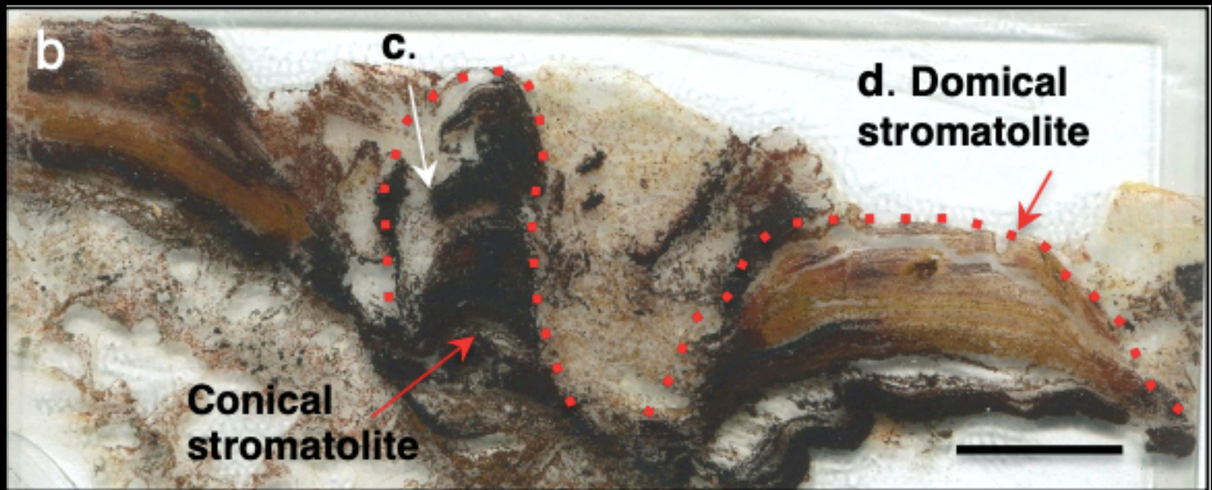
DR CRAIG O'NEILL, ORIGINS RESEARCH INSTITUTE, BUDAPEST

DID THE DESTABILISATION OF DEEP PRIMORDIAL MANTLE DRIVE THE GREAT OXIDATION EVENT?

STROMATOLITES

- Stromatolites are formed from microbial mats of photosynthetic cyanobacteria
- Strong evidence for photosynthesis of some form at 3.5 Ga

Wyoming, Eocene



Dresser Formation, 3.5 Ga, Djokic 2017

PRE-2.4 GA

- Banded-iron formations
- Pyrite and uraninite pebbles in conglomerates

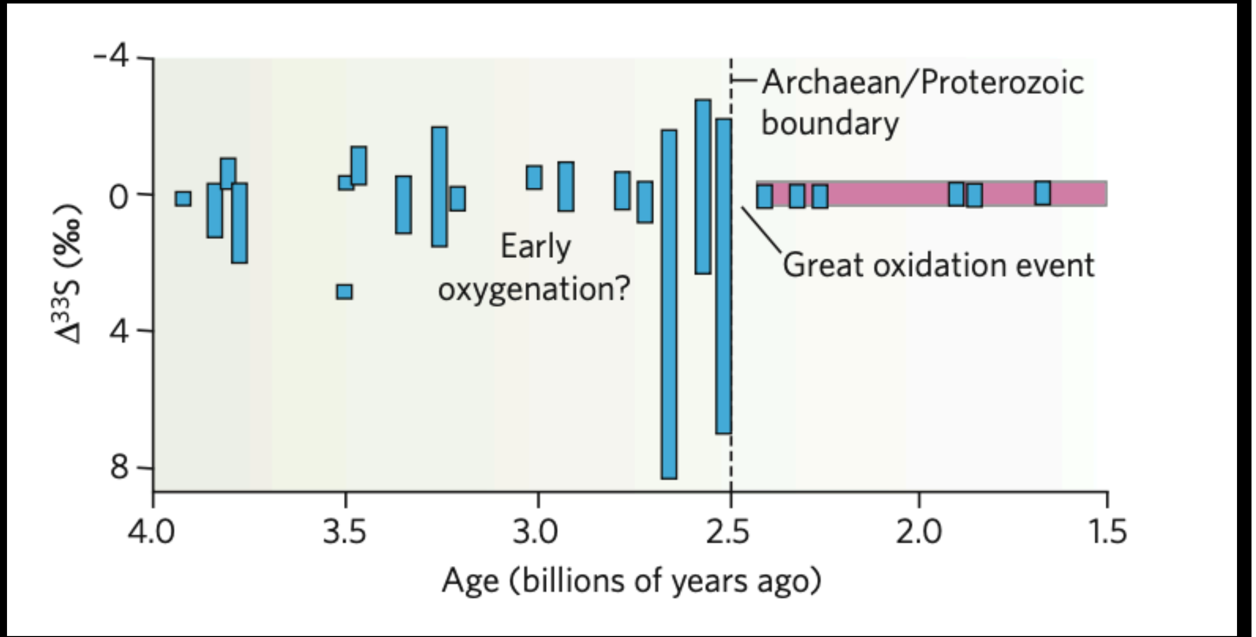

POST-2.4 GA

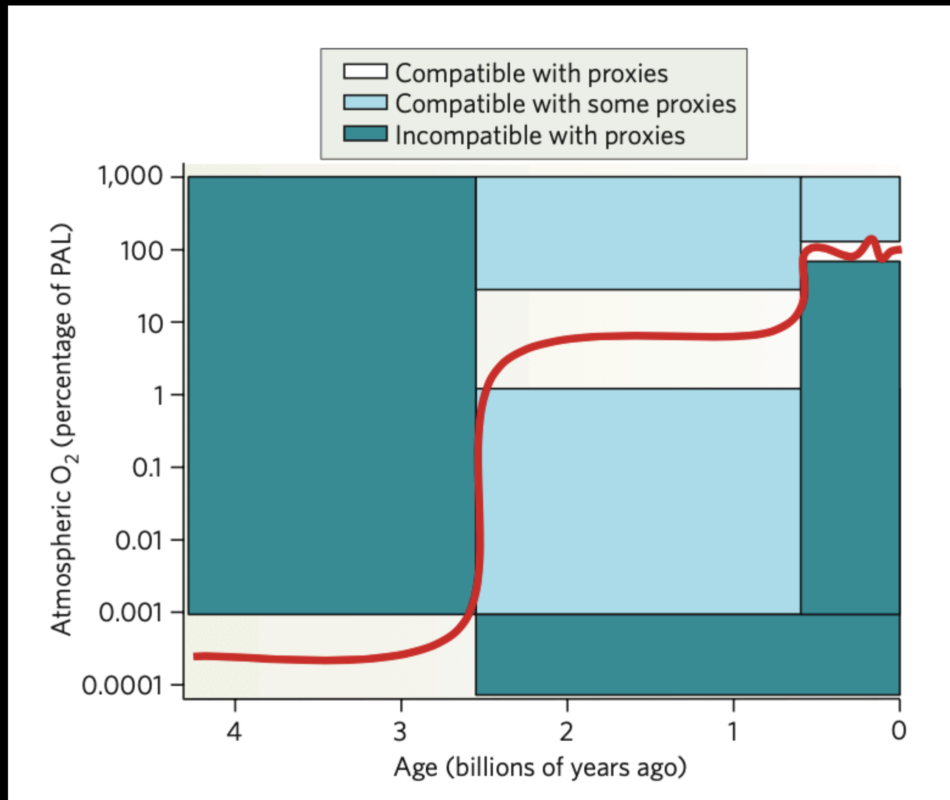
- Red beds
- Oxidised gossan


NO EVIDENCE OF WIDESPREAD ATMOSPHERIC OXYGEN PRIOR TO 2.4 GA

THE GREAT OXIDATION EVENT

- MIF (Mass independent fractionation) of S occurs in upper atmosphere due to S photochemistry
- Rapidly homogenised in presence of oxygen - no MIF post 2.4 Ga
- Quantifies a > 4 order of magnitude jump in atmospheric oxygen at the GOE





Kump, 2008

WHY IS THERE A >1 GYR DELAY BETWEEN THE ONSET OF PHOTOSYNTHESIS AND THE GREAT OXIDATION EVENT?

POSSIBLE ALTERNATIVES:

- Non oxygen producing photosynthesis

Evidence of short-lived oxygen transients suggests oxygenic photosynthesis existed 3.2 Ga (Kadoya et al 2020)

- Slow gradual increase in O_2 till tipping point

Inconsistent with microbial growth and diversification rates

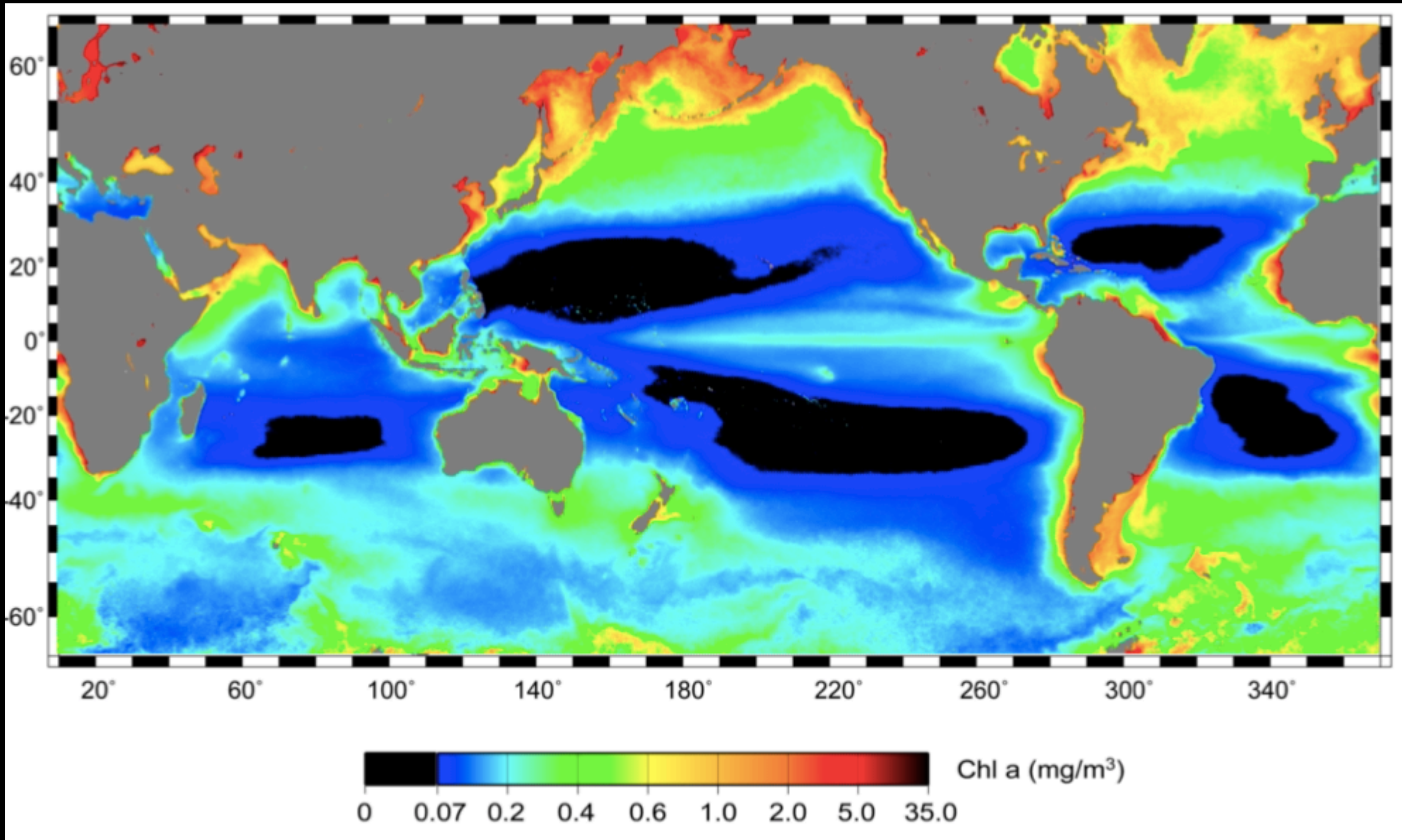
- Restricted biomass / nutrient supply

- Loss of O_2 sink (primarily volcanic reducing gases)

ALTERNATIVE 3: RESTRICTED BIOMASS / NUTRIENT SUPPLY

- Photosynthetic organisms hug the continents - primary source of nutrients (phosphates, nitrates)

- Suggests biomass potential (and O_2 production rate) tied to formation and emergence of continents around 2.7 Ga (Flament et al. 2007)



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Part of the solution. But oxygen would still build up without a sink.

- Loss of O_2 sink (primarily volcanic reducing gases)

ALTERNATIVE 4: LOSS OF O_2 SINK (PRIMARILY VOLCANIC REDUCING GASES)

- Did the style of volcanism change?

  Perhaps (Condie, O'Neill and Aster, 2009) - but a story for another time.

- Did the redox state of volcanic products change?

DID THE REDOX STATE OF VOLCANIC PRODUCTS CHANGE?

- We now know the lithospheric mantle is heavily oxidised by metasomatic events - tendency to drive towards oxidised conditions (Berry et al., 2015)
- Fractionation can drive melts towards oxidation (Foley, 2010)
- "Pristine" Archaean MORB can be estimated from cratonic eclogites (Aulbach and Stagno, 2016)
- Close to "pristine" melt can be derived from obtained from chromite inclusions (extremely refractory - close to source conditions) (Niklas et al., 2018)

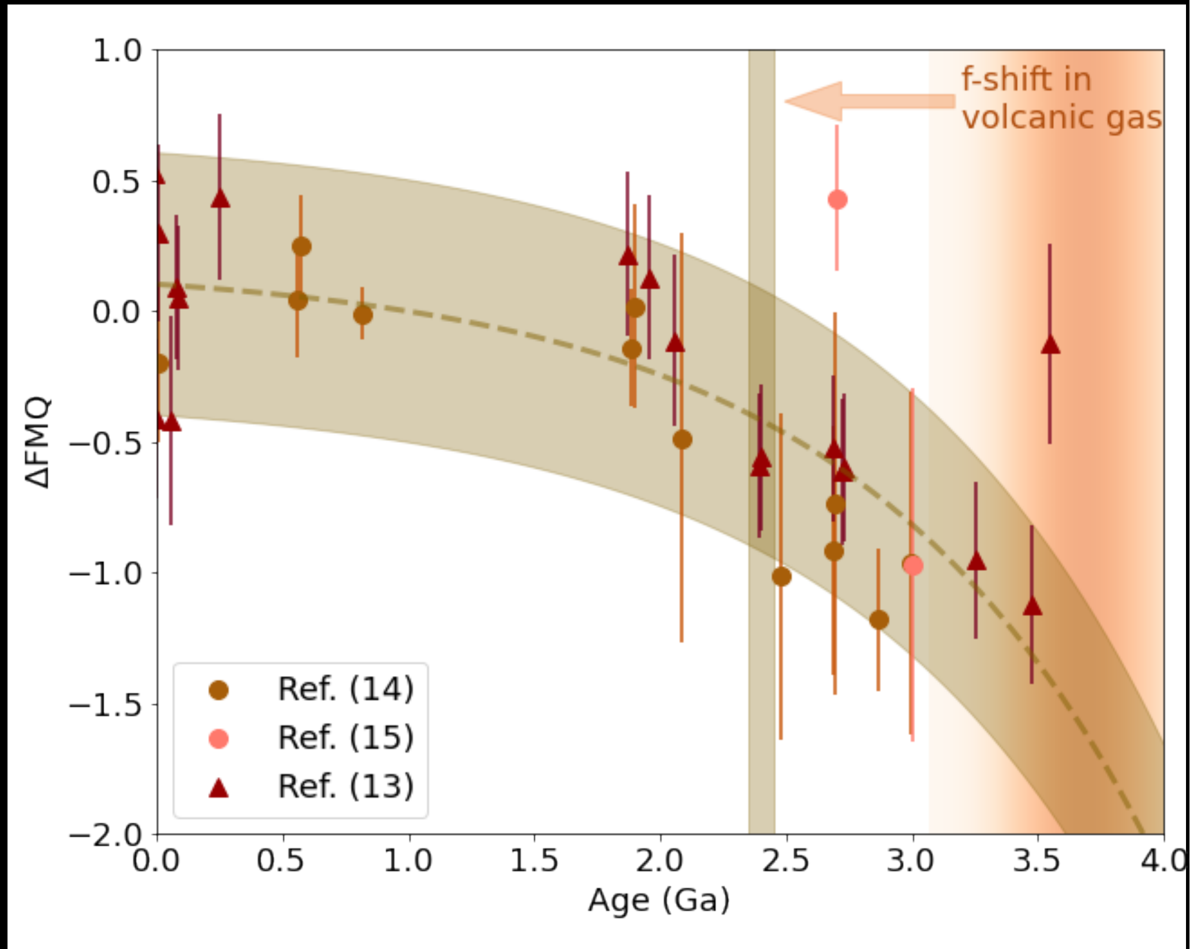
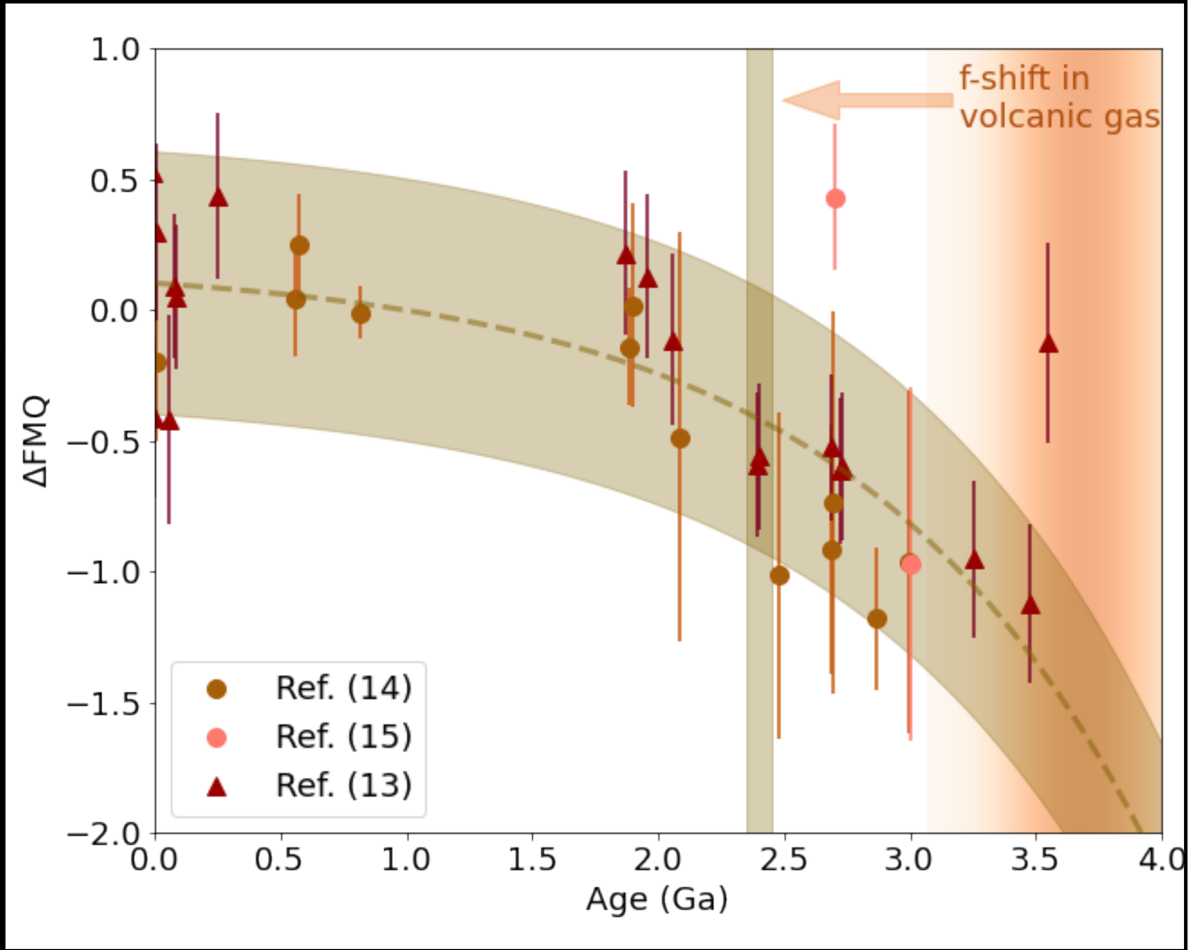


Figure from O'Neill and Aulbach, 2022

DID THE REDOX STATE OF VOLCANIC PRODUCTS CHANGE?

- 0.5 **Delta-**FMQ change in volcanic gasses needed to drive GOE (Holland, 2002)
- Eg. From H_2S -> SO_2, CH_4 -> CO_2, etc.
- Shift of ~ 1.5 dFMQ in mantle source seen over transition, > 0.5 d-FMQ leading up to GOE
- Slow ramp-up before the transition suggests mantle origin (ie. not surface oxidation driven)
- Did the mantle mix-in an oxidised reservoir?



WHAT WAS THE OXIDISED RESERVOIR THE MANTLE MIXED IN?

FORMATION OF OXIDISED MANTLE DURING A MAGMA OCEAN

- Early growth of (Al) bridgmanite (Fe3+)
- Strong disproportionation reaction
- Effectively Fe^{2+} -> Fe^{3+} + Fe^{0}
- Metallic iron (Fe^{0}) is lost to core in magma ocean
- Drives parts of the lower mantle towards high redox state

$$\underset{\text{(silicate)}}{3Fe^{2+}O + Al_2O_3} = \underset{\text{(Mg,Fe)(Si,Al)}O_3\text{ perovskite}}{2Fe^{3+}AlO_3} + \underset{\text{(metal)}}{Fe^{0}} \quad (1)$$

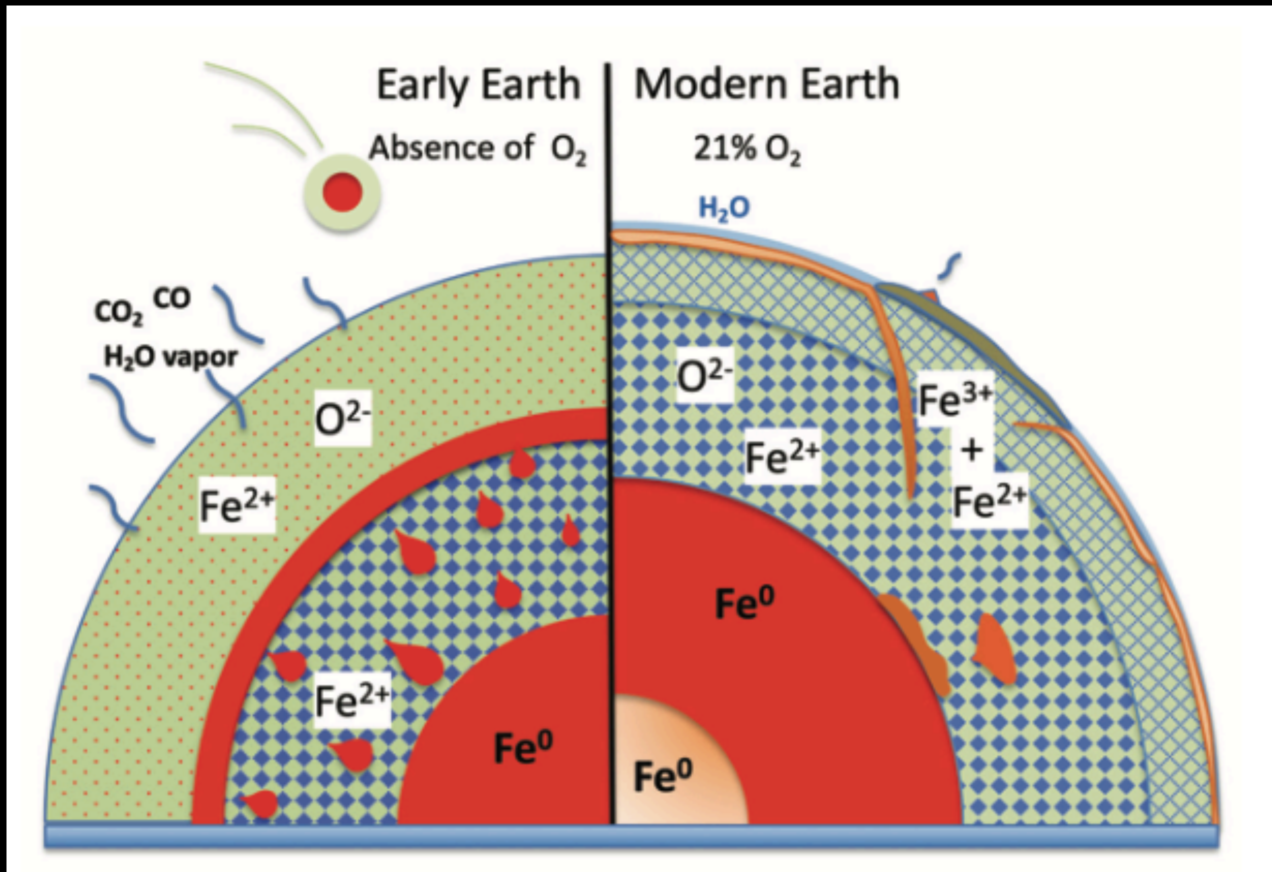
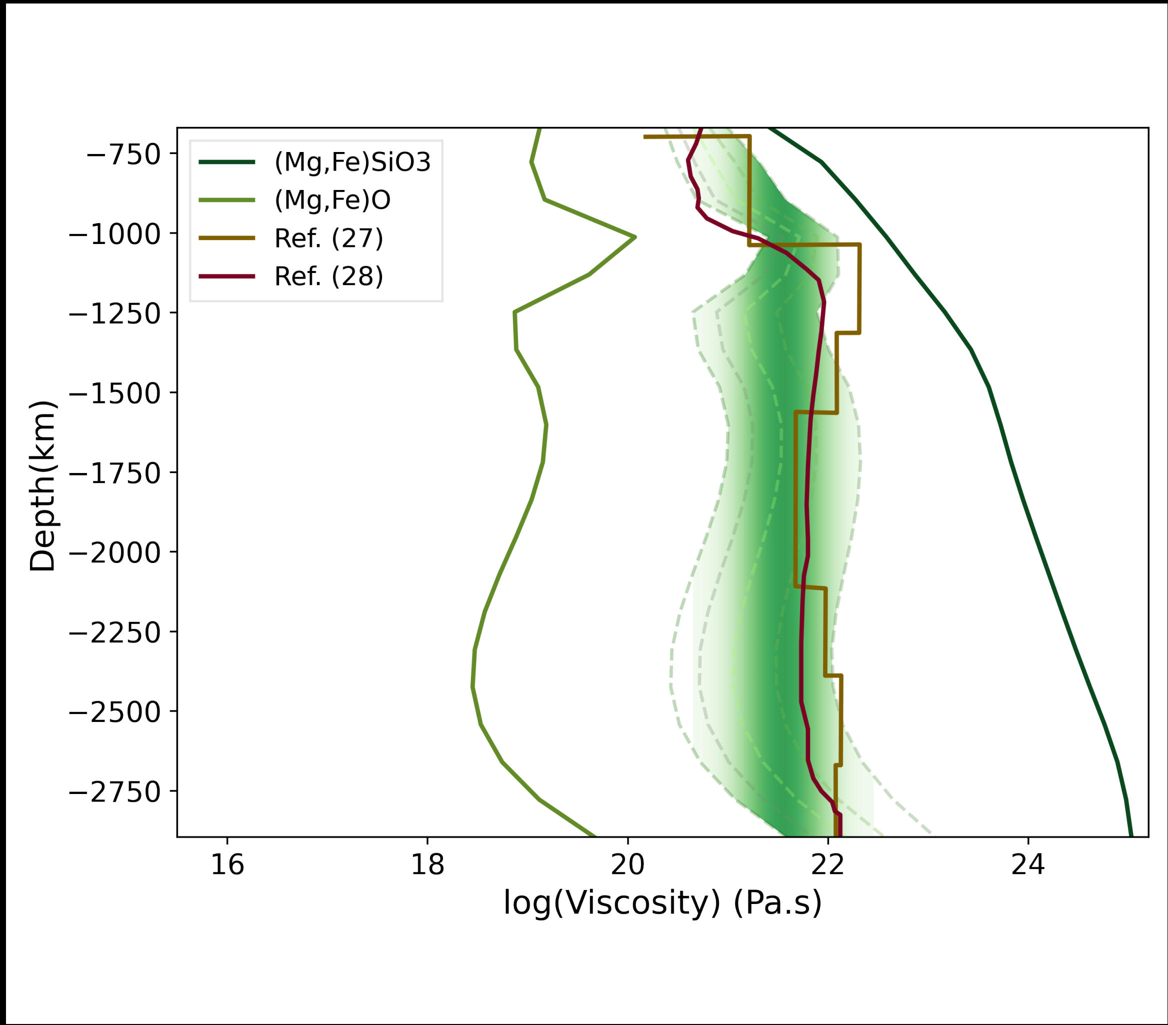


Figure from Stagno and Fei (2020)

WHAT IS THE fO_2 CONTRAST IN THE LOWER MANTLE FROM DISPROPORTIONATION?

- Reaction drives increase in bridgmanite fraction (Fe^{3+}) relative to FeO (Fe^{2+})
- A 10 % contrast in bridgmanite corresponds to a 0.779 shift in $\log(fO_2)$ (modified Kress and Carmichael (1991) relationship, benchmarked with PerPlex).
- Enough to drive the GOE
- Bridgmanite is ~1000 times more viscous than ferripericlase --> major geodynamic implications (Ballmer et al., 2015)

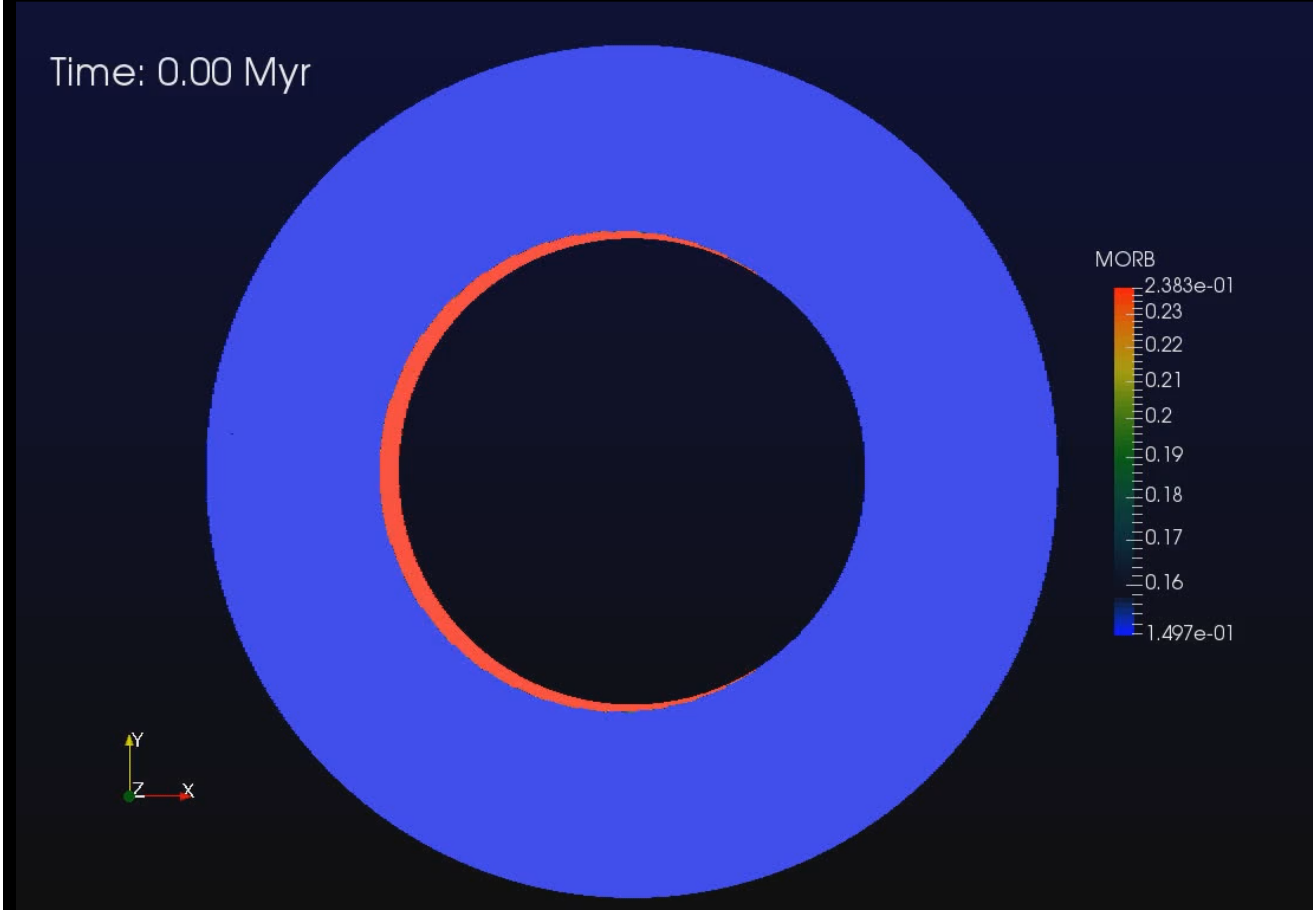
REALISTIC BRIDGMANITE VISCOSITIES



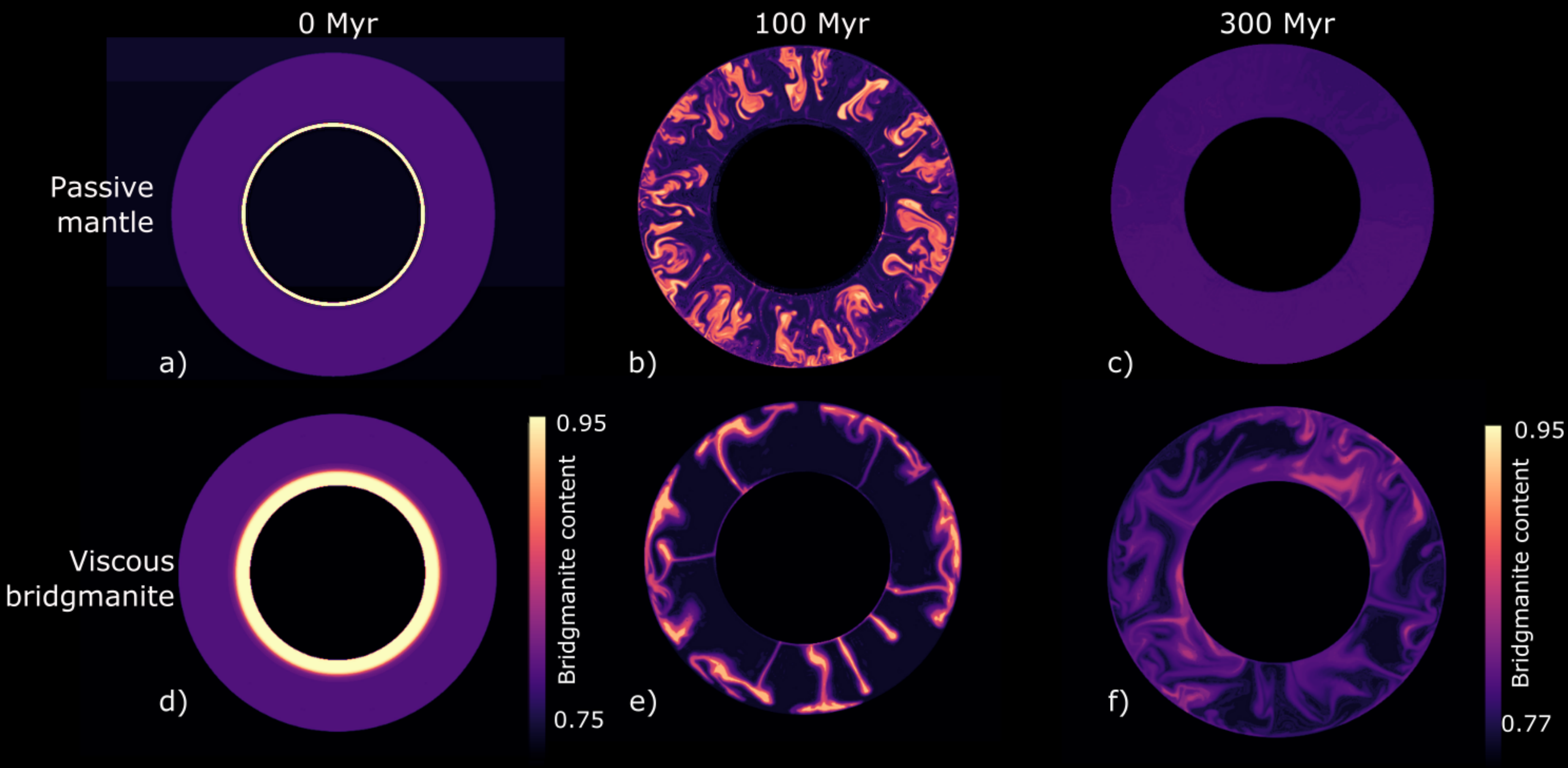
- We calculate individual viscosity curves for bridgmanite and ferropericlase (/magnesiowustite) using an homologous scaling approach (Yamazaki and Karato, 2001)
- And use an experimentally-derived mixing law for high-viscosity contrast granular materials (Ji, 2004).
- Gives a lower mantle viscosity curve very similar to that estimate from geoid+post-glacial rebound

(Forte and Mitrovica, mustard, Rudolph et al., 2015, red)

EXAMPLE SIMULATION - THIN BRIDGMANITE LAYER



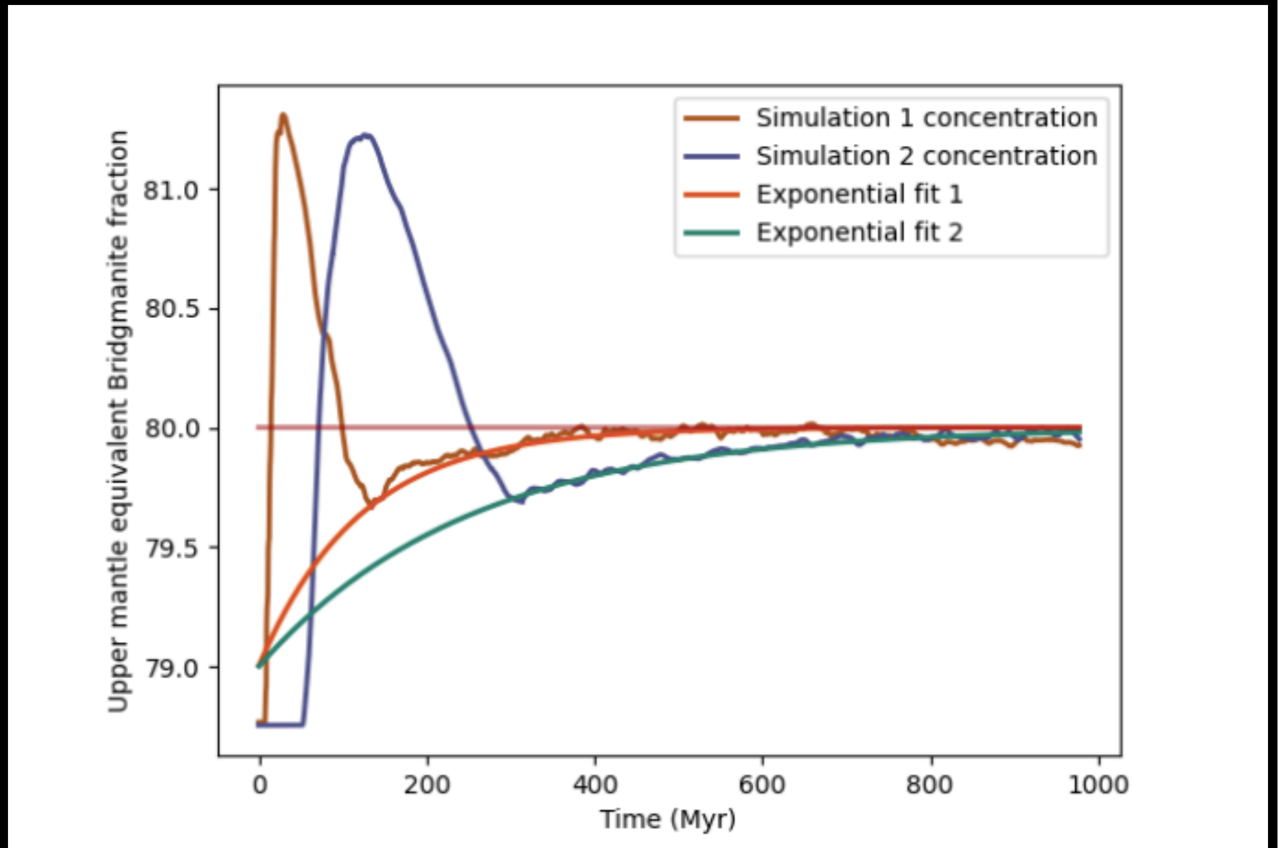
RESULTS



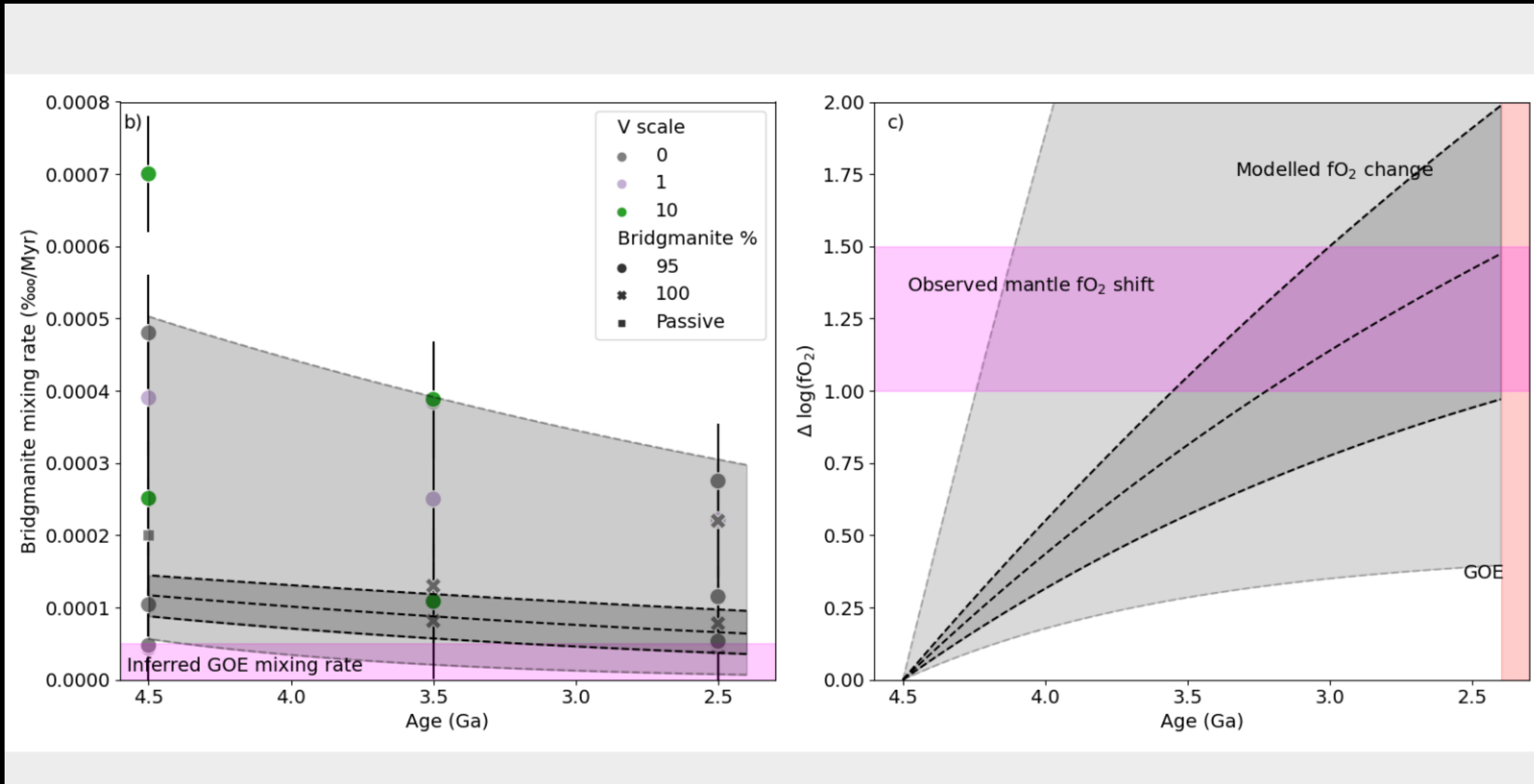
Thick bridgmanite layer retards mantle mixing compared to models without

RESULTS - RATE OF MIXING

- Comparison of two previous simulations
- Without Bridgmanite - mantle full mixed after 400 Myr evolution
- With enriched bridgmanite layer-mantle takes over 1000 Myr to mix.



RESULTS - PREDICTED RATE OF MANTLE fO_2 CHANGE



- Calculated mixing rates for a variety of models with different thermal states and properties, surface velocity scales, bridgmanite enrichment in the oxidised layer, and mixing law exponent.
- The light grey shaded: uncertainty region of our models,
- Central dark dashed line: is a curve through the kernel density estimate maxima at each time, +/-1 standard error of median (dark fill).

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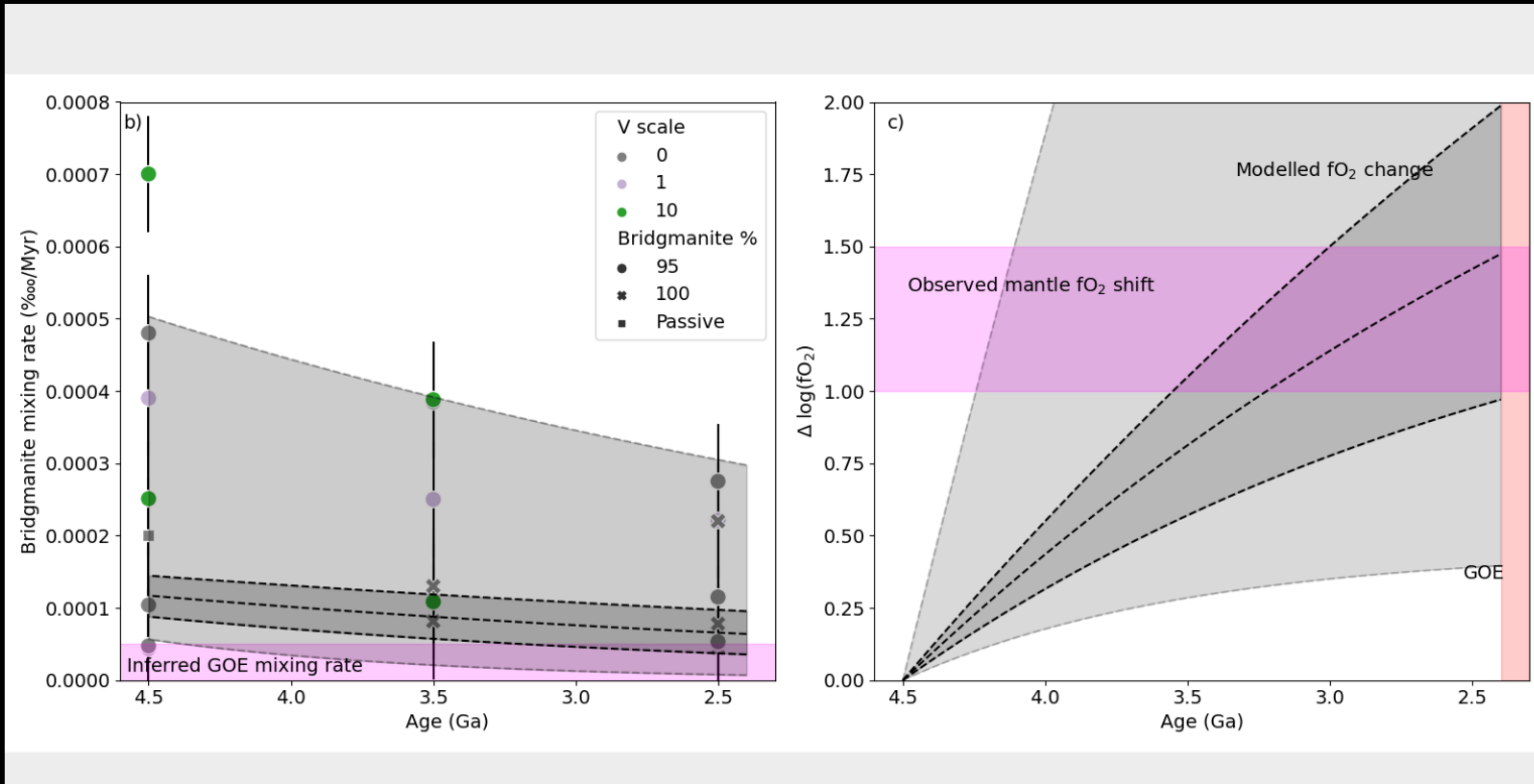

- Evolution of upper mantle Δlog(fO2), calculated from the grey bounding mixing curves in (b).
- Also plotted is the timing of the GOE (red), and the inferred mantle Δlog(fO2) shift from geological constraints
- Model median range satisfies geological constraints

DISCUSSION

- Predicted rates of mixing of oxidised bridgmanite reservoirs - leftovers of magma ocean differentiation - match the timing required for the GOE
- Predicts a mantle shift of over $> 1 \log(fO_2)$ for reasonable (~15%) bridgmanite variations
- Supports the idea that the GOE was in part due to shifting composition of volcanic degassing products, and decreased methane.
- The GOE was sudden - the mantle shift slower. But - this is consistent with tipping point models of how non-linear Earth Surface systems respond to long-term drivers (Ostrander et al, 2021)

SUMMARY

- Evidence and modelling suggests the GOE at 2.4 Ga was driven by a change in oxygen sinks - primarily volcanic gas compositions

- The Great Oxidation Event at 2.4 Ga appeared to have been preceded by a long rise in mantle fO_2.

- Oxidised deep mantle expected from magma-ocean core formation models - would be high in bridgmanite, and strong

- Our models suggest long lag times mixing this material could explain the long delay between the evolution of oxygen photosynthesis, and the GOE.