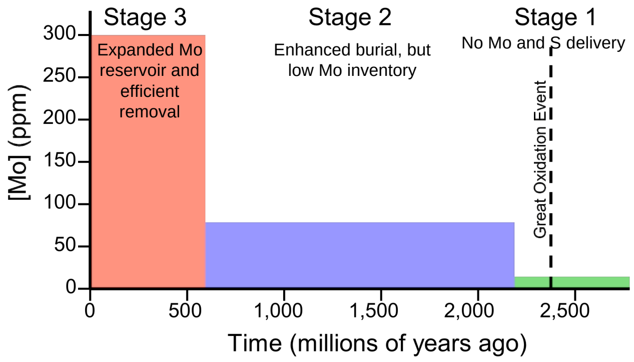
Neoproterozoic “ferringuous ocean”



Used very detailed iron speciation (by chemical extraction) to determine if primary iron mineral was ferric, ferrous or pyritic.

Canfield et al., Science 321, 949 (2008)

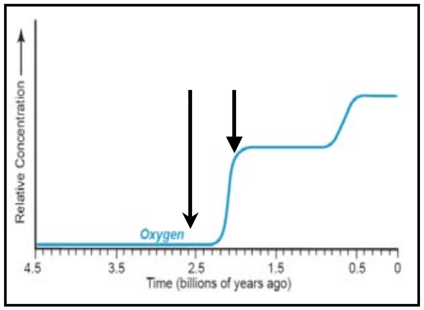
Beyond iron... Molybdenum

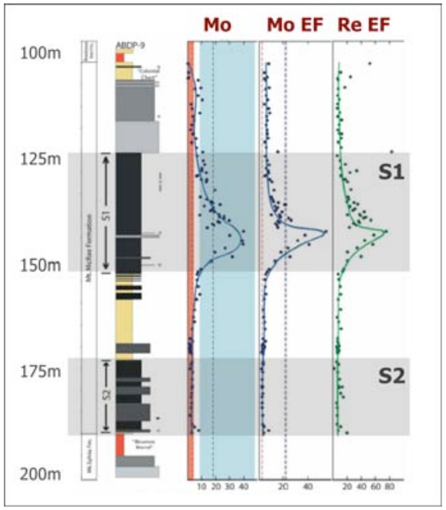


(Anoxic) Mo chemistry 101: Mo removal to the sediments is closely tied to sulfide availability; Mo concentration in the sediments therefore reflect the efficiency of the removal, or the availability of Mo in the ocean.

Scott *et al.*, *Science* **452**, 456 (2008)

So when did oxygen first appear?





Mo delivery to the ocean is dependent on continental oxic weathering (similar to sulfur).

Anbar *et al.*, *Science* **317**, 1903 (2007)

Reading:

take another look at:

Canfield D., Rosing M., and Bjerrum C. (2006) Early anaerobic metabolisms. Philos. Trans. R. Soc. B 361, 1819-1836.

Walker, J.C.G. (1987) Was the Archean biosphere upside down? Nature 329, 710-713.

Canfield D. E. (1998) A new model for Proterozoic ocean chemistry. Nature 396, 450-453.

Kappler A., Pasquero C., Konhauser K. O., and Newman D. K. (2005) Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria. Geology 33, 865-868.

Anbar A. D., Duan Y., Lyons T. W., Arnold G. L., Kendall B., Creaser R. A., Kaufman A. J., Gordon G. W., Scott C., Garvin J., and Buick R. (2007) A Whiff of Oxygen Before the Great Oxidation Event? Science 317, 1903-1906.