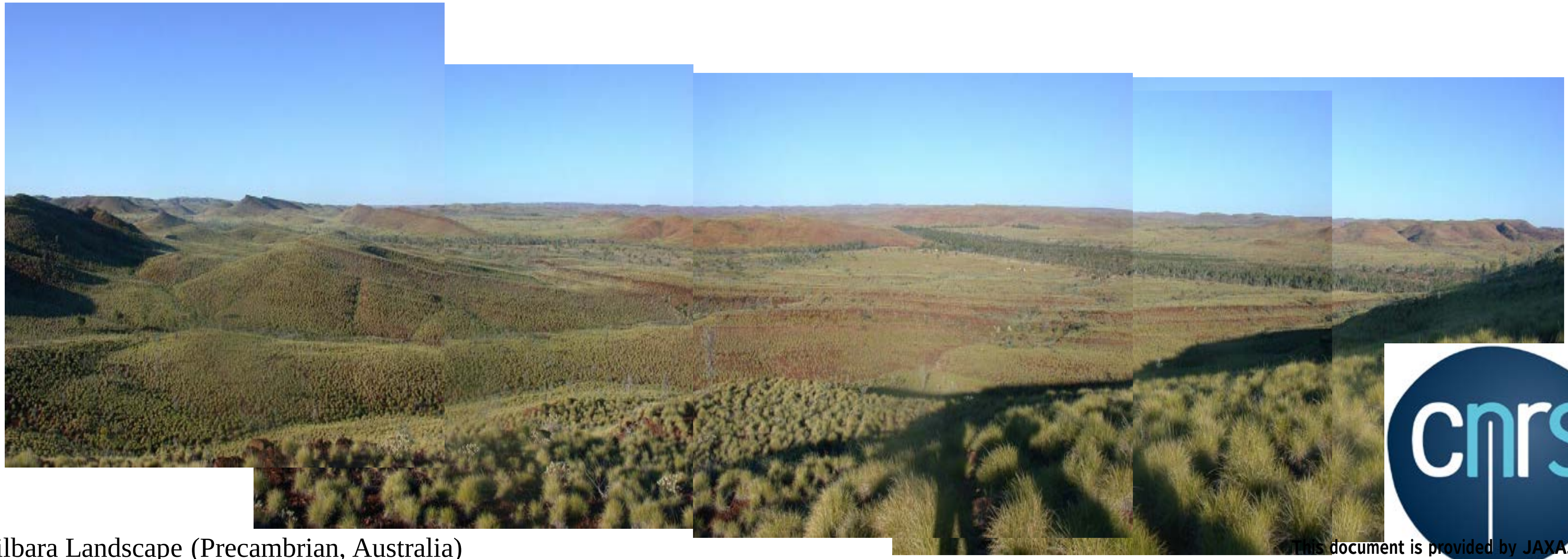
International Astrobiology Workshop 2013

Did oceanic biogenic methane cycling regulate the evolution of Early Earth atmospheric chemistry?



Pilbara Landscape (Precambrian, Australia)

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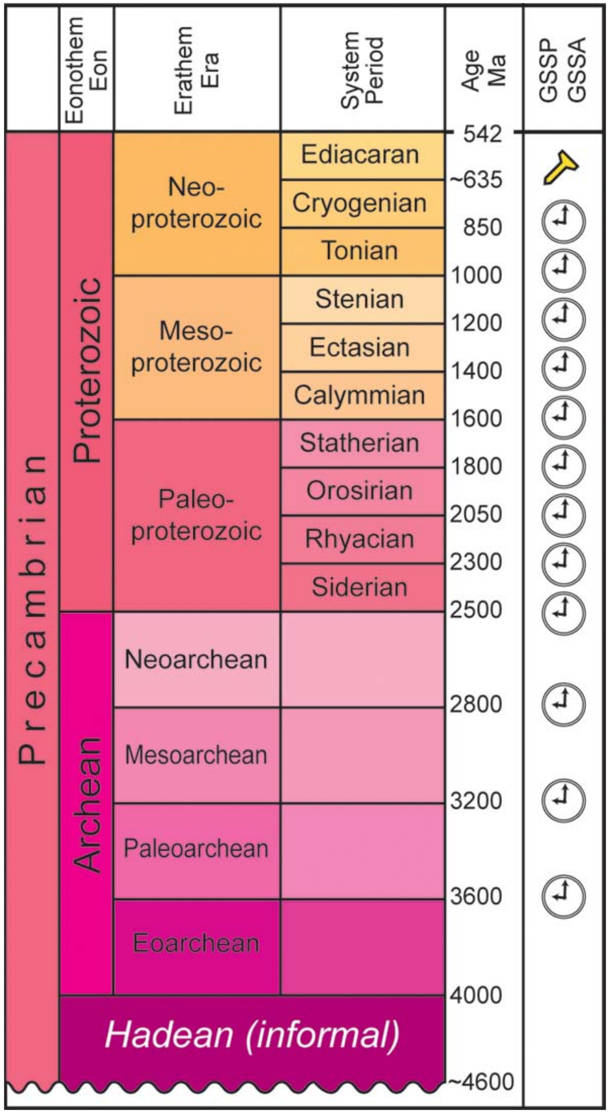

- Ocean formation
- **Oxidation of the environment *Ocean and Atmosphere***
- Continental crustal growth
- **Development of life**

~ Half of the geological record

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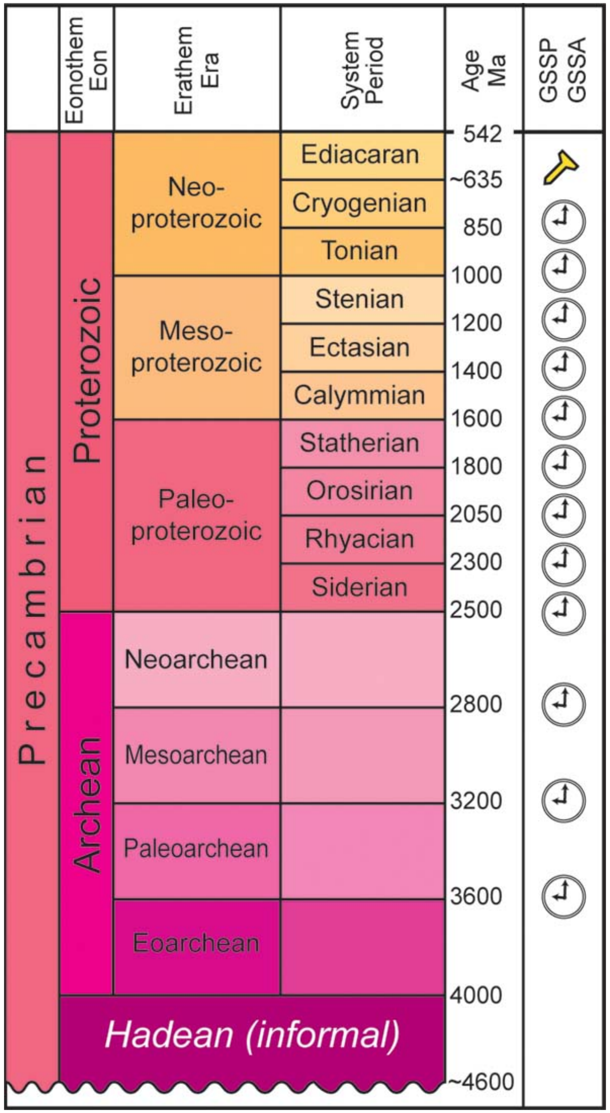
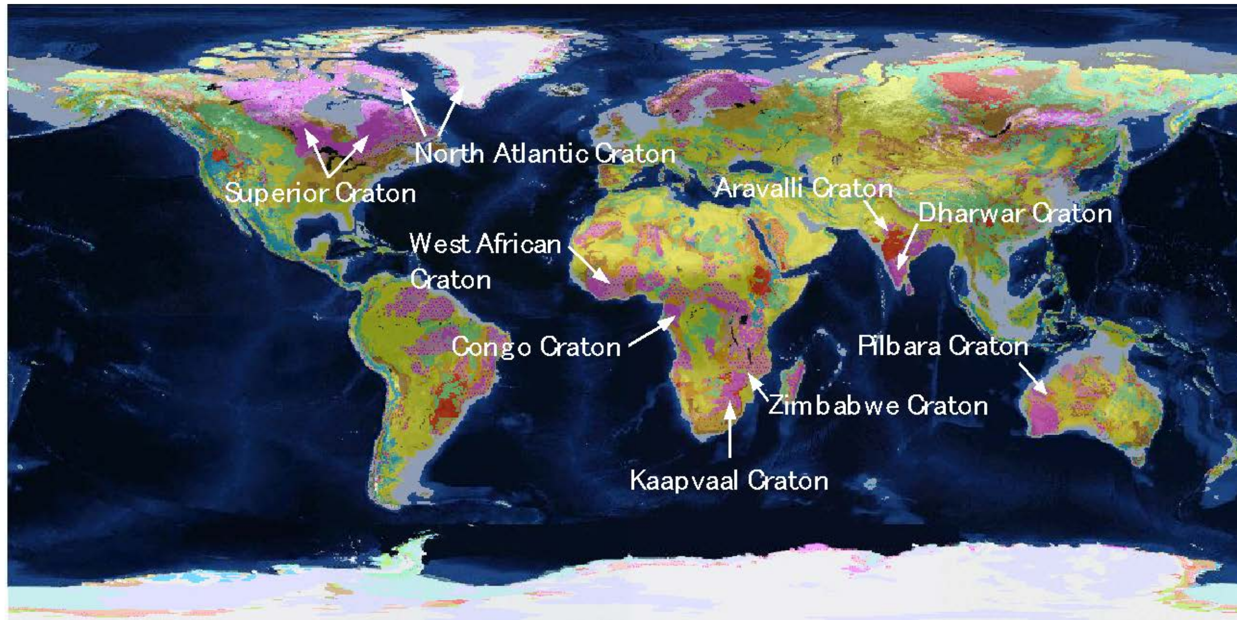


~ Half of the geological record



Poorly archived, few sediments, metamorphosed at T >200°C

Early life and its environment remains poorly characterized

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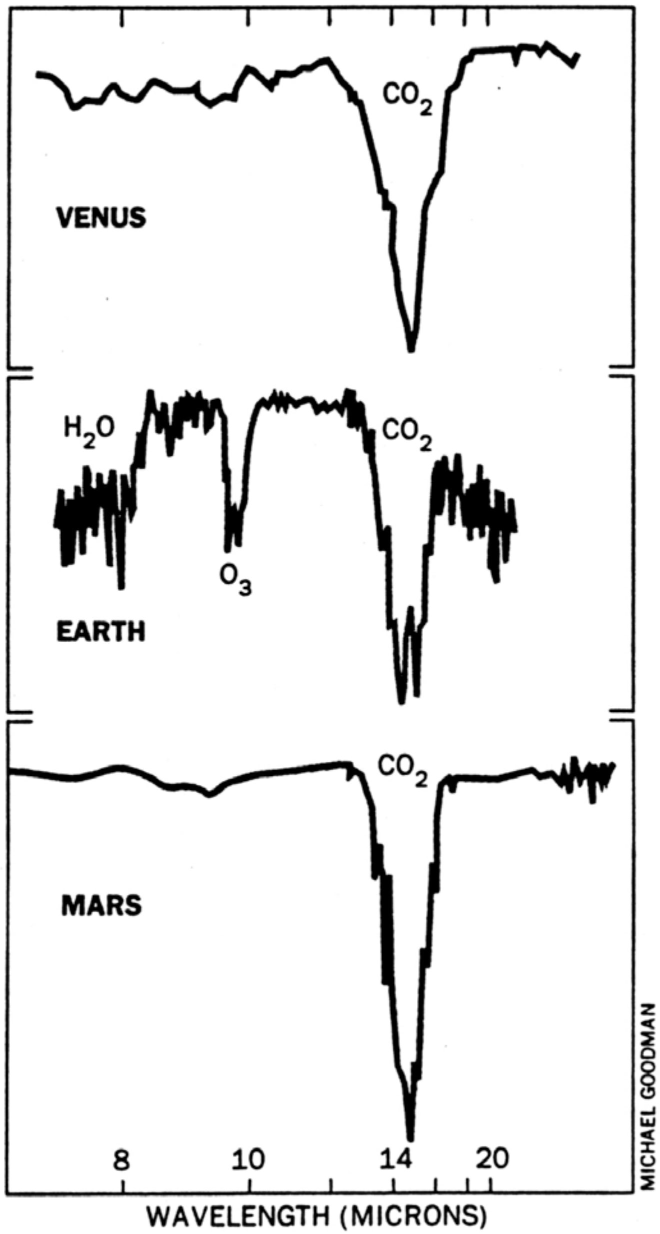
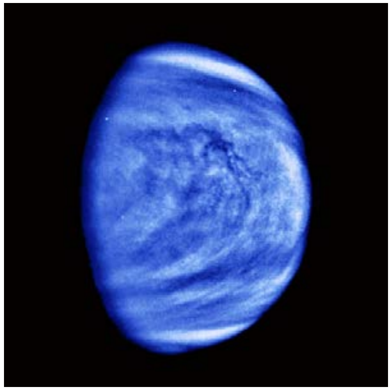
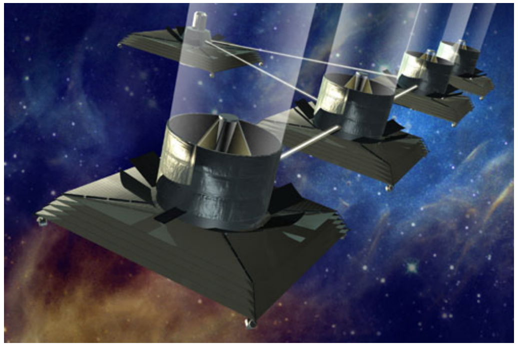




Thermal IR Spectra using TPF



R. Hanel, Goddard Space Flight Center

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A decade of multiple sulfur isotope studies bring new insights in the timing of the Earth system oxygenation

Science AAAS

Atmospheric Influence of Earth's Earliest Sulfur Cycle
James Farquhar, *et al.*
Science **289**, 756 (2000);
DOI: 10.1126/science.289.5480.756

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Theory of Mass dependent/Independent Fractionation of sulfur isotopes

4 isotopes :

^{32}S : 95,02%

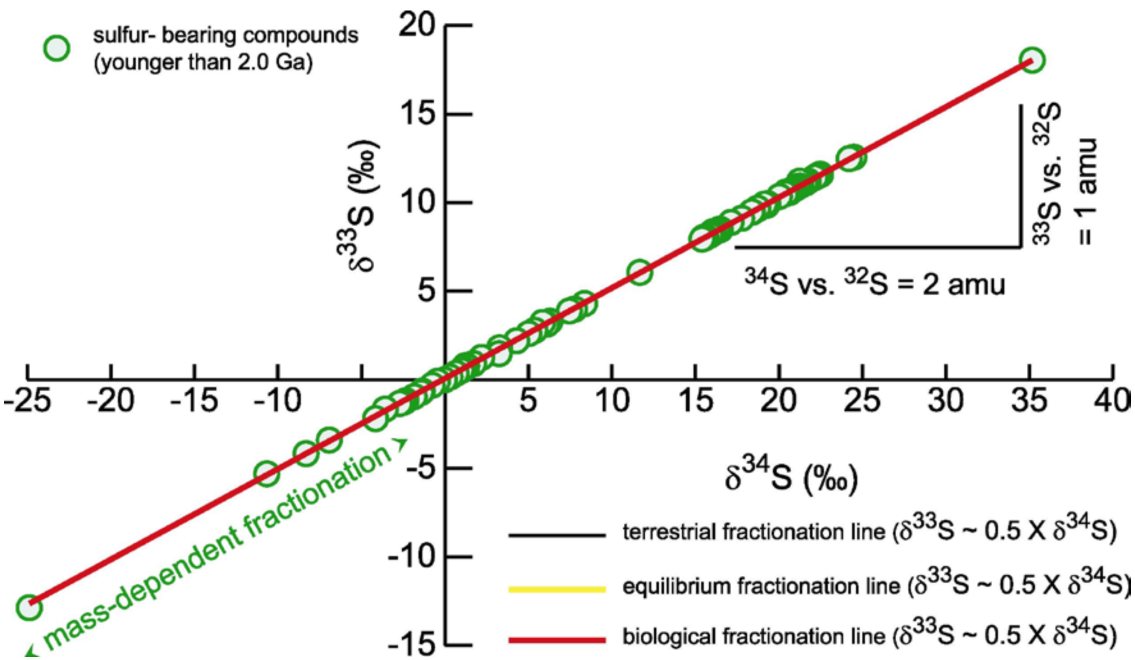
^{33}S : 0,75 %

^{34}S : 4,21%

^{36}S : 0,02%

Mass (^{34}S)-Mass (^{32}S)= 2 X Mass (^{33}S) - Mass (^{32}S)

← isotopic fractionation depends on mass …



Prediction from theory:

$$\delta^{34}S = 2 \times \delta^{33}S$$

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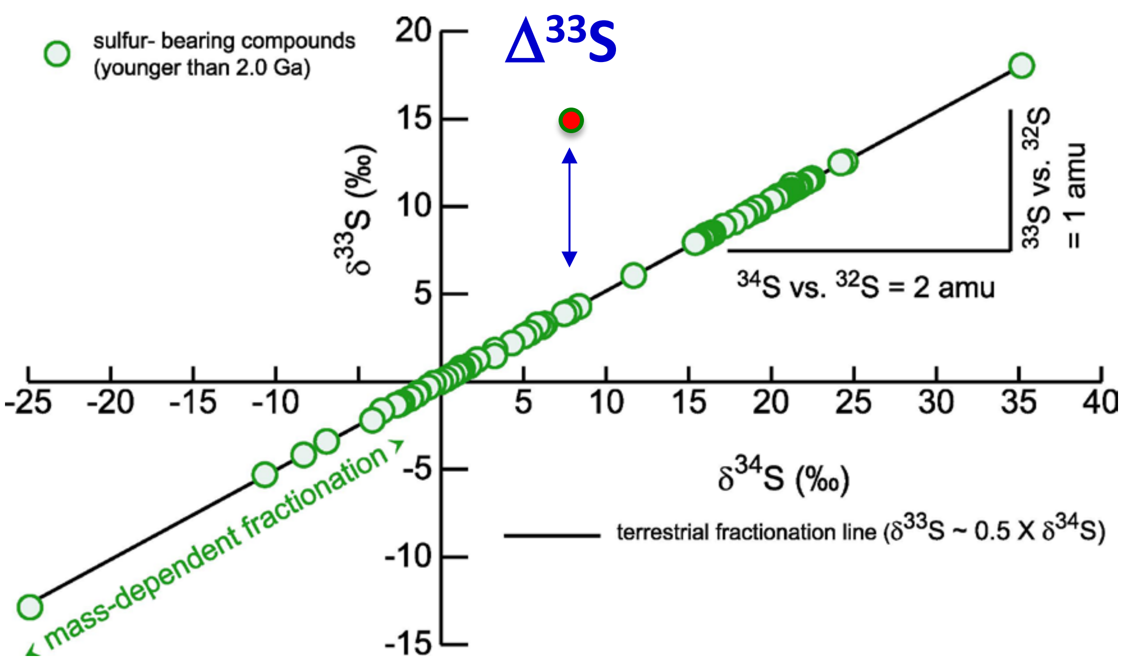
^{34}S : 4,21%
^{36}S : 0,02%

Mass (^{34}S)-Mass (^{32}S) ≠ 2 X Mass (^{33}S) - Mass (^{32}S)

← isotopic fractionation independent on mass …



Prediction from theory:

$\delta^{34}S \neq 2 \times \delta^{33}S$

←$\Delta^{33}S \approx \delta^{33}S - 0.515\ \delta^{34}S$

deviation with regard to the terrestrial fractionation line = (**MIFs**)

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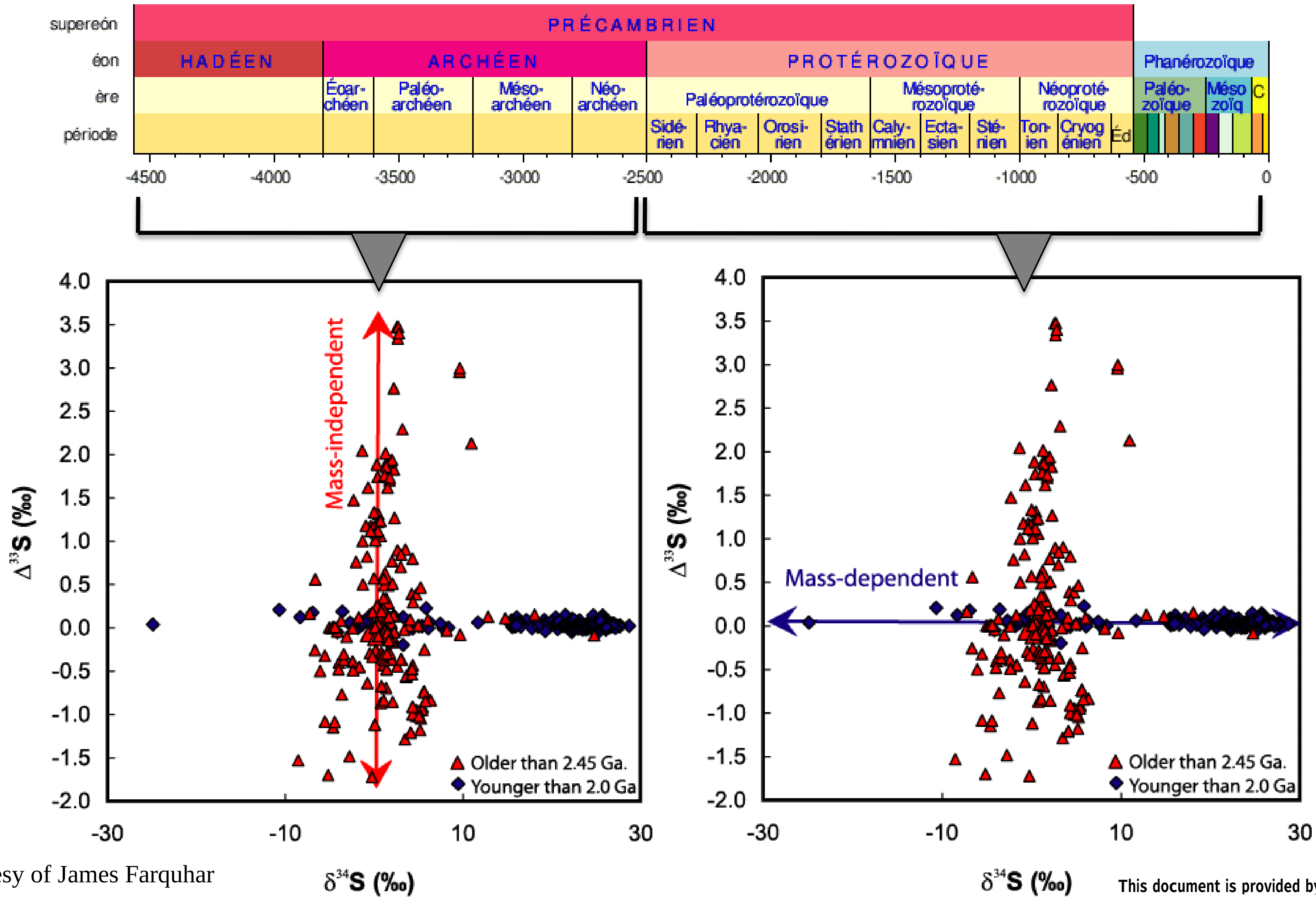
Geological record



Courtesy of James Farquhar

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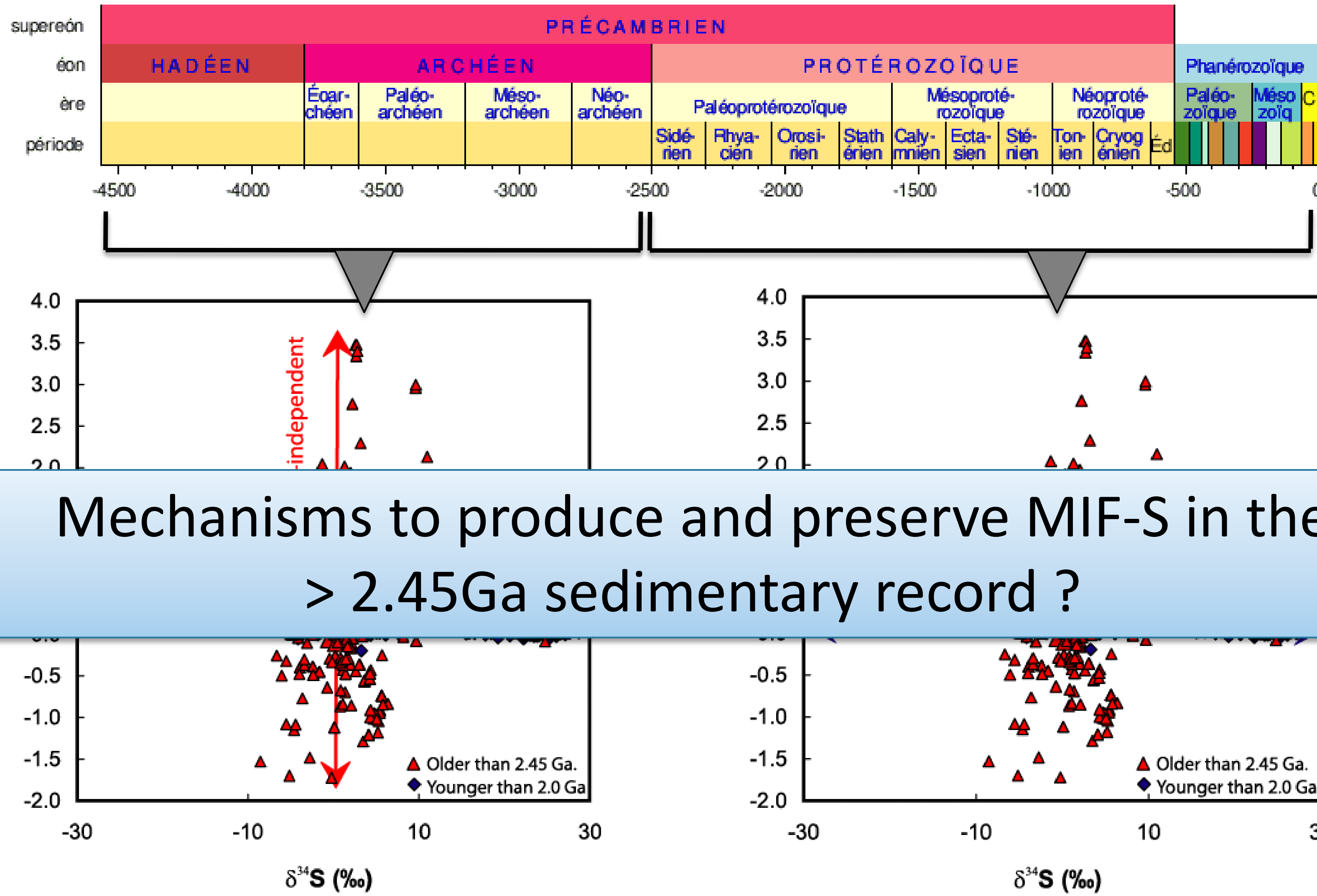
Geological record



Mechanisms to produce and preserve MIF-S in the > 2.45Ga sedimentary record ?

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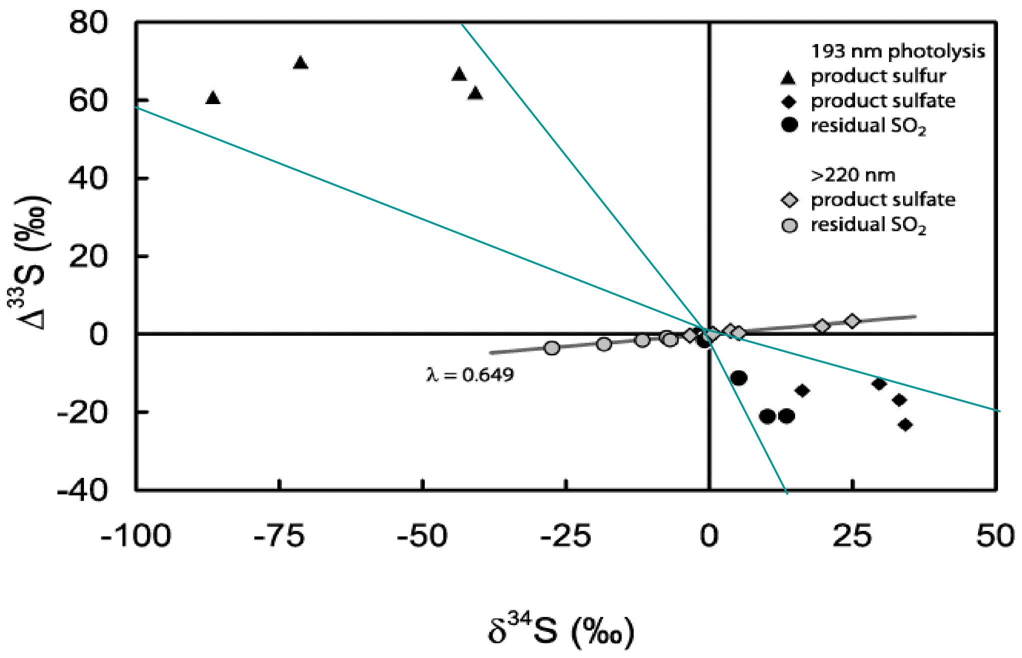
- MIF-S are produced in lab experiment during UV photolysis of SO_2

Farquhar et al, 2000



Photolytic reaction of S in anoxic atmosphere

Without O_2 (O_3)

Science AAAS
Atmospheric Influence of Earth's Earliest Sulfur Cycle
James Farquhar, *et al.*
Science **289**, 756 (2000);
DOI: 10.1126/science.289.5480.756

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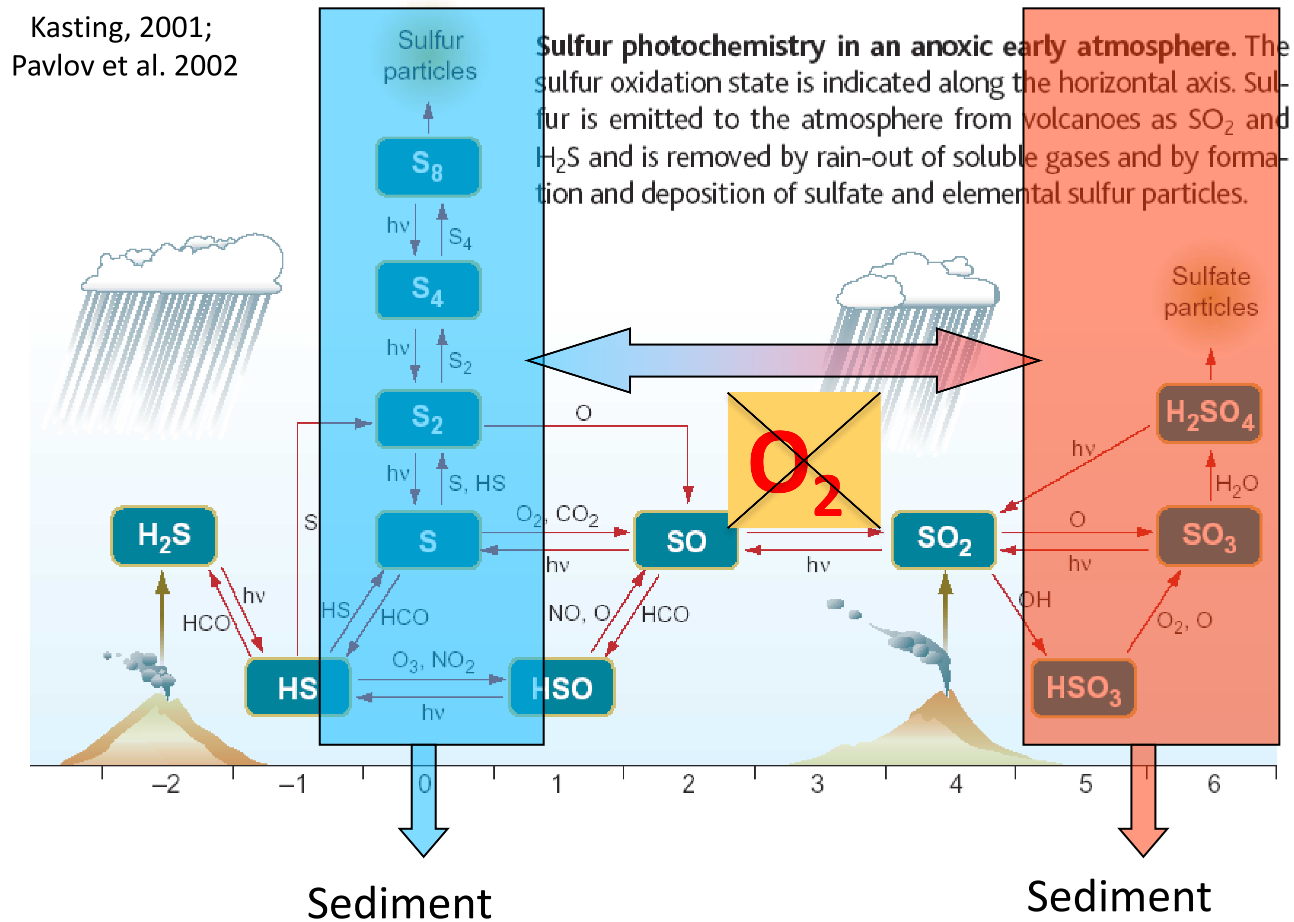
Preservation in the sedimentary record?



➢ Two exit channels of sulfur species is required and imply low O_2 (< 10^{-5} PAL) in the Archean environment

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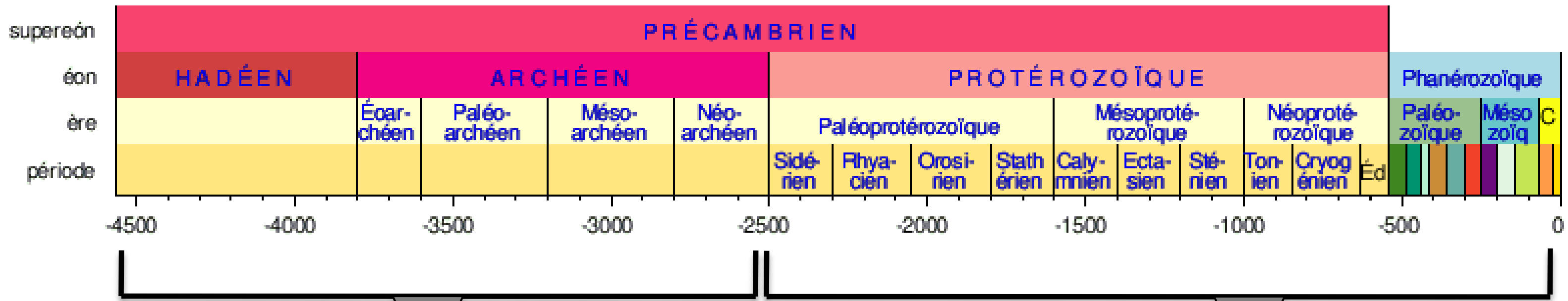
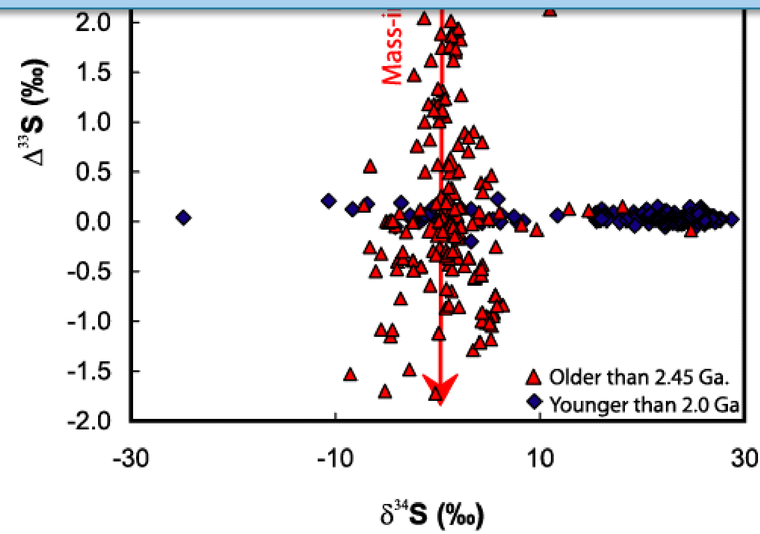
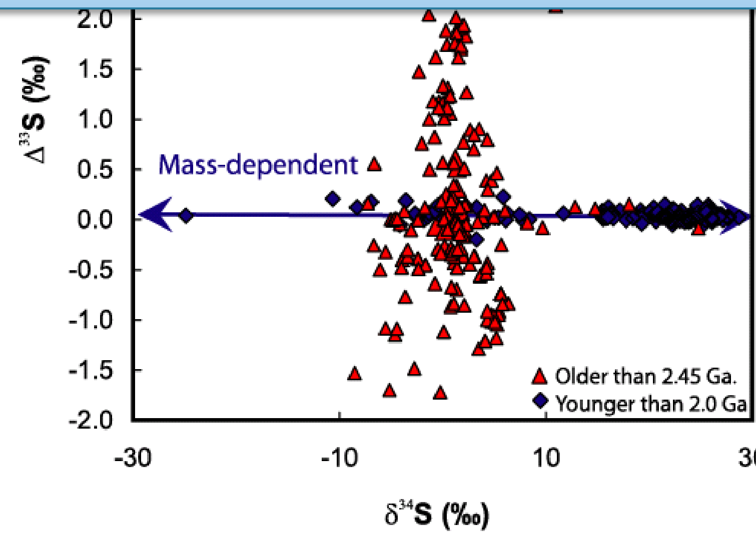
Geologic record



The transition at ~ 2.4 Ga are interpreted by most of the authors as the GOE (Great Oxidation Event)





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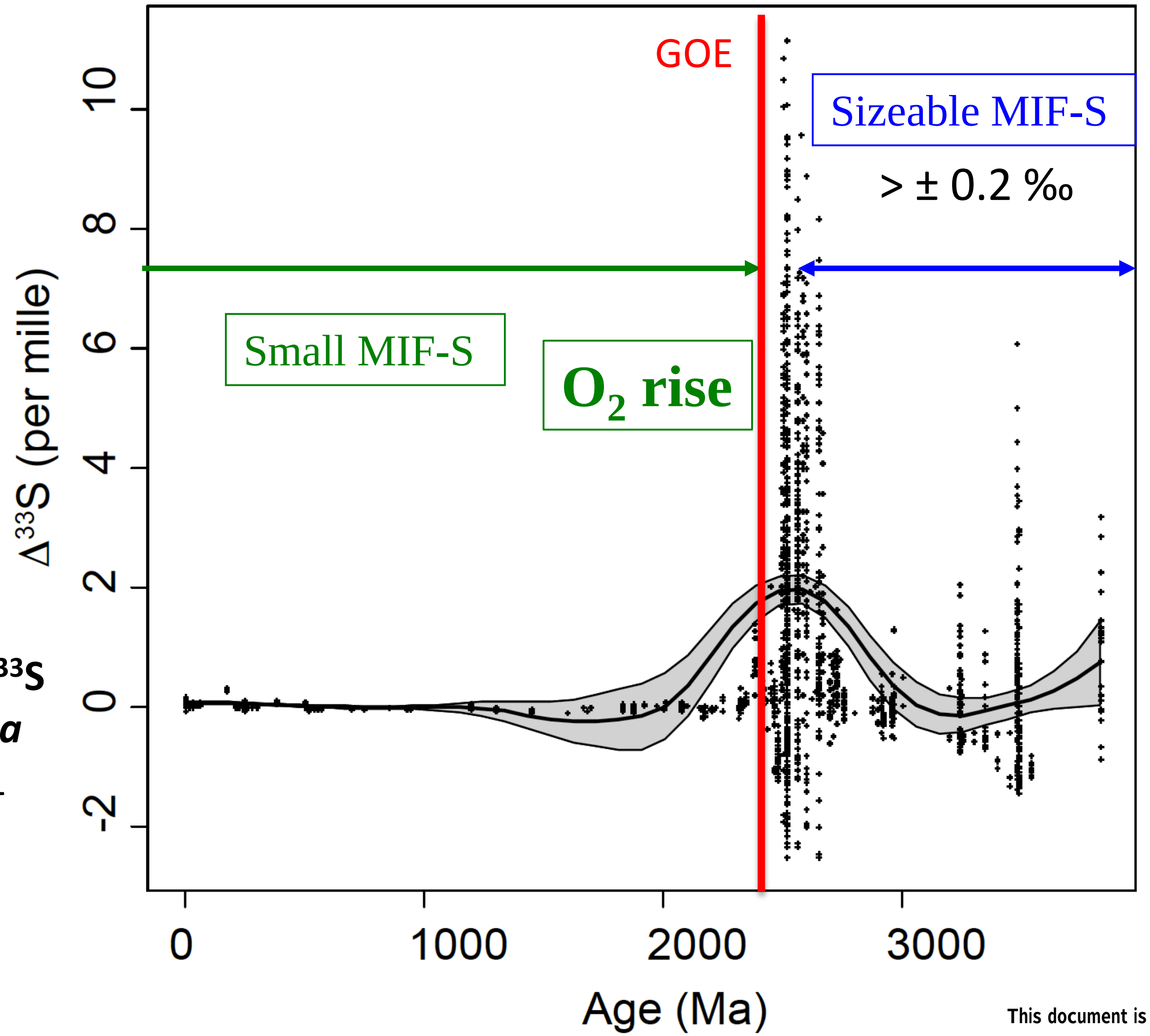
…. But in details there is some secular variations in the MIF-S record during the Precambrian …



NB: **dampen down $\Delta^{33}S$ between *3.1 to 2.7 Ga*** (i.e. value between -1 to +1 ‰)

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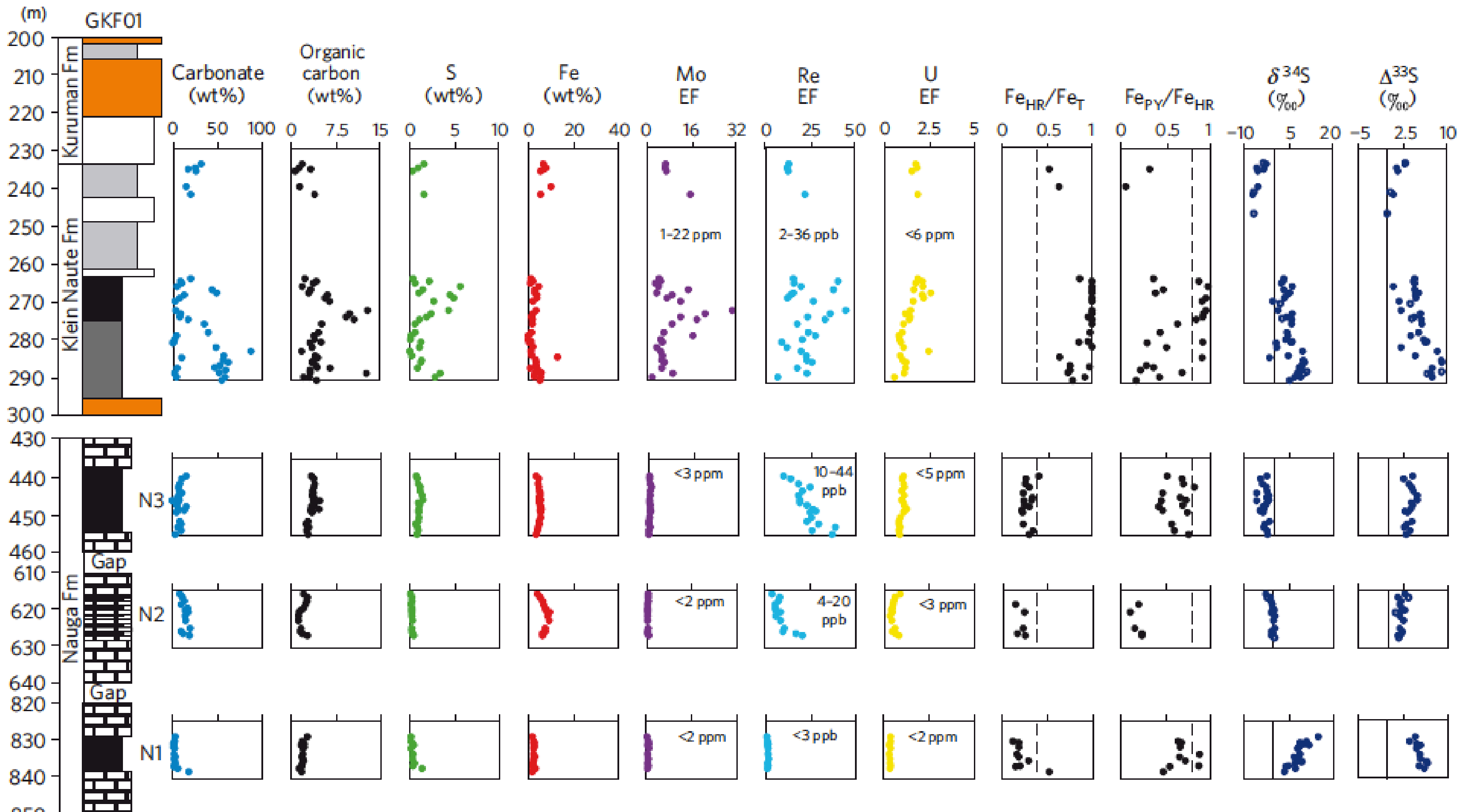
…. But in details there is some secular variations in the MIF-S record during the Precambrian … AND some evidences for a « *whiff of oxygen* » *before the GOE*



Kendall et al, 2010

➢ Re enrichment and iron speciation point to oxidative weathering at around 2.6 Ga

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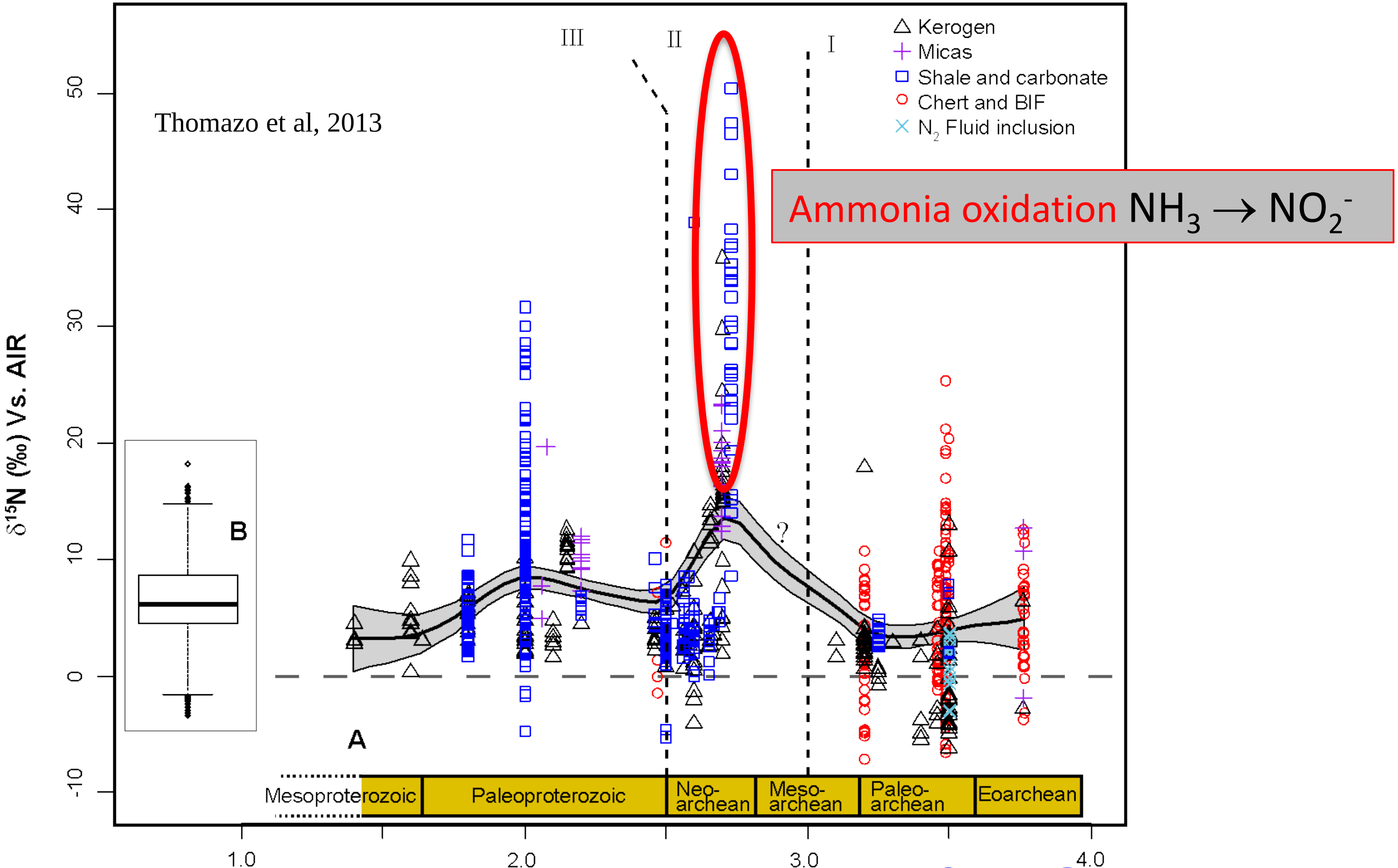
…. But in details there is some secular variations in the MIF-S record during the Precambrian … AND some evidences for a « *whiff of oxygen* » *before the GOE*



➢ The oxidative part of the nitrogen cycle is recorded SINCE 2.7 Ga

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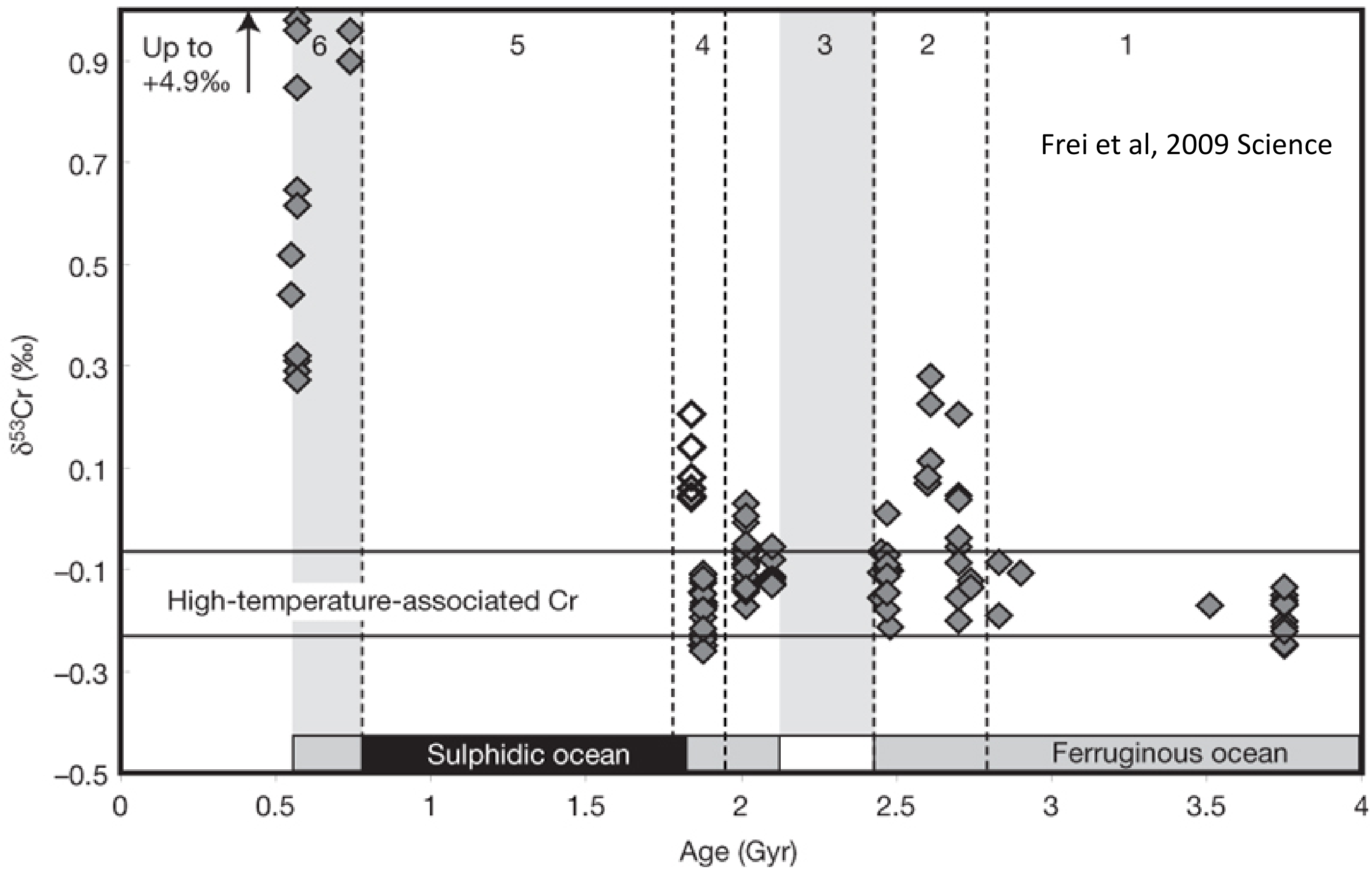
…. But in details there is some secular variations in the MIF-S record during the Precambrian … AND some evidences for a « *whiff of oxygen* » *before the GOE*



➢ accumulation of Cr(VI) in ocean surface waters ~2.8 to 2.6 Gyr ago

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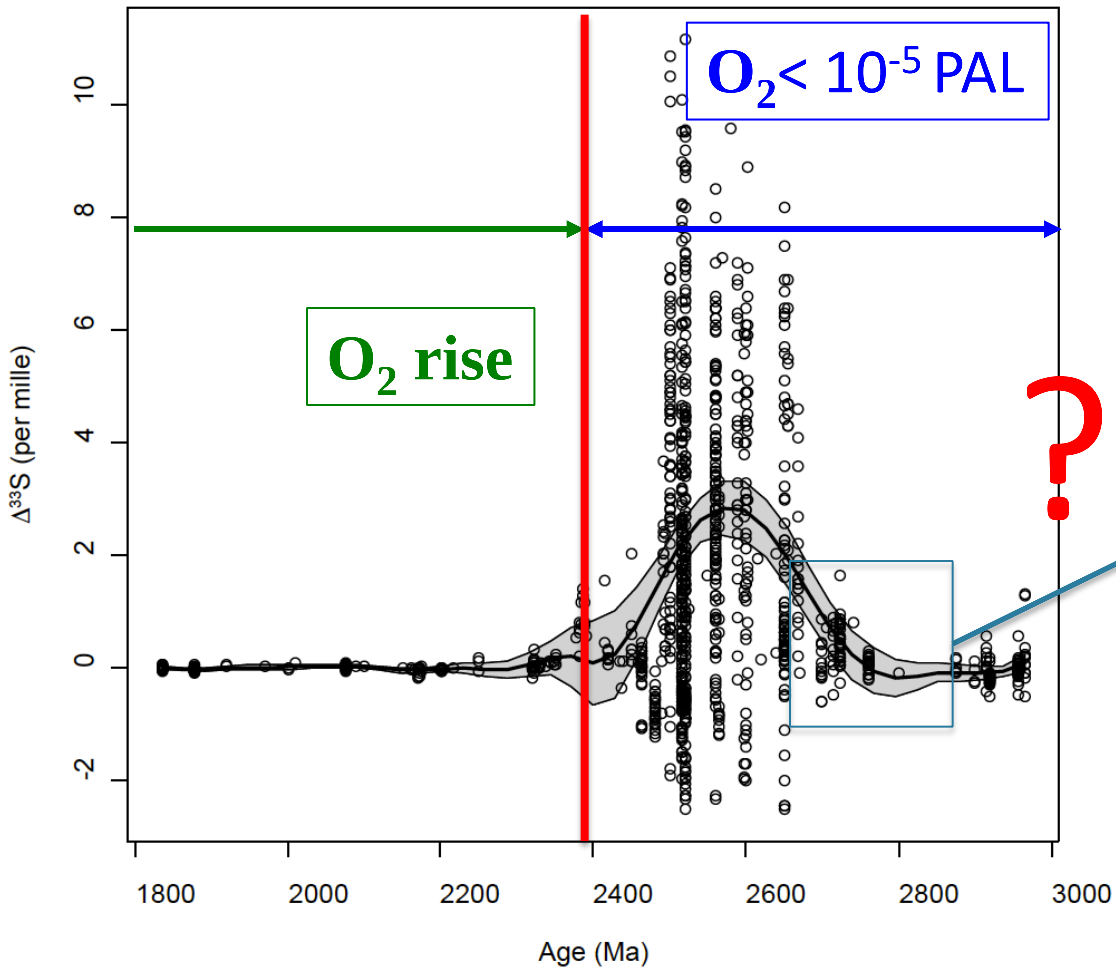
How to council MIF-S secular variations (magnitude and sign) and a transient elevation in atmospheric and surface ocean oxygenation as early as 2.7 Ga ?



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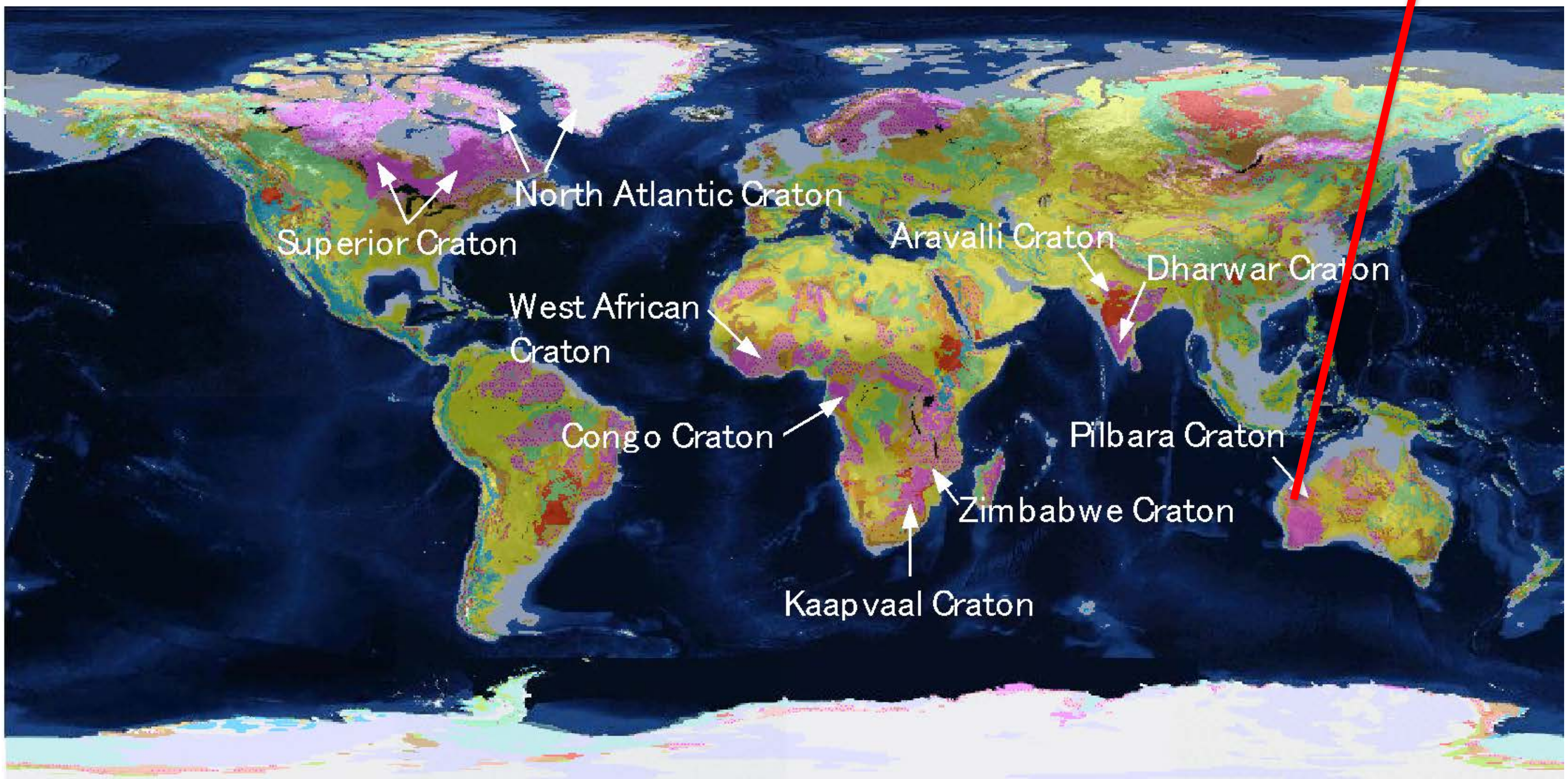
1/ Tumbiana Fm. (Pilbara Craton, Australia)



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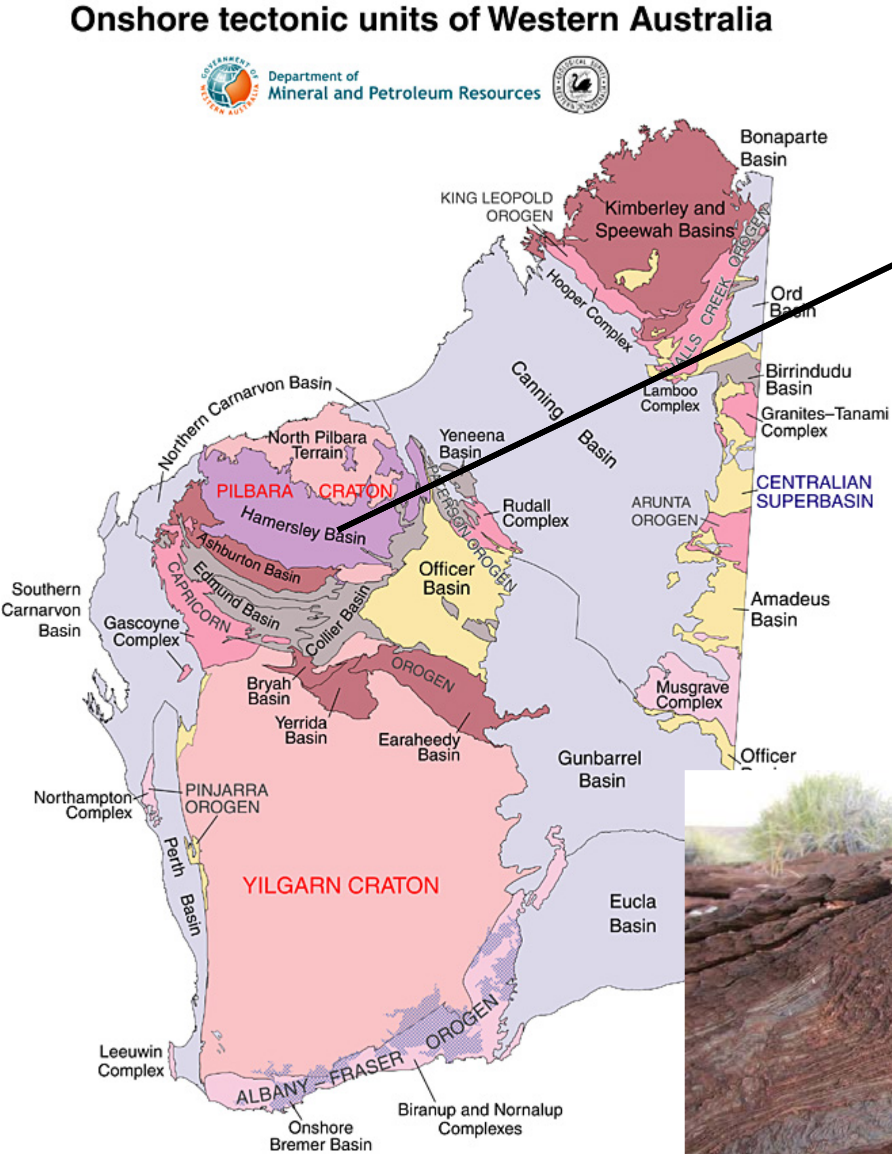
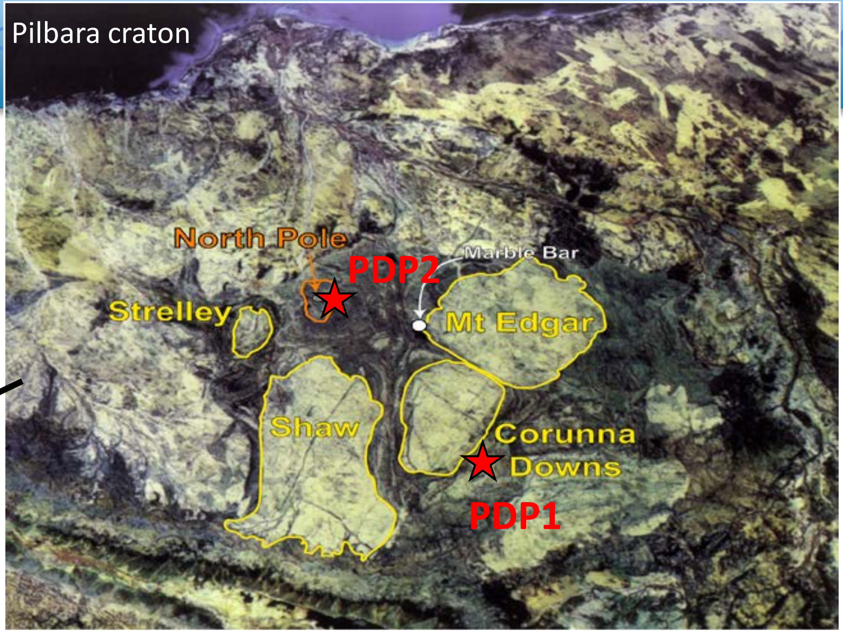
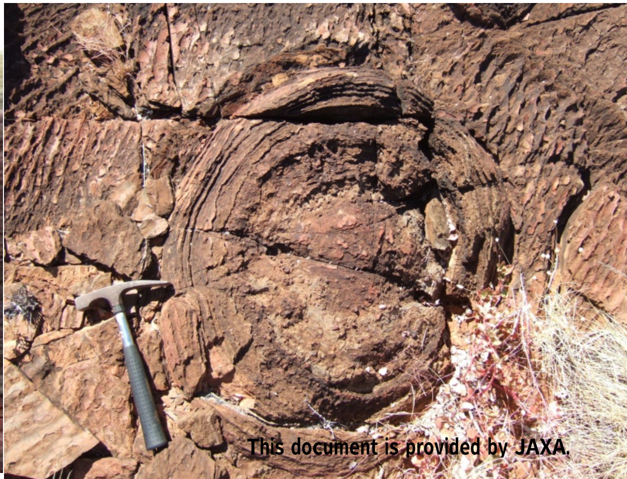


Philippot et al, 2009



- PDP 1 Drill core (2004)
- 2.73 Ga Tumbiana Formation
- Shallow marine environment
- Subgreenschist facies



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2/ Kidd Creek Fm. (Abitibi Subprovince, Canada)

1/ Tumbiana Fm. (Pilbara Craton, Australia)

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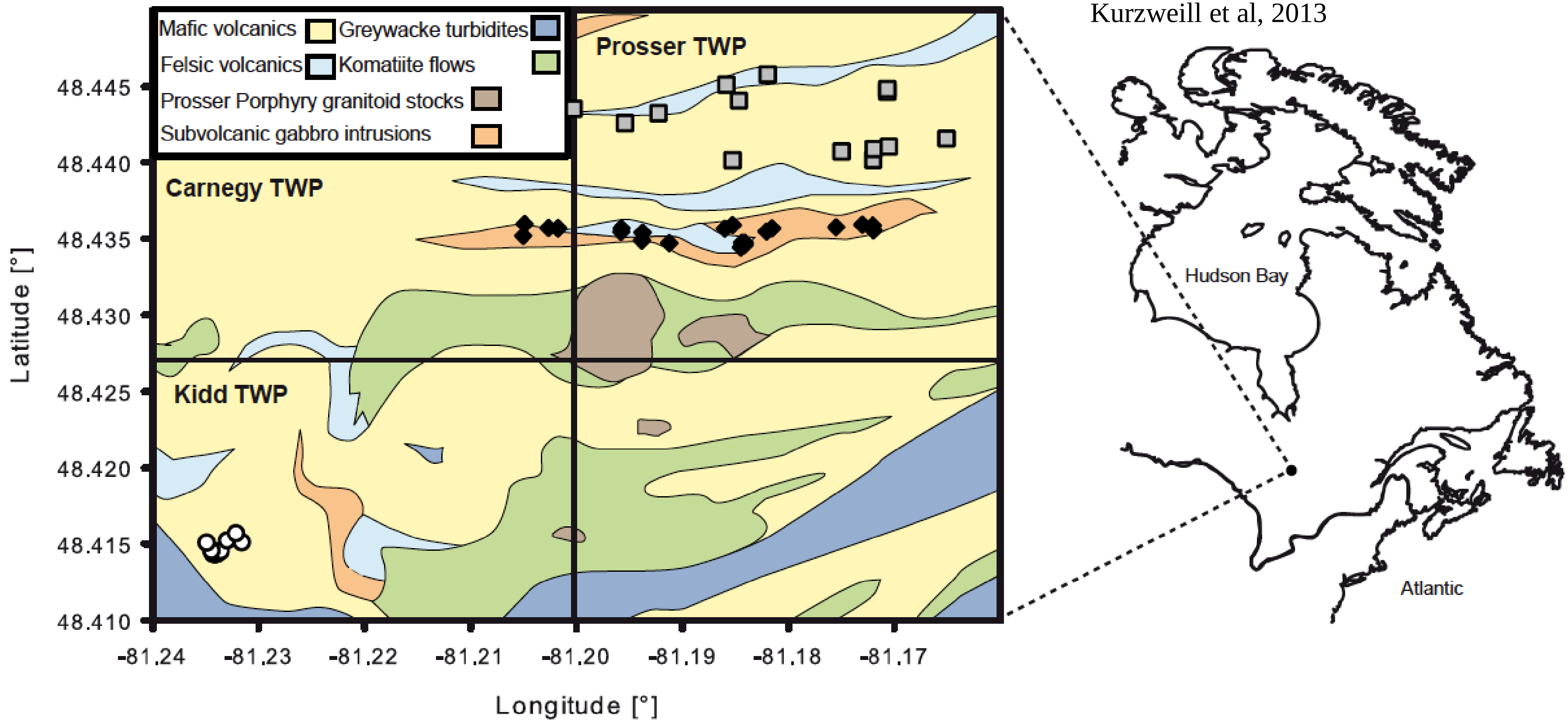
Kurzweill et al, 2013

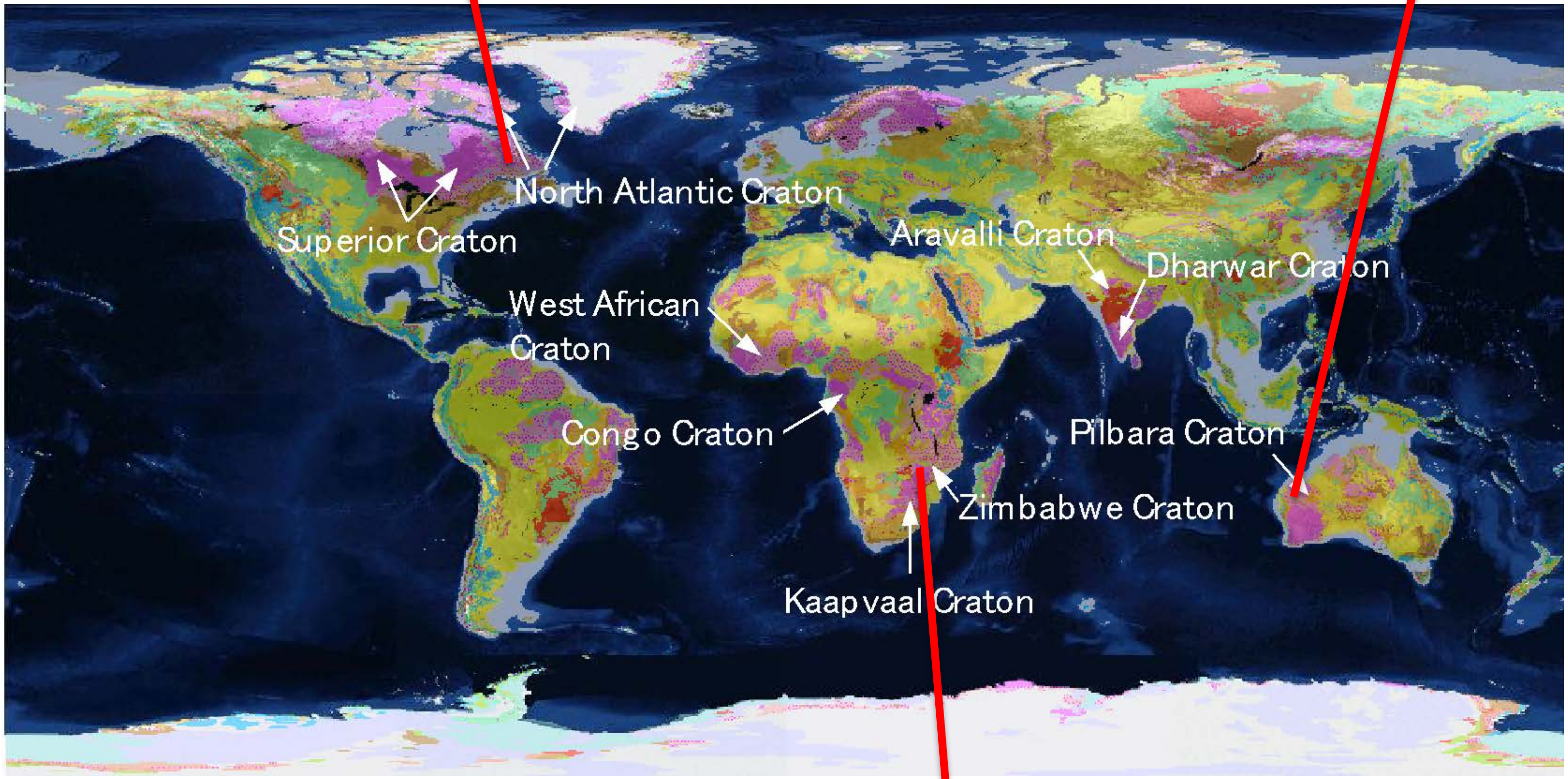


- Outcrop samples (sedimentary argillite layers in between felsic volcanics)
- 2.71 Ga for the sedimentary rocks of the Kidd Creek area
- Deposition in biologically active areas close to hydrothermal vents (Wellmer et al., 1999)
- Hydrothermal alteration bellow 250°C (Hannington et al., 1999b)
- The metamorphic grade of the Kidd Creek is sub-greenschist to lower greenschist

This document is provided by JAXA.

2/ Kidd Creek Fm. (Abitibi Subprovince, Canada)

1/ Tumbiana Fm. (Pilbara Craton, Australia)



3/ Cheshire Fm. (Ngezi Group, Zimbabwe)

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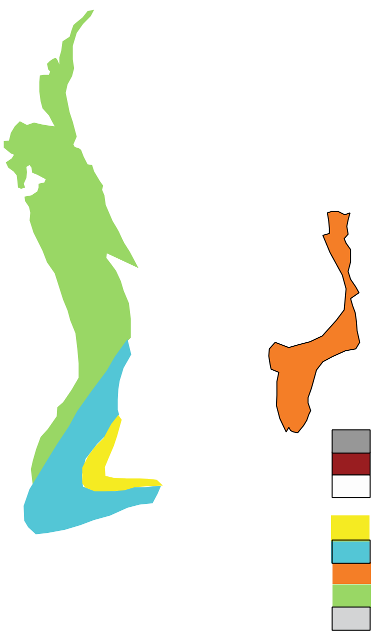
Thomazo et al, 2013

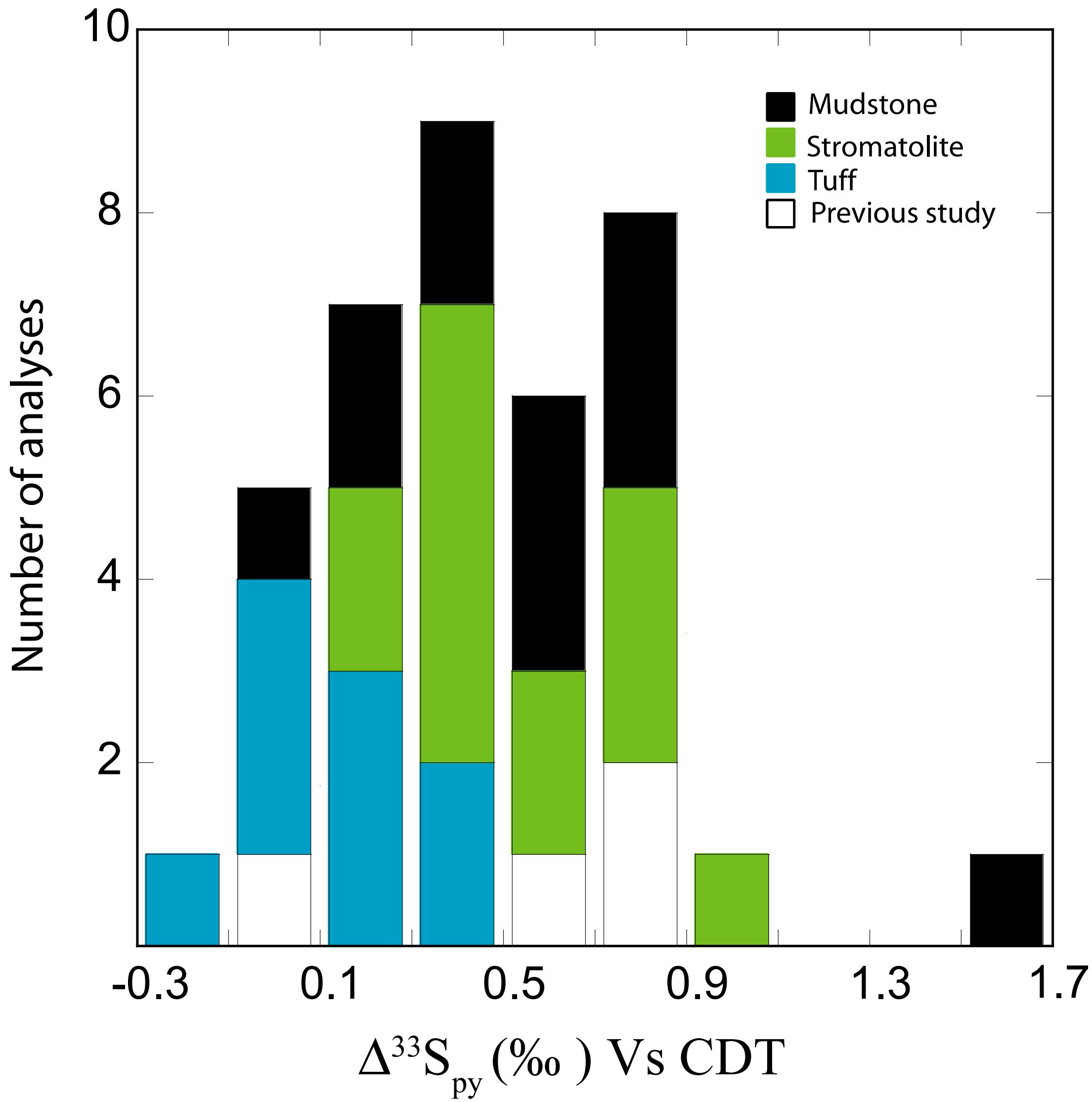


- Nercmar core
and Saskmar holes (80’)
- 2.65 Ga Cheshire Formation
- Shallow marine environment
- Samples are unstrained and in the subgreenschist facies

This document is provided by JAXA.

Thomazo et al, 2009

1/ 2.73 Ga Tumbiana Formation



$\Delta^{33}S_{py}$ between -0.3 and 1.6 ‰

Sizeable (> ± 0.2 ‰)

BUT LOW MIF-S

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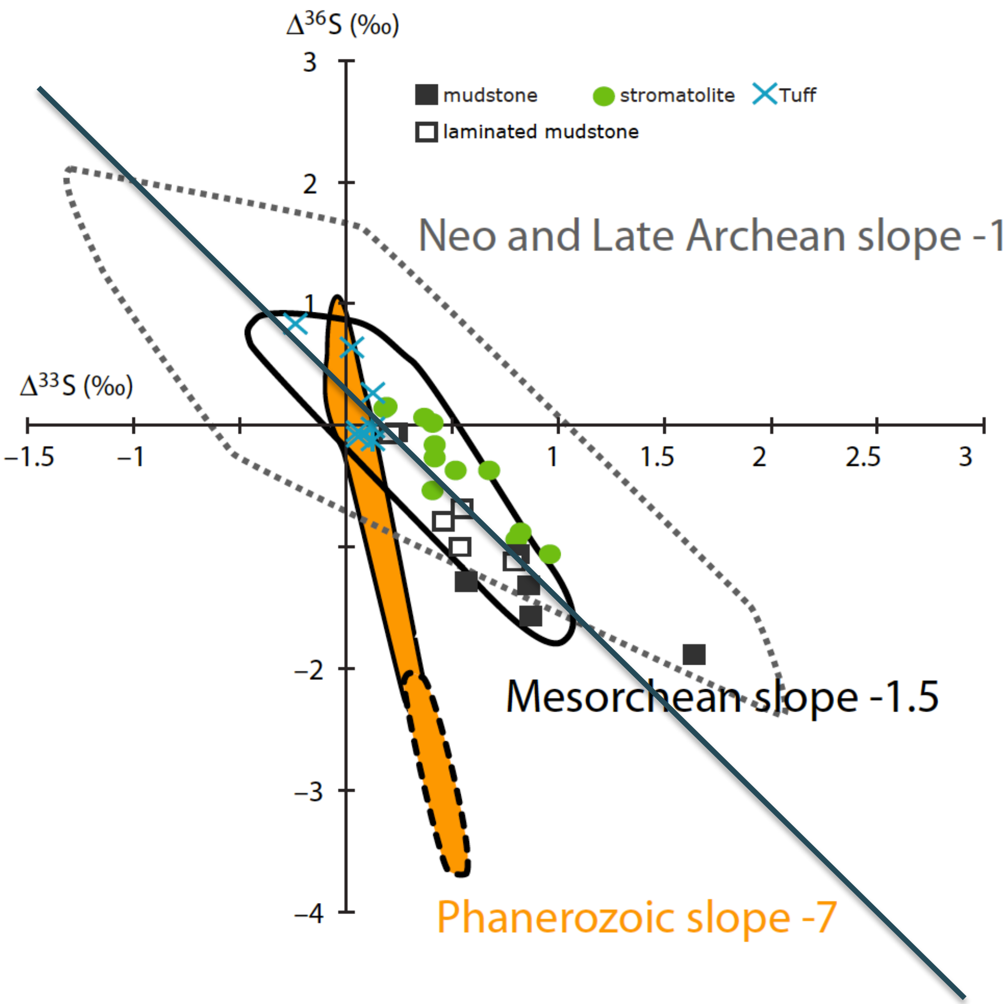
1/ 2.73 Ga Tumbiana Formation

Thomazo et al, 2009



$\Delta^{33}S_{py}$ between -0.3 and 1.6 ‰
Sizeable (> ± 0.2 ‰)
BUT LOW MIF-S

$\Delta^{36}S/\Delta^{33}S$ array fall on a typical **Mesoarchean slope** of ~ -1.5

- Argue for the preservation of a Mass Independent signal and thus **O_2**< 10^{-5} PAL

Y=-1.57x + 0.26
R^2=0.82

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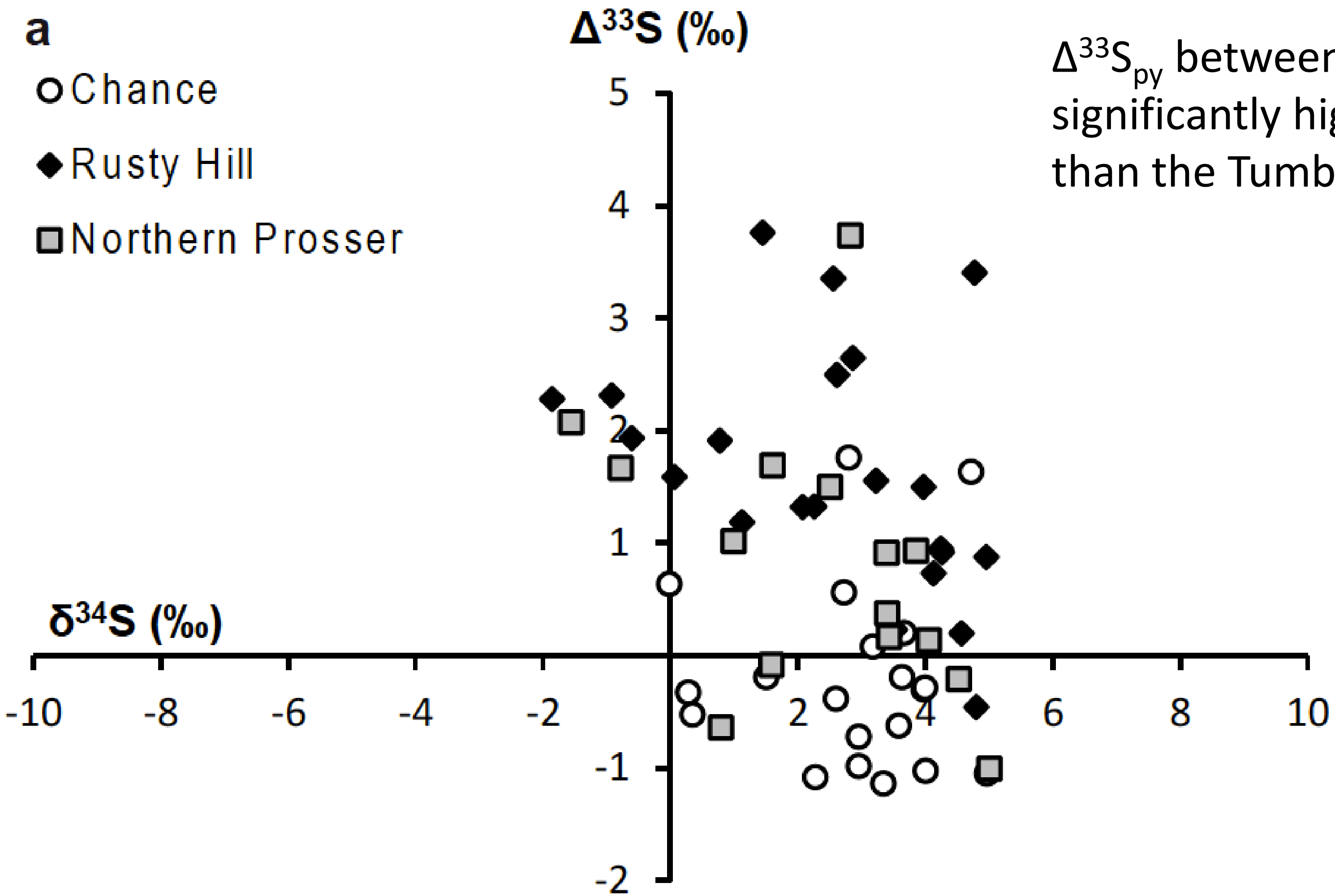
Kurzweill et al, 2013

2/ 2.71 Ga Kidd Creek Argillite layers



$\Delta^{33}S_{py}$ between -1.2 and 3.8 ‰ significantly higher in magnitude than the Tumbiana …

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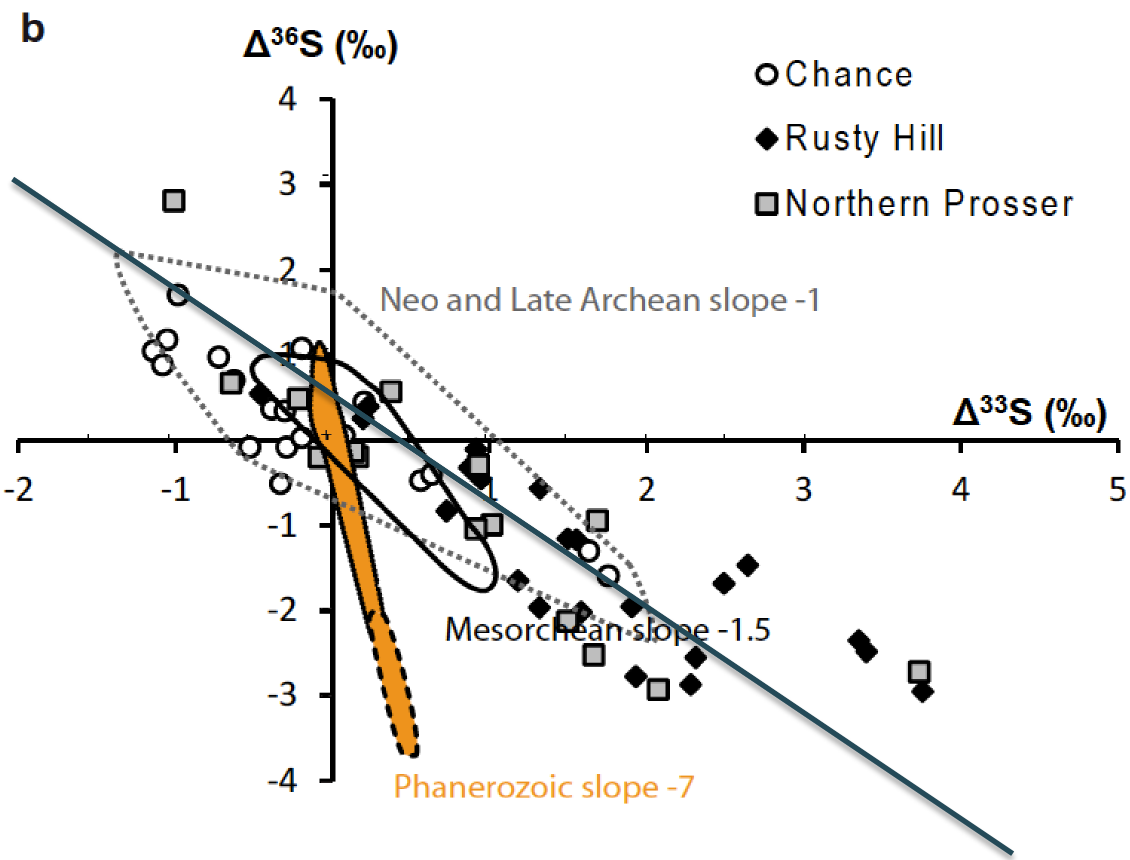
2/ 2.71 Ga Kidd Creek Argillite layers

Kurzweill et al, 2013



Y=-0.93x + 0.12
R^2=0.81

$\Delta^{33}S_{py}$ between -1.2 and 3.8 ‰ significantly higher in magnitude than the Tumbiana …

$\Delta^{36}S/\Delta^{33}S$ array fall on a typical **Latearchean slope** of ~ -1.0

- ➢ Argue for the preservation of a Mass Independent signal and thus O_2< 10^{-5} PAL

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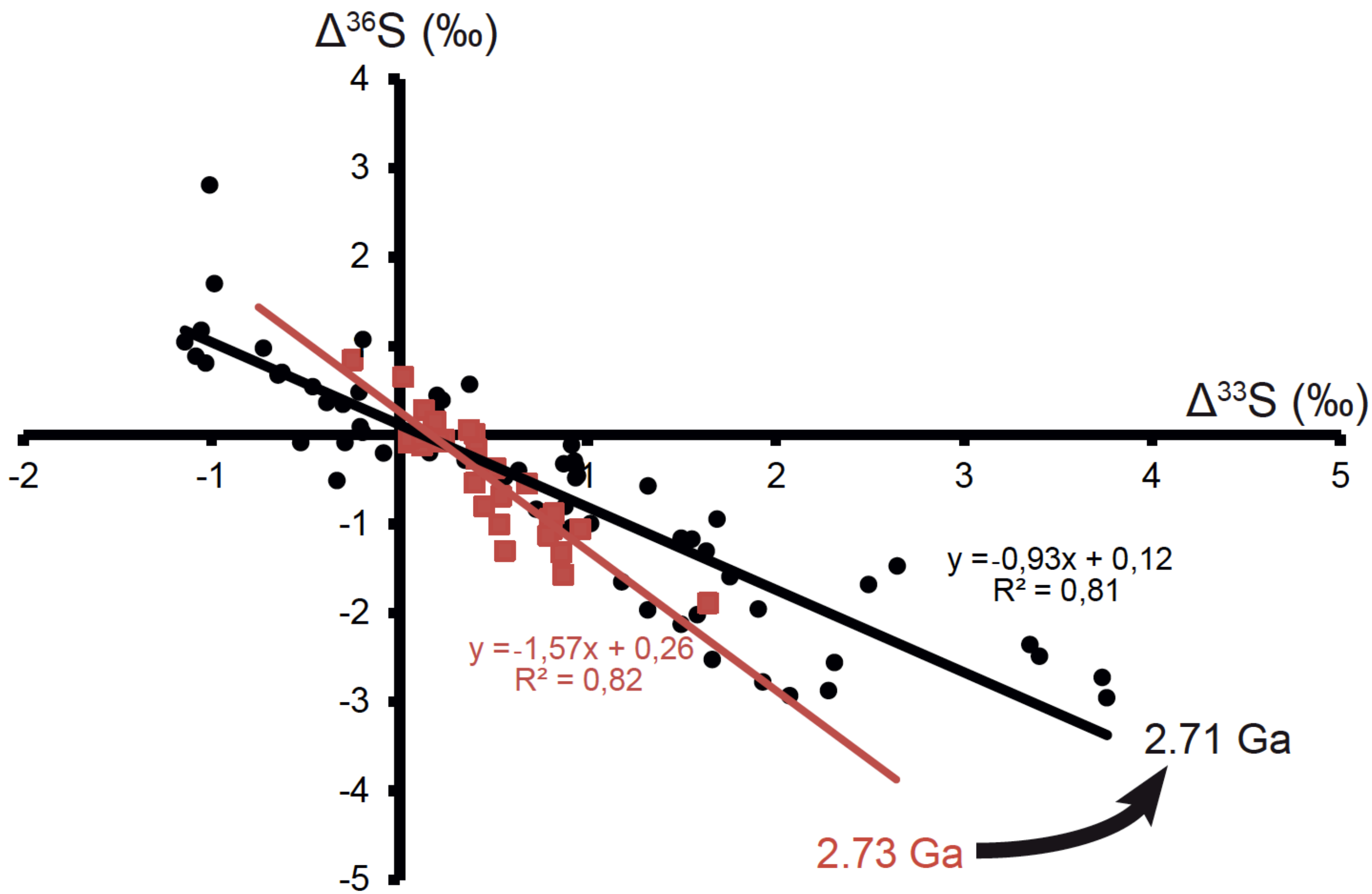
Slope of $\Delta^{36}S/\Delta^{33}S$ change between 2.73 and 2.71 Ga !!



Kurzweill et al, 2013

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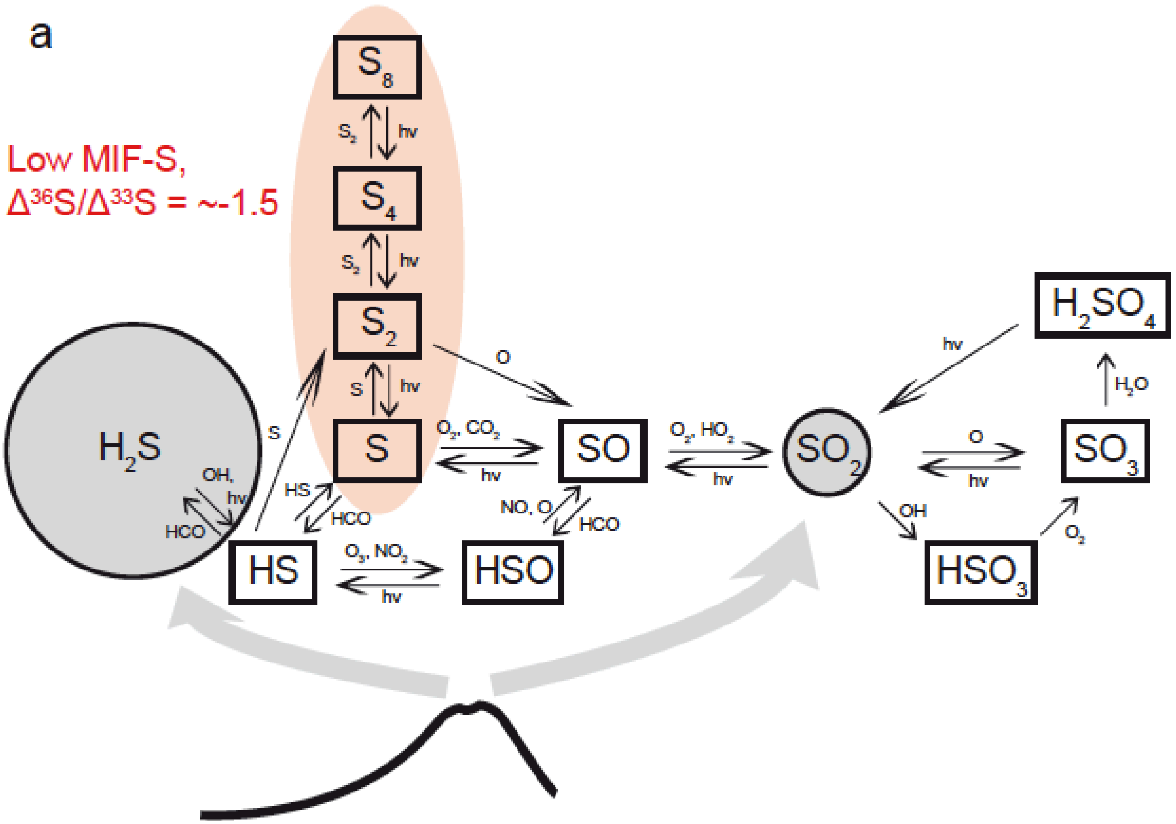
We need some photochemical model ...



Kurzweill et al, 2013

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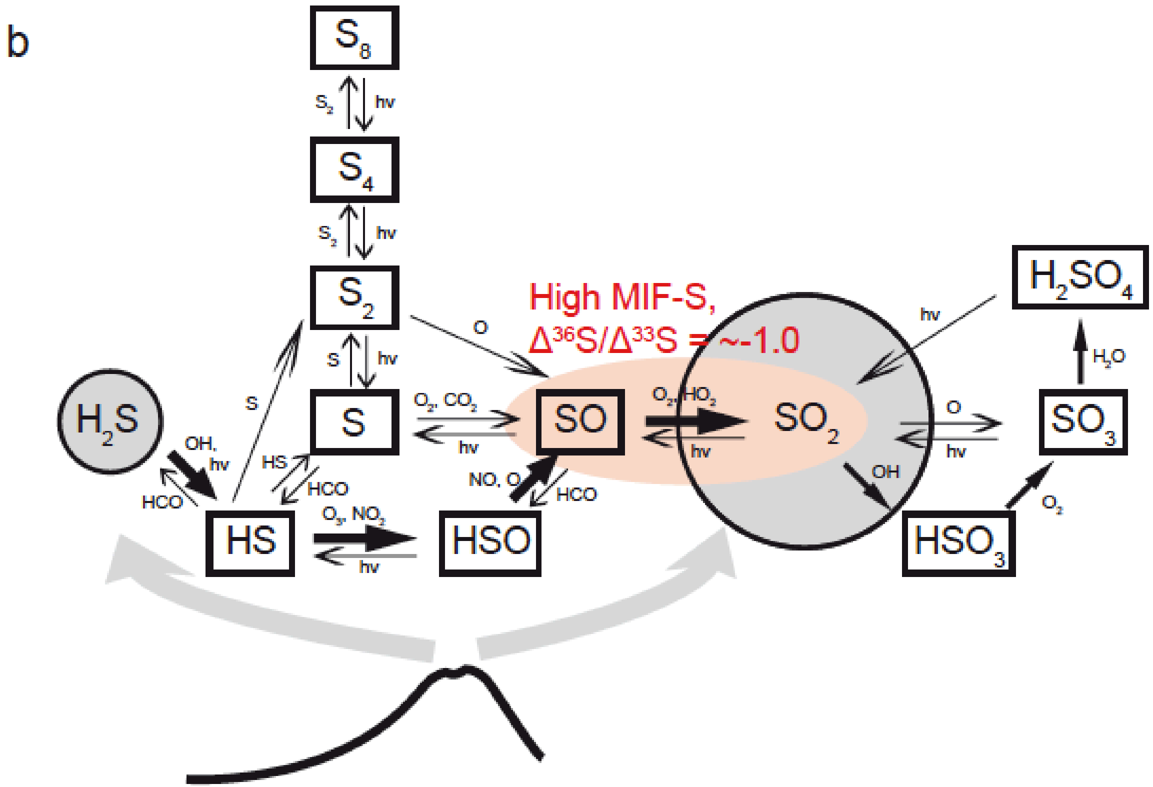

Kurzweill et al, 2013

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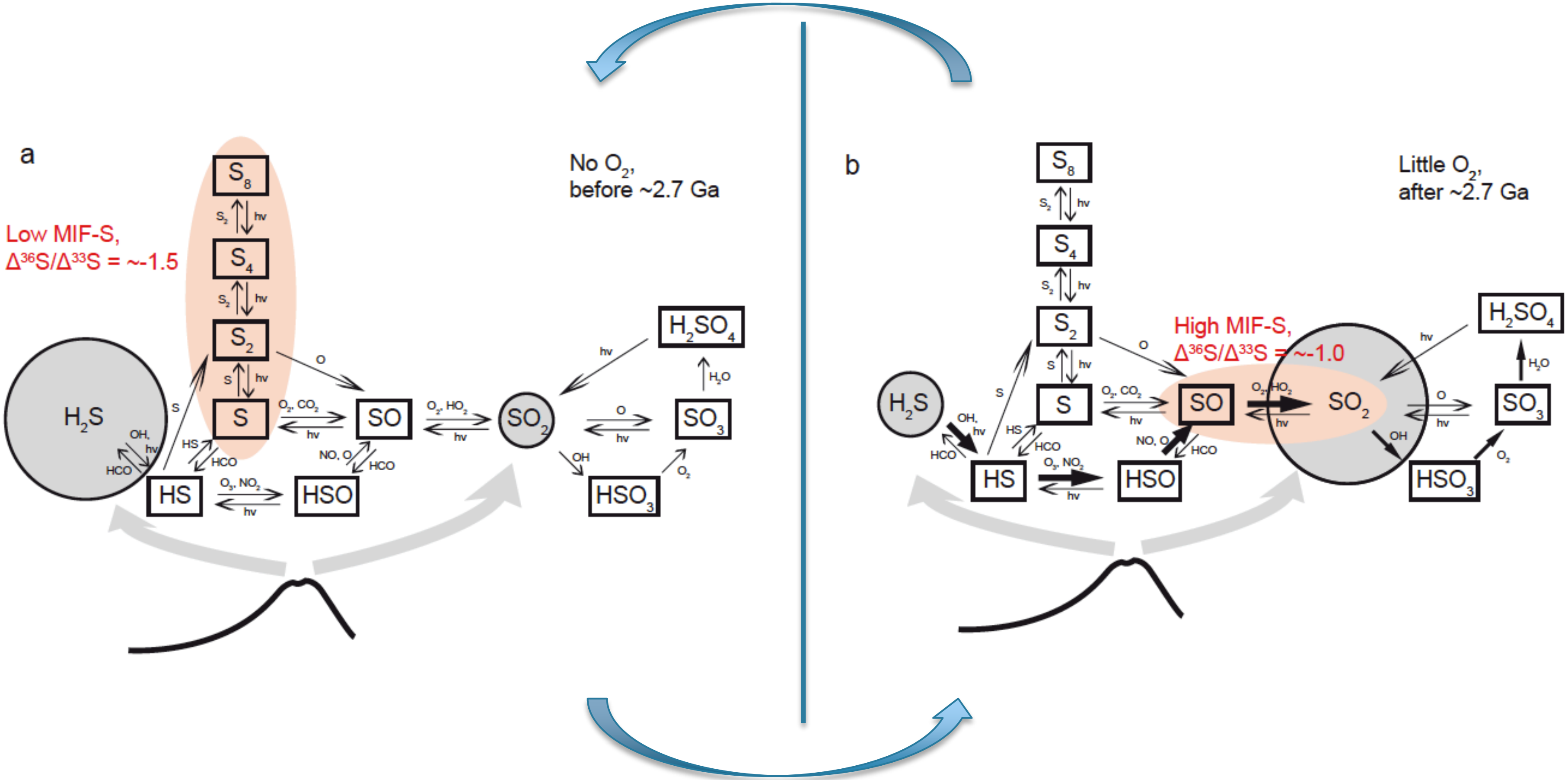

Depends on O_2 mixing ratios

Kurzweill et al, 2013

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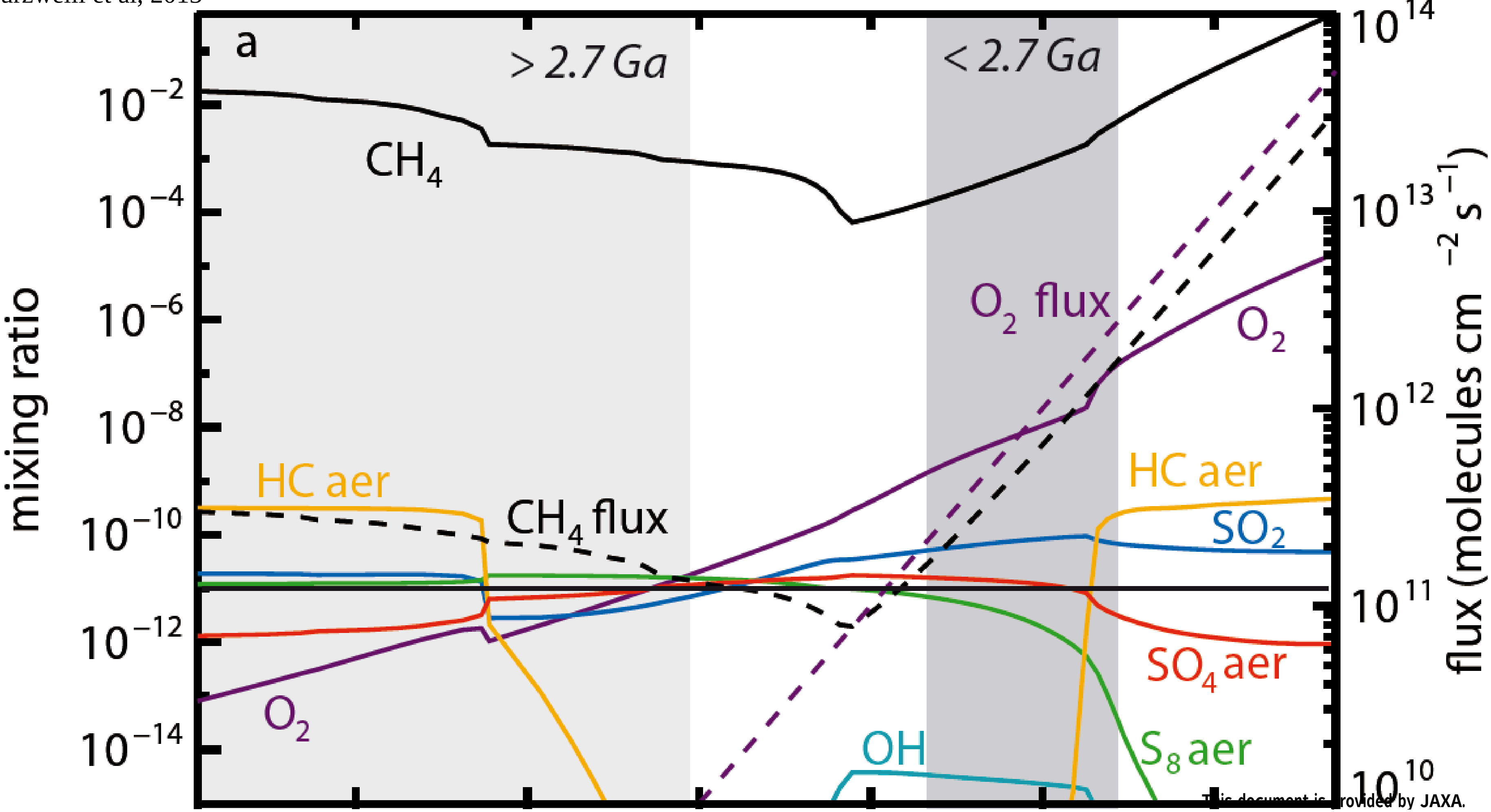
S_8 exit channel starts to decrease at O_2 mixing ratios $>10^{-9}$ consistent with previous estimates of photosynthetic flux into a predominantly reducing atmosphere (Claire et al., 2006)

Kurzweill et al, 2013



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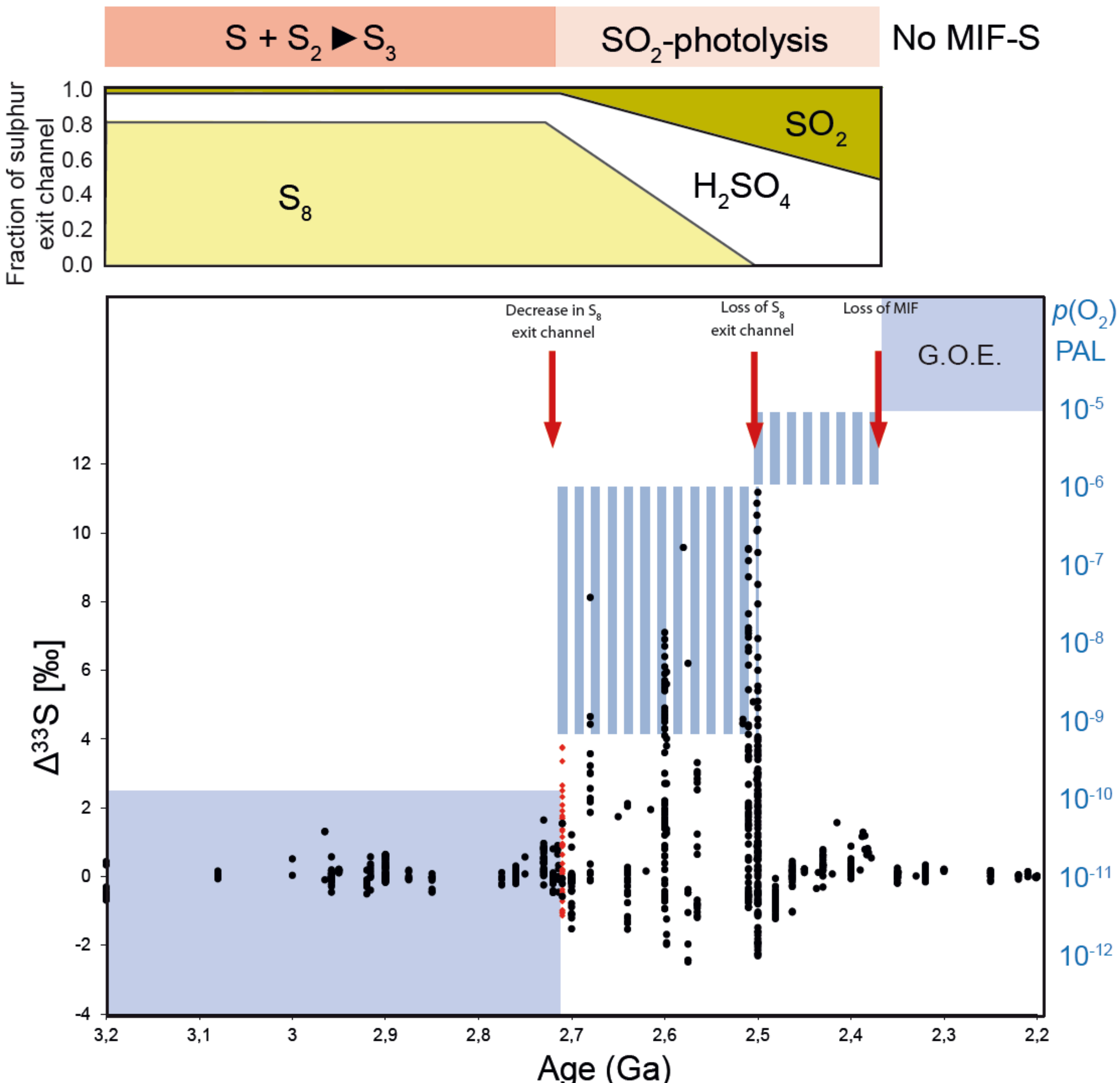

- ➢ We may have a quantitative model linking MIF-S secular variation and **the long term oxygenation of Earth**!

Kurzweill et al, 2013

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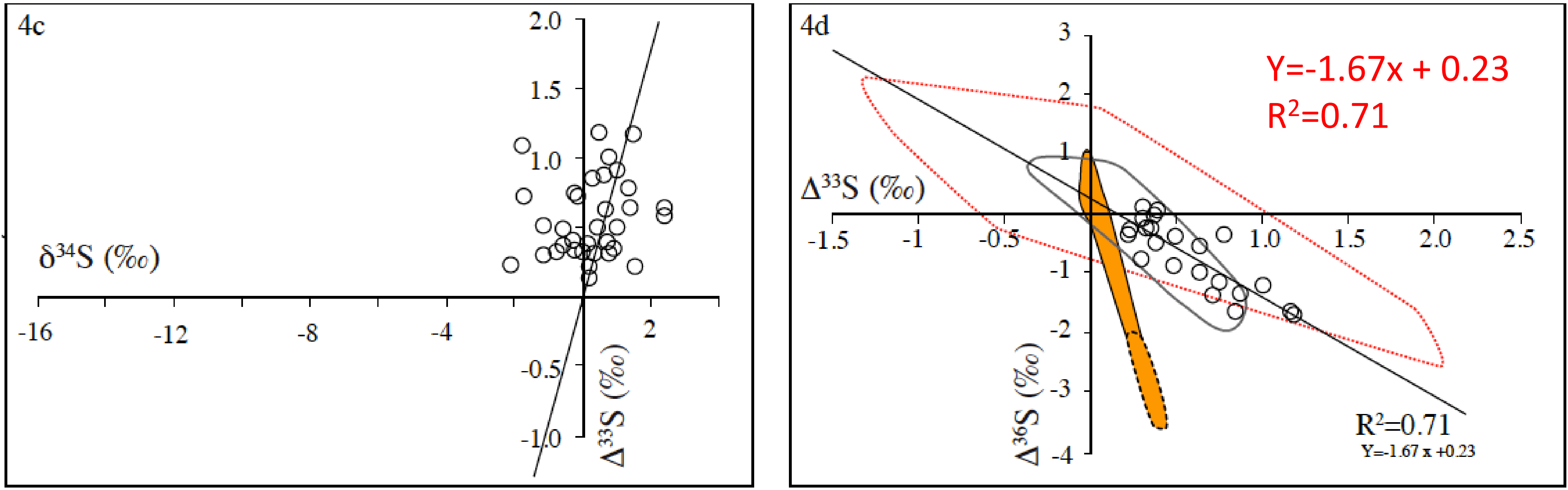
However at 2.65 Ga Manjeri and Cheshire formations

Thomazo et al, 2013



$\Delta^{33}S_{py}$ between 0.14 and 1.17 ‰ = Sizeable (> ± 0.2 ‰) BUT LOW MIF-S!!!

$\Delta^{36}S/\Delta^{33}S$ array fall on a typical **Mesoarchean slope** of ~ -1.5!!!

➢ **Our model is wrong / atmosphere is bi-stable / local conditions ?**

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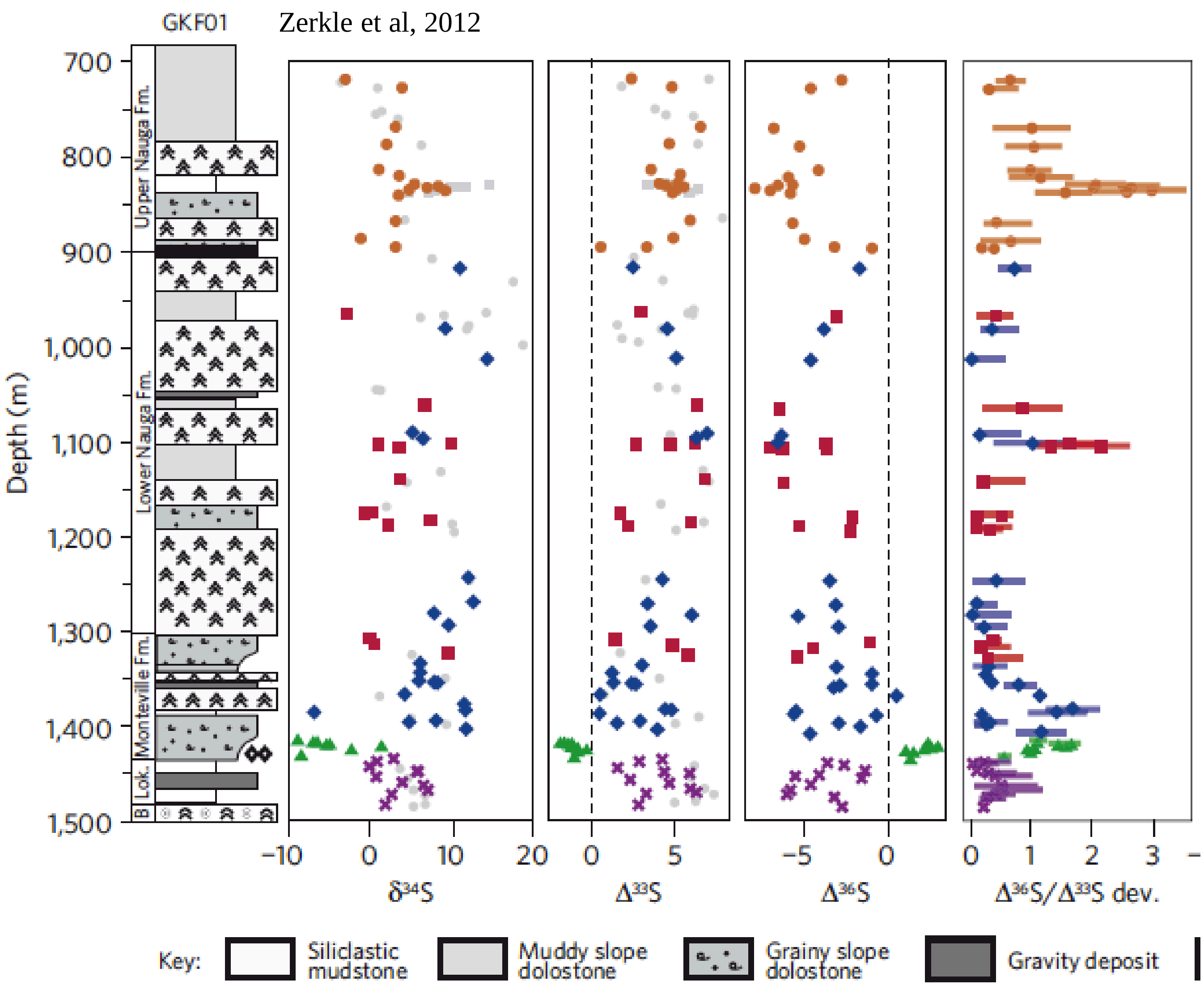

Short term deviation in the $\Delta^{36}S/\Delta^{33}S$ are **also observe** in the Campbellrand-Malmani platerofrm deposits (Transvaal Supergroup, South Africa) at around 2.5 Ga.

➢ **Our model is wrong / atmosphere is bi-stable / local conditions ?**

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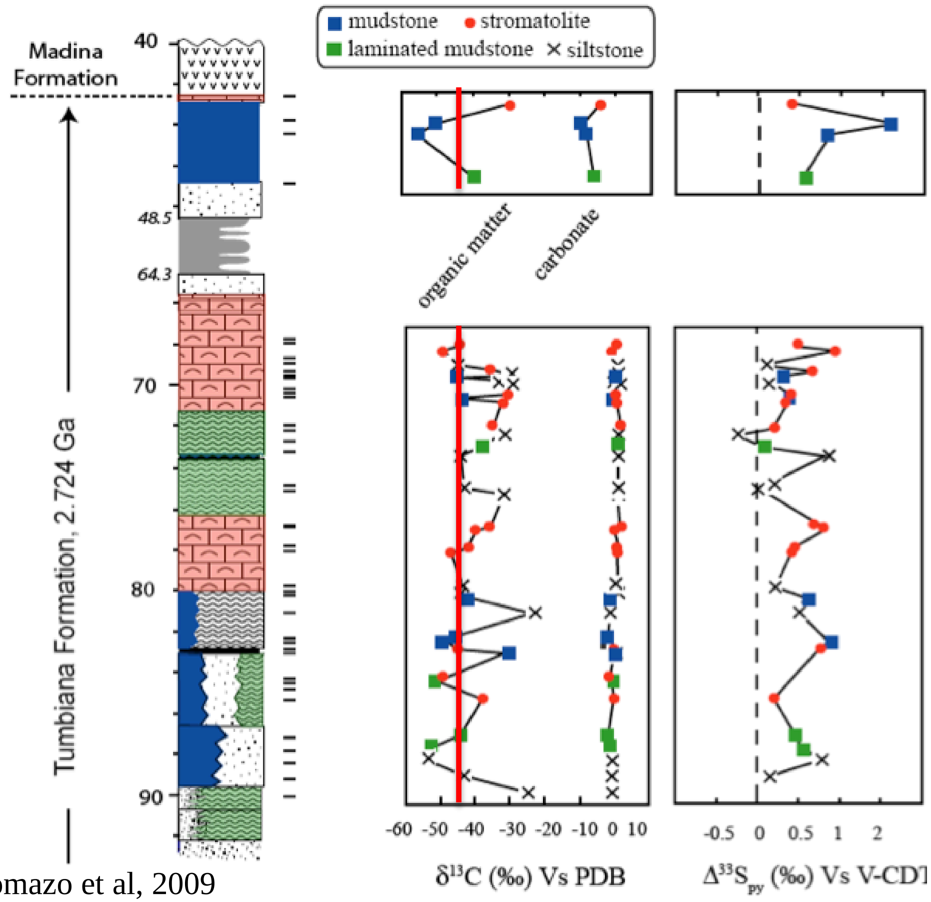
Neoarchean MIF-S oscillations (low MIF-S and $\Delta^{36}S/\Delta^{33}S$ array of -1.5) are often link to $\delta^{13}C_{org}$ variations!

In the Tumbiana Formation



Thomazo et al, 2009

- The ~2.72 Tumbiana Fm. record $\delta^{13}C_{org}$ range between -55.9 and -23.8 ‰

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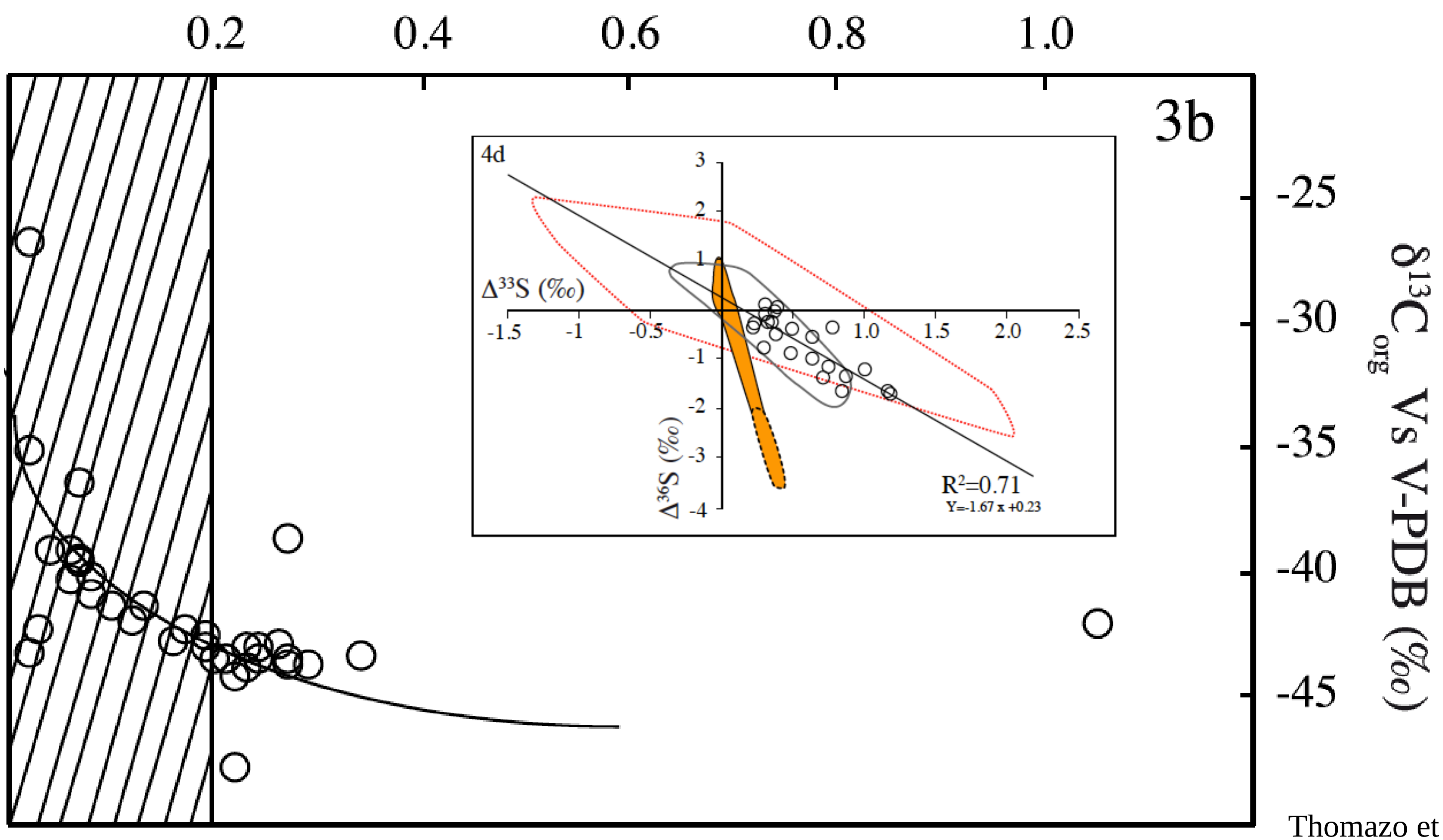
Neoarchean MIF-S oscillations (low MIF-S and $\Delta^{36}S/\Delta^{33}S$ array of -1.5) are often link to $\delta^{13}C_{org}$ variations!

In the Tumbiana Formation
In the Cheshire Formation

- The ~2.65 Cheshire Fm. record $\delta^{13}C_{org}$ of -41.3 ± 3.5‰



Thomazo et al. 2013

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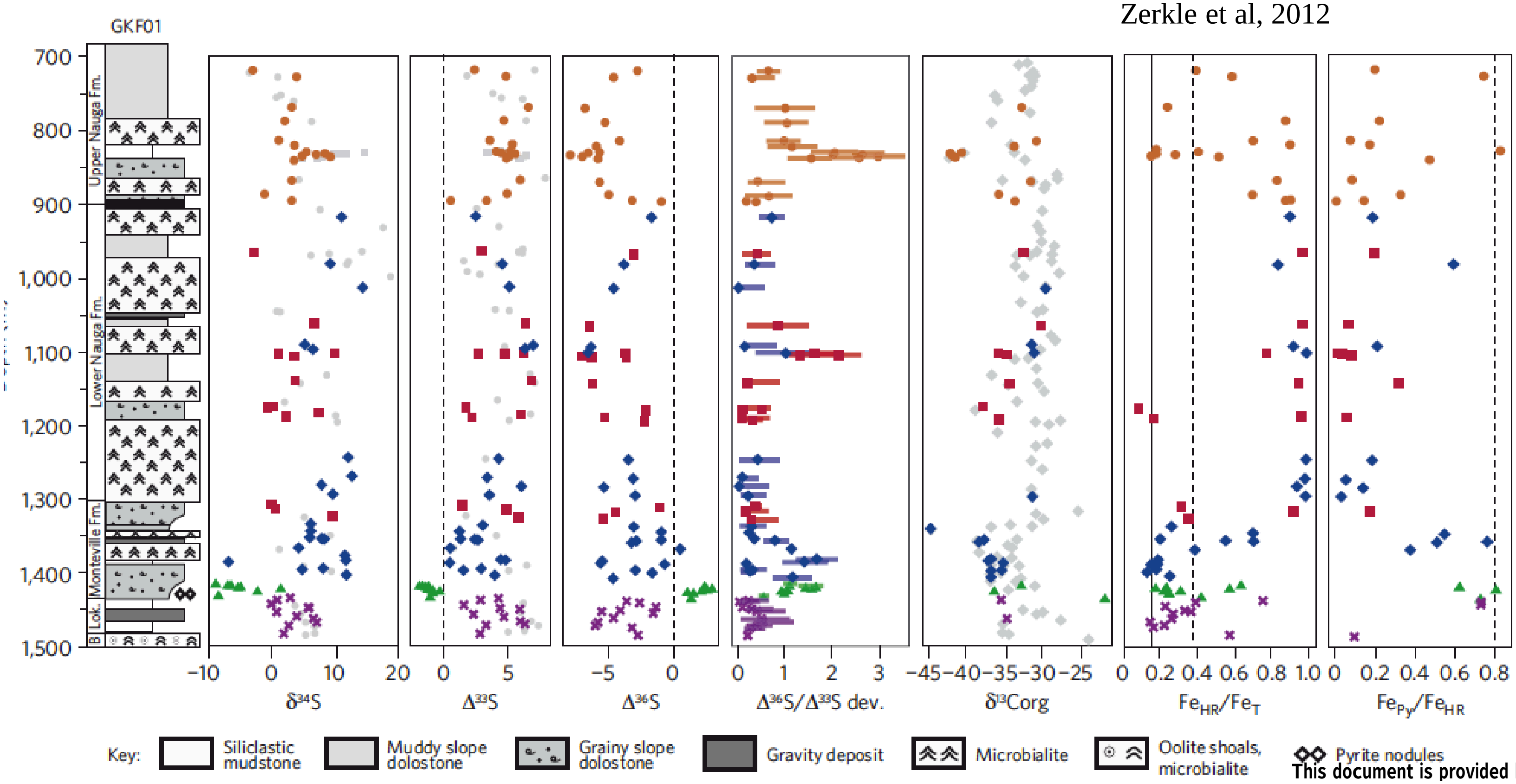
Neoarchean MIF-S oscillations (low MIF-S and $\Delta^{36}S/\Delta^{33}S$ array of -1.5) are often link to $\delta^{13}C_{org}$ variations!

In the Tumbiana Formation
In the Cheshire Formation
In the Campbellrand-Malmani platerofrm

Zerkle et al, 2012



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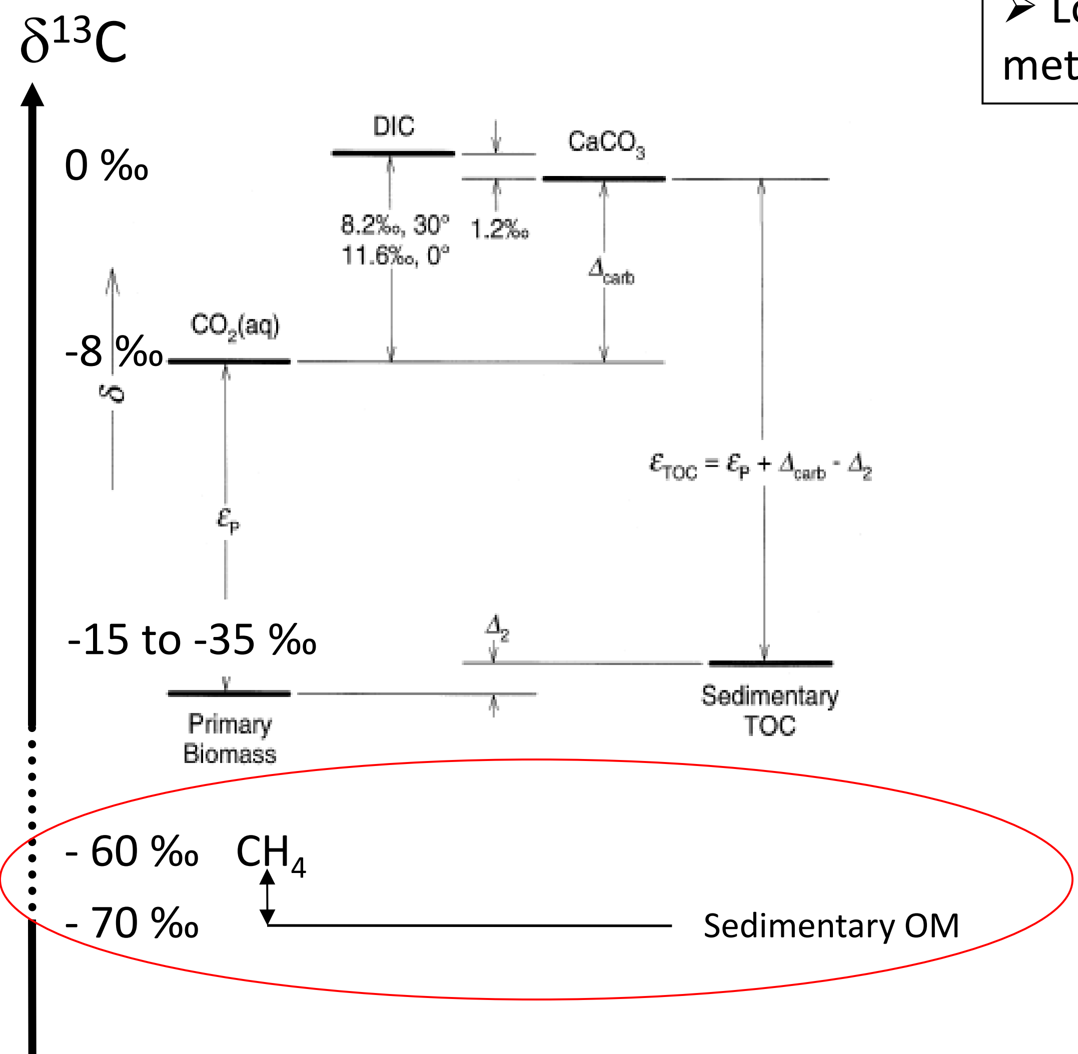
> ➢ Low $\delta^{13}C_{org} < 40‰$ is interpreted as methane incorporated in organic matter …



Modified from Hayes et al, 1998

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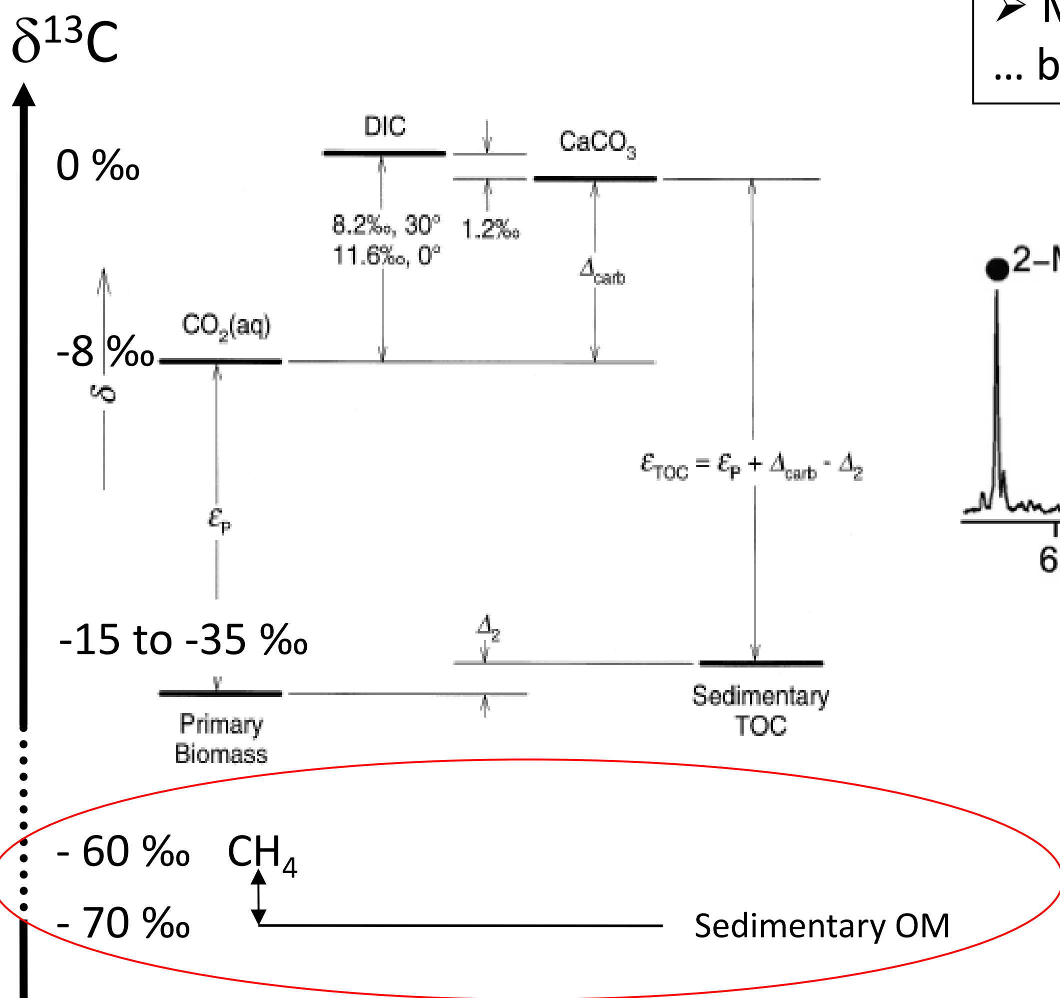
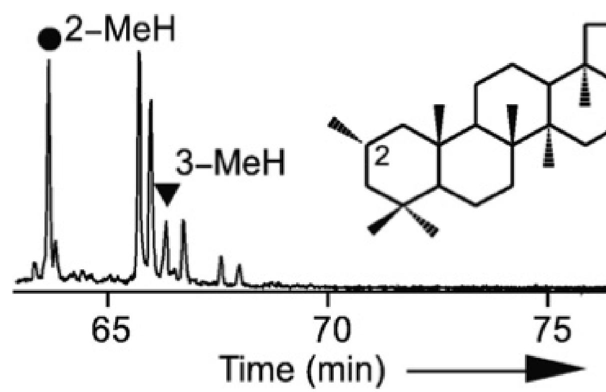
- Methane incorporated in organic matter
… by **Microbial oxidation of methane**



Modified from Hayes et al, 1998

2- α methyl hopane



Eigenbrode et al, 2008

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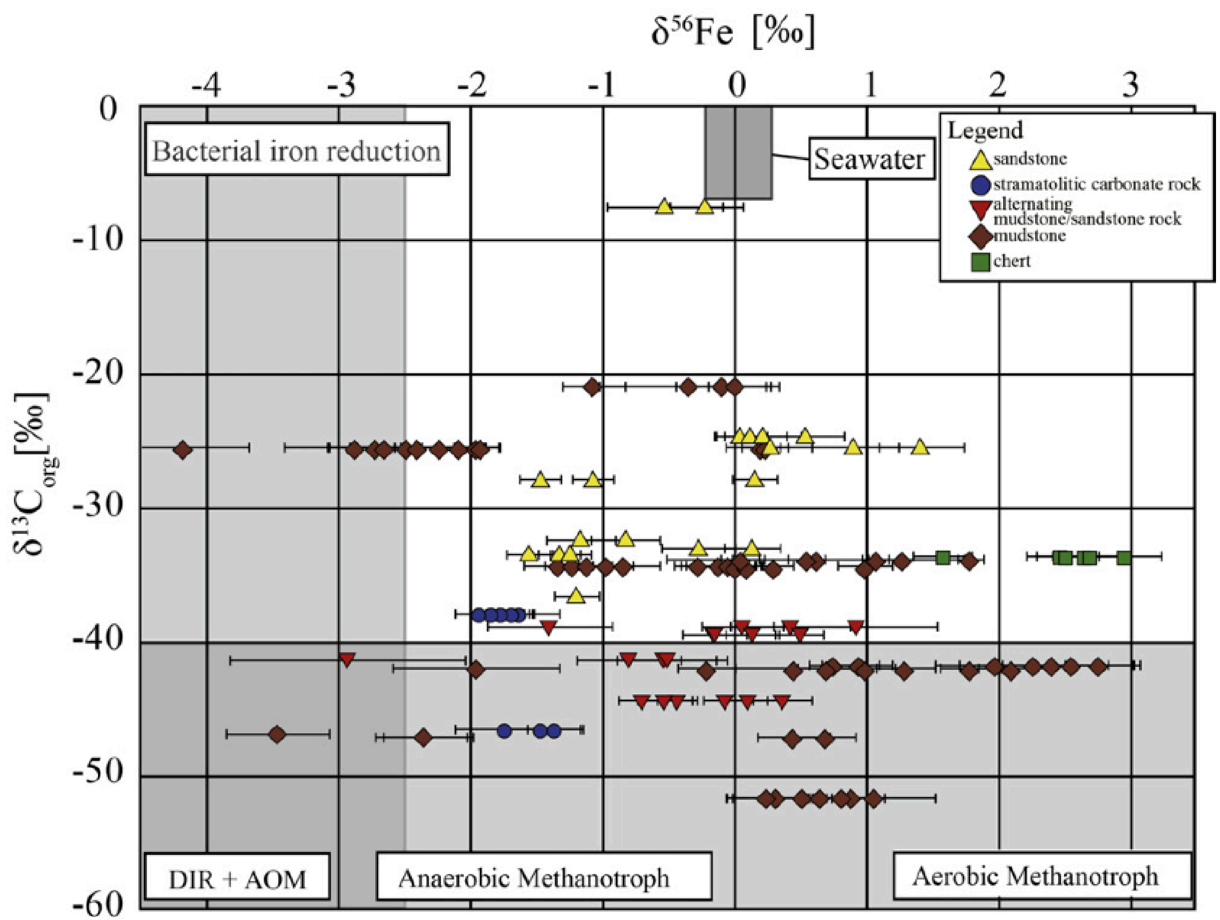
➢ Methanotrophs using **Anaerobic Oxidation of Methane** couple to **iron reduction, sulfate reduction, nitrate reduction** ??



Yoshiya et al, 2012

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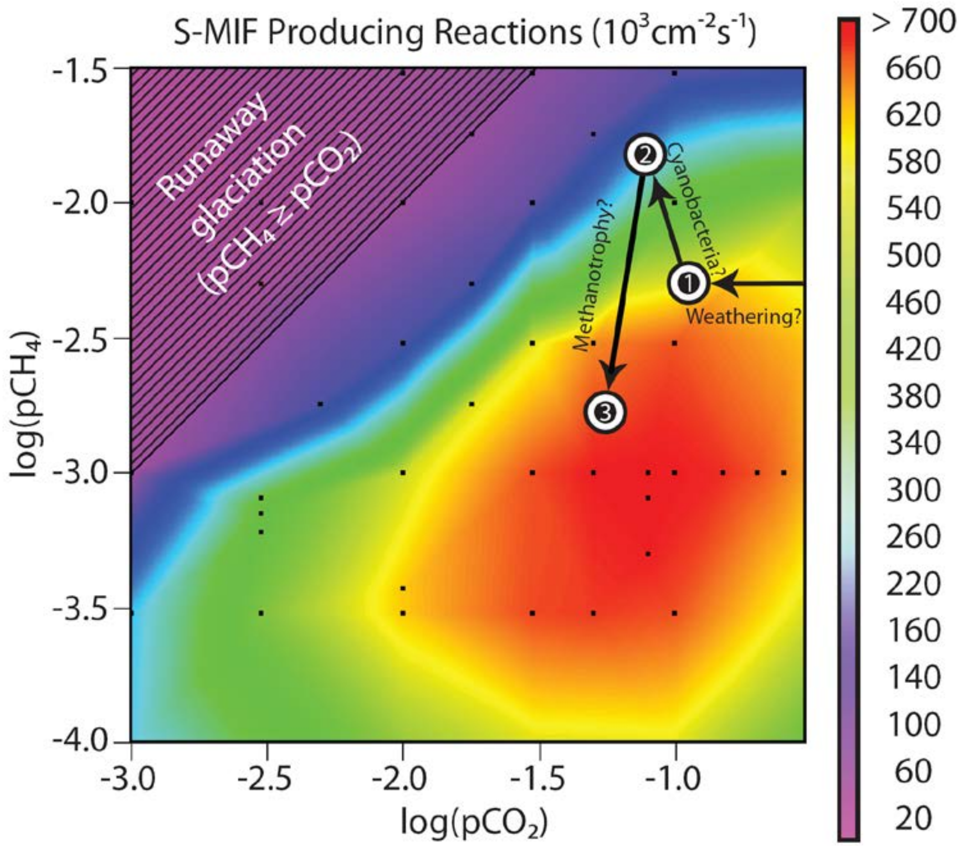
Methanotrophy could have decrease the flux of CH_4 to the atmosphere and modulate the amplitude, sign and reaction rate of sulfur isotopes …



Domagal-Goldman et al. EPSL (2008)

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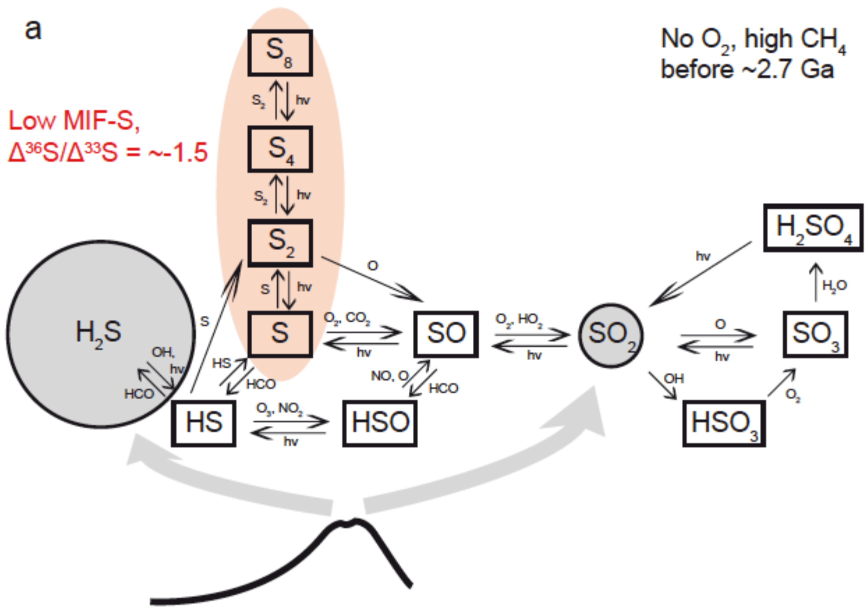
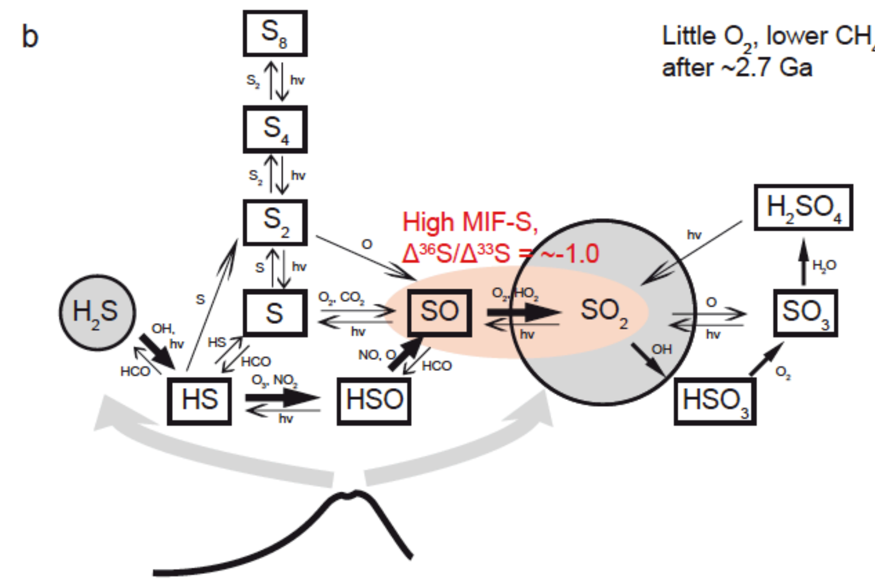
High Atmospheric CH_4

Low Atmospheric CH_4





Depends on O_2 and CH_4:CO_2 mixing ratios

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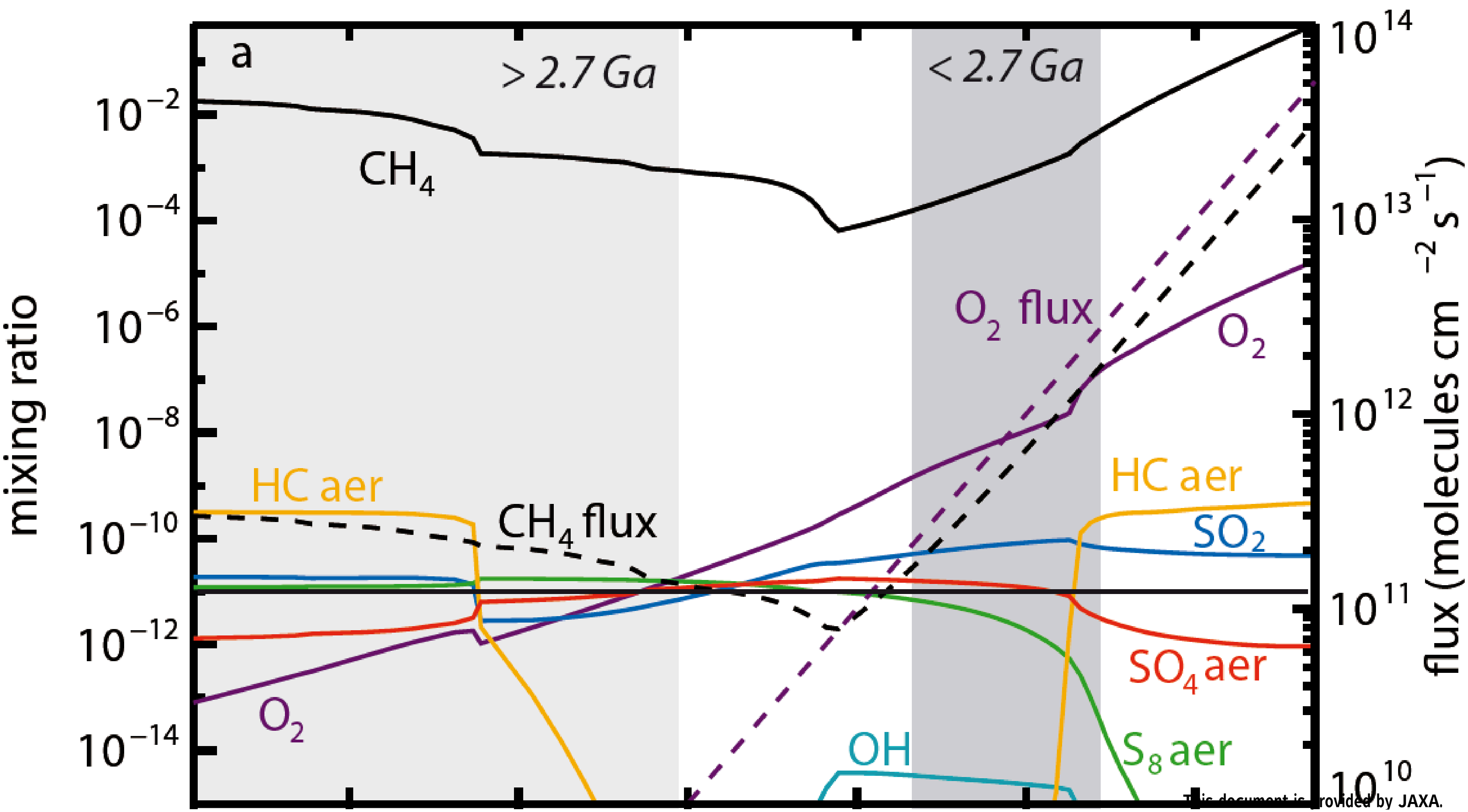
S_8 exit channel decrease once the oxygen flux becomes larger than the methane flux …

Kurzweill et al, 2013



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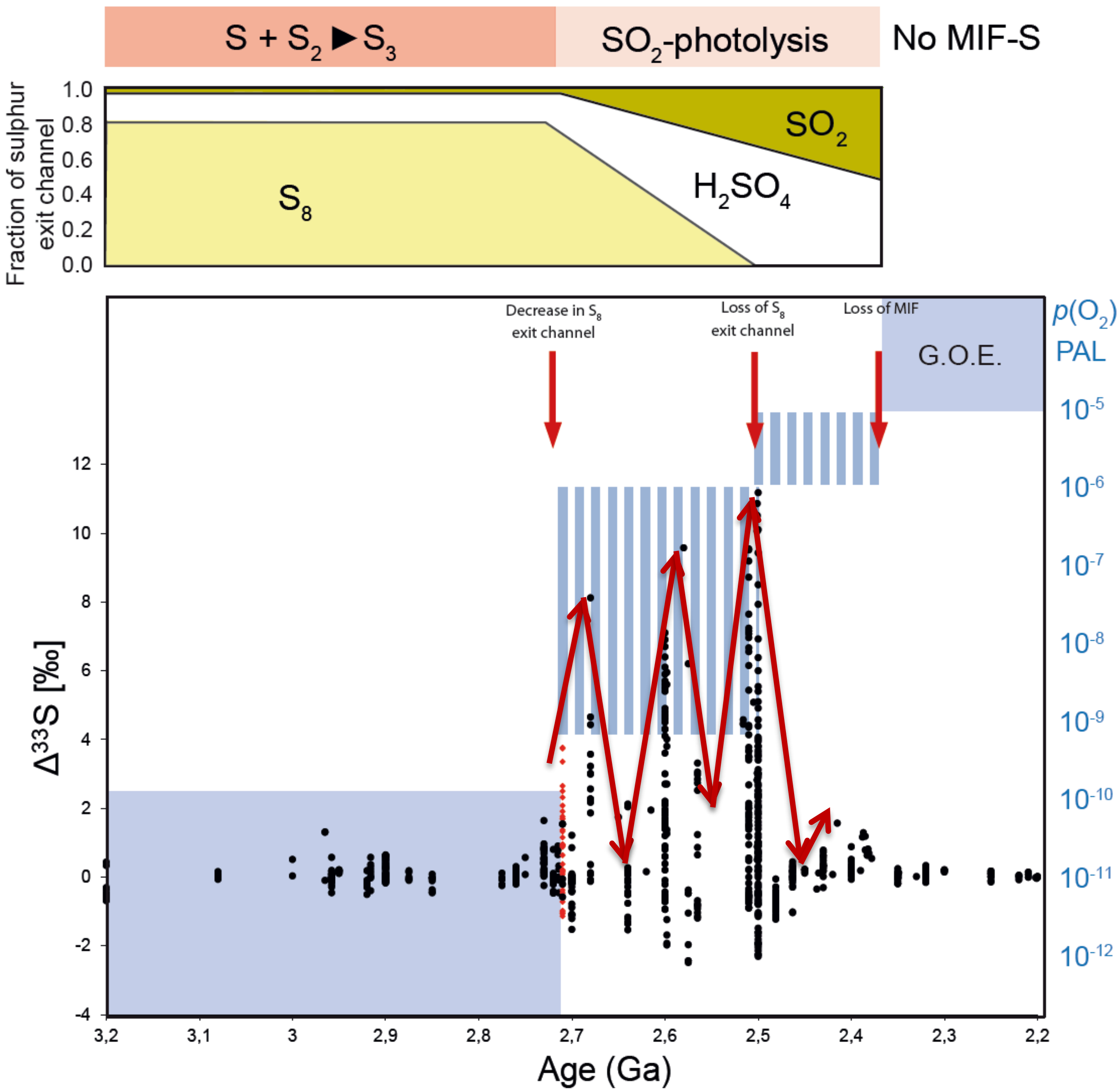

- We may have a quantitative model linking MIF-S secular variation and the long term oxygenation of Earth!

- Some of the observed variations might be directly link to the oceanic biological methane cycling (in response to a growing oceanic oxidants reservoir : nitrate, sulfate, iron)

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Conclusions :

- Model MIF-S secular variations are consistent with a first « whiff of oxygen » at around 2.7 Ga (10^{-11} to 10^{-7} PAL for O_2) in a still largely reducing atmosphere and suggest a strong air–sea gas exchange disequilibrium with respect to O_2

- Some of the observed MIF-S variations might reflect changes in methane flux to the atmosphere regulated by biological process (i.e. the microbial oxidation of methane) …

*BUT our atmospheric model is yet unrealistic / oversimplified, other gases might have been important : **H_2S (Halevy et al, 2010); OCS (UENO et al. 2009)** etc…*

…there is a few 300 Ma of biological and geological feed back loop to decipher ! (sulfur, nitrogen, iron, methane, OM burial, climate) before the GOE!

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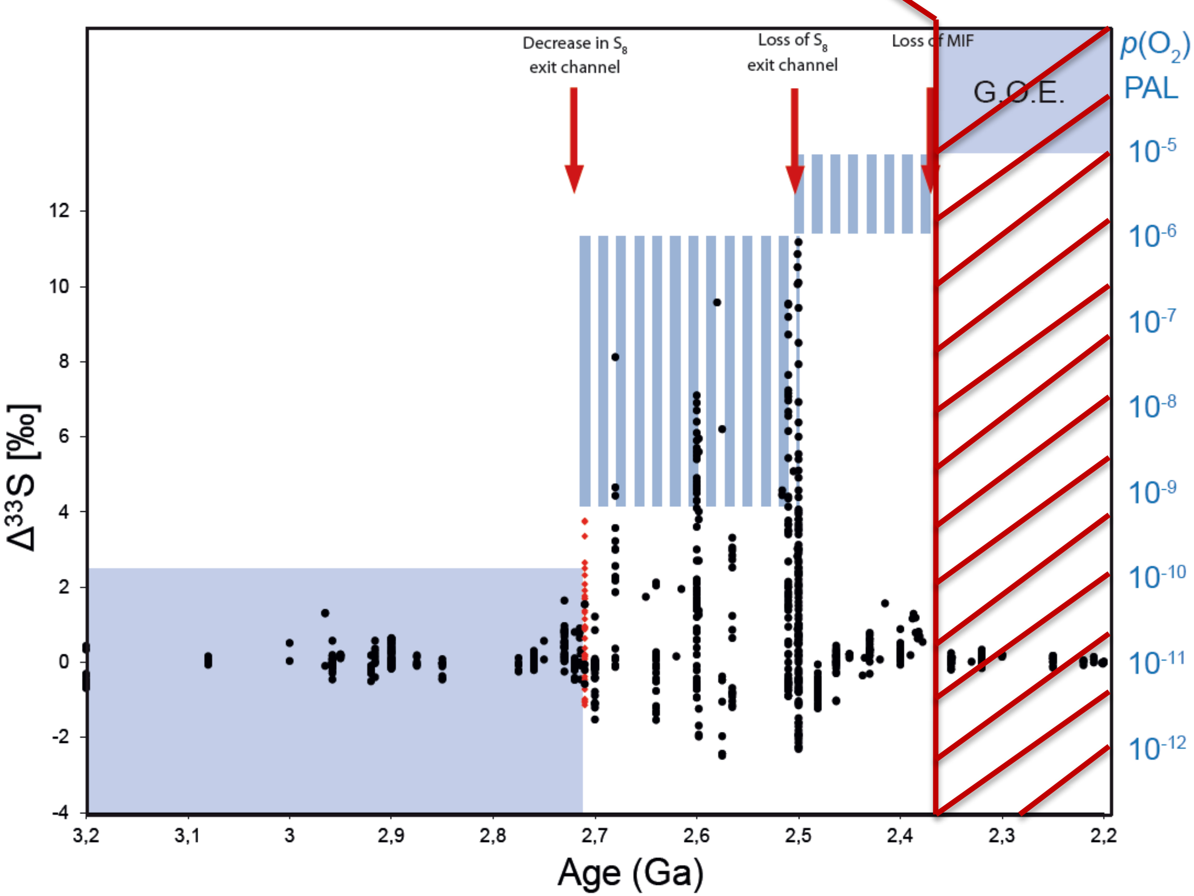
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$



- After the GOE methane lifetime decrease drastically (atmospheric methane cycle is regulated by abiotic oxidation)

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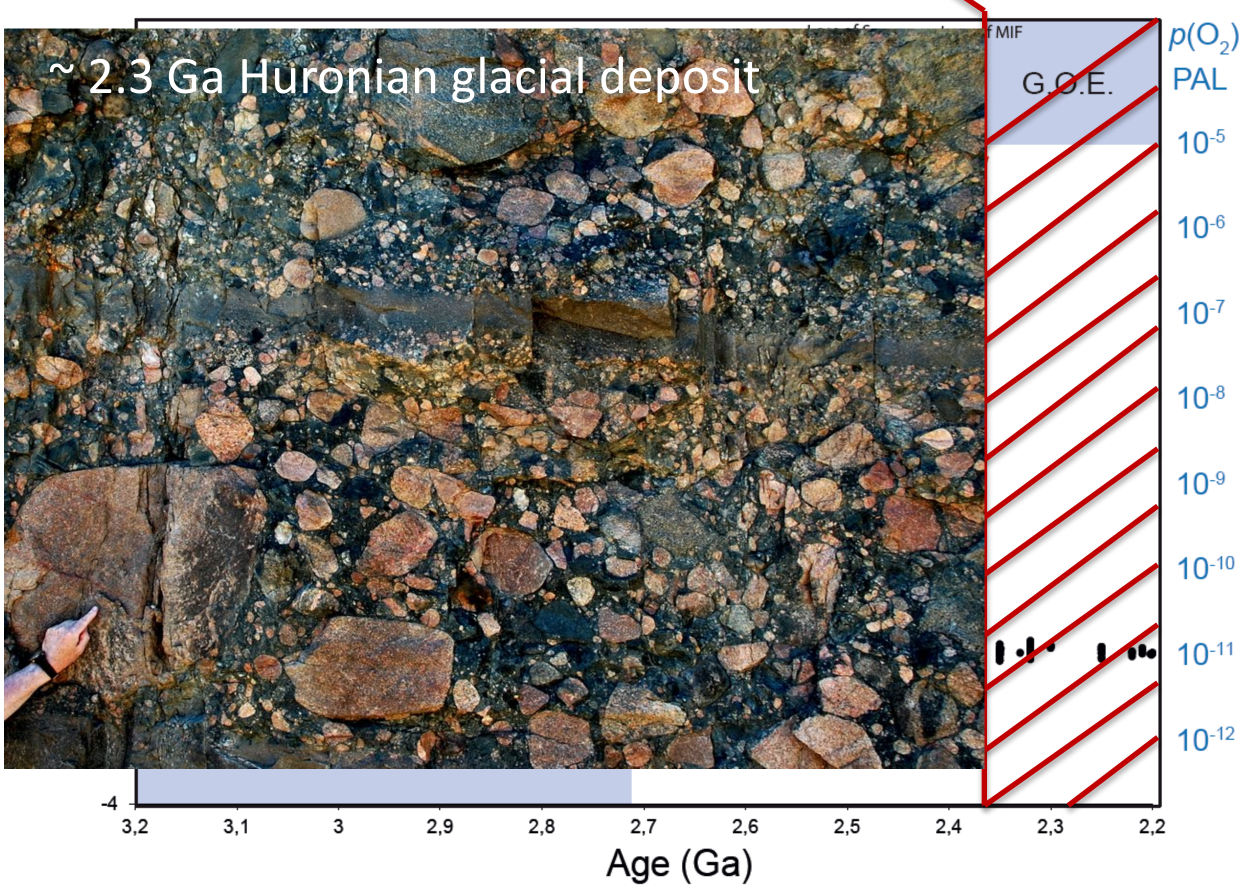

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