

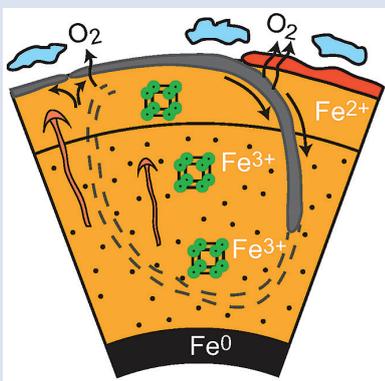
# Large oxygen excess in the primitive mantle could be the source of the Great Oxygenation Event

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## Abstract



Before the Archean to Proterozoic Transition (APT) the tectonic regime was dominated by microplates floating on a low viscosity mantle. Such a regime restricted chemical exchange between the shallow and deeper mantle reservoirs. After the APT, a more global convection regime led to deep subduction of slabs. We propose that the improved vertical mixing of the mantle favoured the release to the Earth's surface of an oxygen excess initially trapped in the deep mantle. This excess built up when the primordial lower mantle was left with a high  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio ( $\# \text{Fe}^{3+}$ ), after metallic iron segregated down into the core. Our synchrotron-based *in situ* experiments suggest a primordial  $\text{Fe}^{3+}$  excess of  $\sim 20\%$  for the mantle iron. By comparison with the  $\# \text{Fe}^{3+}$  of the present mantle, this  $\text{Fe}^{3+}$  excess would correspond to 500–1000 times the  $\text{O}_2$  content in the Earth's atmosphere. The tectonic transition greatly facilitated the ascent of oxidised lower mantle material towards the Earth's surface, inducing a continuous arrival of  $\text{O}_2$  at the Earth's surface and into the atmosphere.

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## Introduction

The main lower mantle phase, bridgmanite (Bg:  $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ ) can easily incorporate  $\text{Fe}^{3+}$ . This effect is related to a strong coupling of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  cations on the A and B sites of the  $\text{ABO}_3$  perovskite-type lattice. The Al- $\text{Fe}^{3+}$  interaction in this phase is so favourable that it can induce the disproportionation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  (which is incorporated into Bg) and metallic iron ( $\text{Fe}^0$ ) (Fig. 1) (Frost *et al.*, 2004). Such electron transfer occurs when a predominantly  $\text{Fe}^{2+}$ -bearing upper mantle material is buried below the 660 km discontinuity by mantle convection. In the solid lower mantle, the Fe droplets are expected to remain relatively small and separate (Yoshino *et al.*, 2003). Thus, they are gravitationally metastable in the lower mantle. When this mineral mixture migrates upwards to the upper mantle, the coexisting  $\text{Fe}^{3+}$  and  $\text{Fe}^0$  can eventually recombine with each other (*i.e.*  $2\text{Fe}^{3+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+}$ ), leading to a dominantly  $\text{Fe}^{2+}$ -bearing upper mantle with a true  $\text{Fe}^{3+}$  excess of only 2–3% (Frost *et al.*, 2008). This ongoing cycle of  $\text{Fe}^{2+}$  disproportionation followed by  $\text{Fe}^{3+}$  plus  $\text{Fe}^0$  recombination results in a neutral budget of the cation/oxygen ratio of the mantle. It remains difficult, however, to provide quantitative estimates of the  $\# \text{Fe}^{3+}$  in the deep mantle, because different studies present a controversial range of  $\# \text{Fe}^{3+}$  values from 10%

to 60% or more, for pressures up to the 135 GPa found at the core-mantle boundary (see Shim *et al.*, 2017).

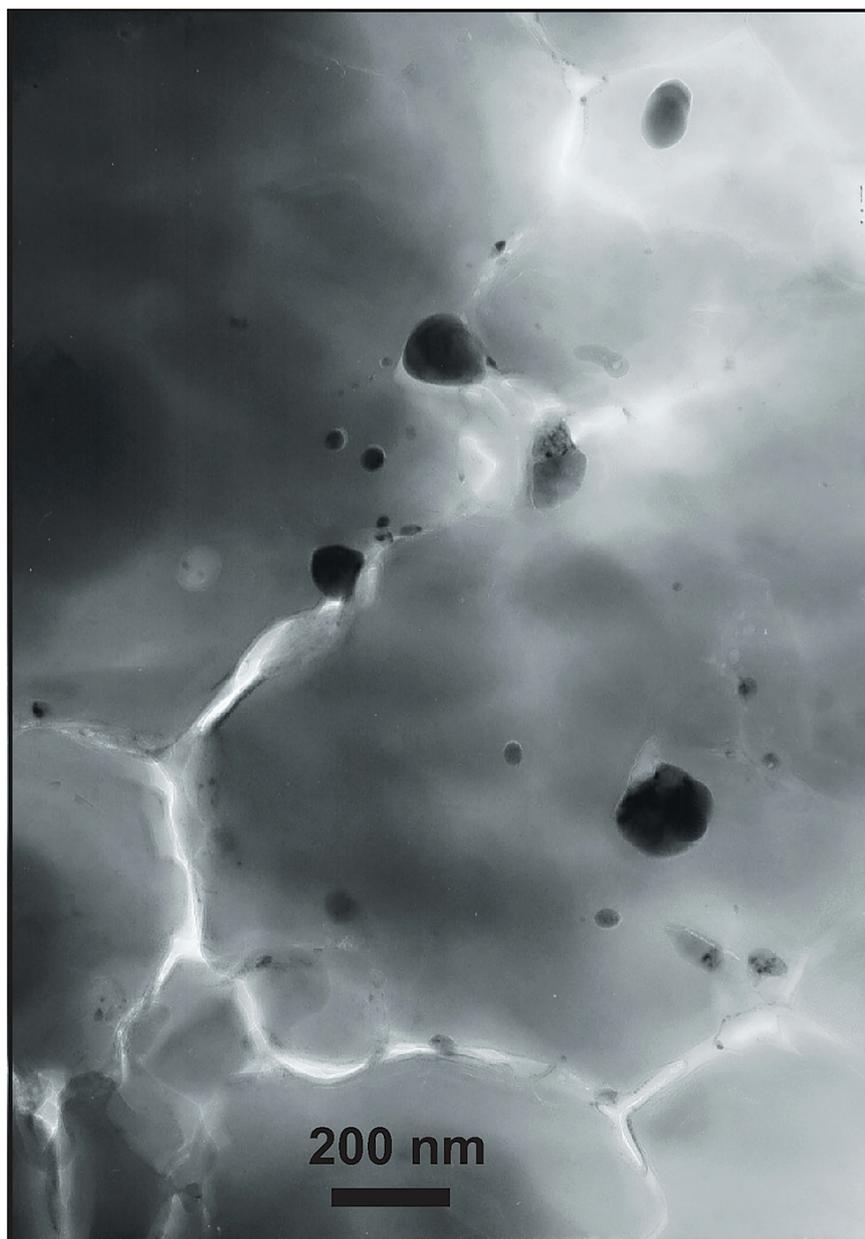
The redox equilibrium between Bg with a high  $\# \text{Fe}^{3+}$  and metallic  $\text{Fe}^0$  was established early in the Earth's history. However, the core-mantle segregation induced drainage of  $\text{Fe}^0$  droplets from the molten mantle down into the core, which resulted in a large  $\text{Fe}^{3+}$  excess in the primordial lower mantle (Frost *et al.*, 2008). This excess became a potential source of oxygen for the shallow mantle and the Earth's surface. This is highly important with respect to the Great Oxygenation Event (GOE) which occurred 2.2–2.5 Ga ago (Bekker and Holland, 2012). Different scenarios were proposed to explain the major change in redox state at the Earth's surface at this time, including the emergence of oxygenic cyanobacteria (Buick, 2008), and, in relation to the deep Earth, to a change in the oxidation state of sulphur in volcanic gases (Gaillard *et al.*, 2011). This subject is still hotly debated.

## Experimental Determination of the $\# \text{Fe}^{3+}$ in the Deep Lower Mantle

Our experiments were aimed at refining the  $\# \text{Fe}^{3+}$  in the Earth's lower mantle. Starting materials consisted of homogeneous

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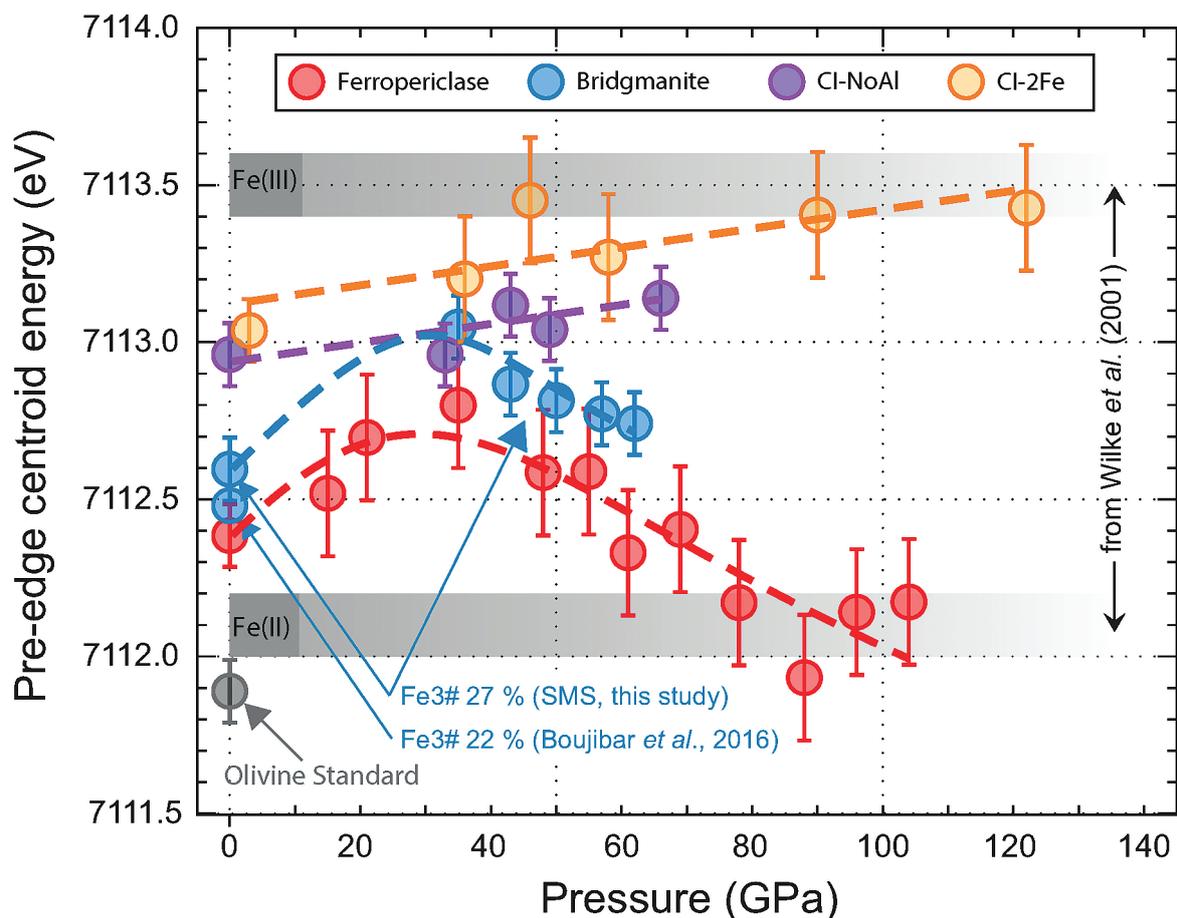
**Figure 1** Micrograph of an Al-bearing (Mg,Fe)SiO<sub>3</sub> bridgmanite. The starting material consisting of a mixture of (Mg,Fe)SiO<sub>3</sub> pyroxene and Al<sub>2</sub>O<sub>3</sub> corundum was compressed to 40 GPa and heated to 2500 K, using the LH-DAC. The reaction between the two phases induced the Fe<sup>2+</sup> disproportionation into a mixture of Fe<sup>3+</sup>-rich, Al-bearing bridgmanite (large grey areas) and metallic Fe<sup>0</sup> (dark droplets). Early in the Earth's history, core segregation drained the metallic Fe<sup>0</sup> away from the Fe<sup>3+</sup>-rich Bg, thus leaving the deep mantle with a large oxygen excess.

glasses with a primitive mantle composition, but different Fe and Al contents (Tables S-1 and S-2). Their #Fe<sup>3+</sup> was typically 7–8 % (Fig. S-5). Samples were synthesised at P-T conditions ranging from 25 to 140 GPa and 2000 to 3500 K, using a laser-heated diamond-anvil cell (LH-DAC). The DAC provides a closed system in which the cation/oxygen ratio remains constant. This represents a good proxy for natural conditions. During laser heating, chemical segregation associated with temperature gradients was minimised thanks to scanning of the lasers over the sample surface on both sides of the DAC. The valence state of Fe was determined *in situ* using synchrotron-based X-ray absorption (Fe K-edge XANES) and Mossbauer (SMS) spectroscopy (see Supplementary Information).

**XANES measurements.** We modelled the pre-edge features (Figs. S-1 to S-4, Wilke *et al.*, 2001) to retrieve information on the sample #Fe<sup>3+</sup> as a function of pressure. To apply this technique, we first determined the centroid energy

position (PCE) of the pre-edge features in two Fp and Bg reference compounds, before comparing them to samples which contained a mixture of both phases. PCEs for both Fp and Bg increase with pressure by 0.3–0.4 eV up to ~30 GPa, before decreasing progressively at higher pressures. Because the iron valence of the reference compounds does not change under compression, such an evolution is likely to be due to pressure effects which are as yet undocumented in the literature.

XANES spectra of our samples (Fig. 2) show PCE values slightly higher than our Bg reference, which suggests an #Fe<sup>3+</sup> higher than 27 %, as found in our Bg reference using SMS (Fig. S-6). PCEs of both samples increase regularly with pressure up to more than 120 GPa, in strong contrast with decreasing trends observed for Fp and Bg references. This observation clearly supports a progressive increase in #Fe<sup>3+</sup> in CI-NoAl and CI-2Fe samples with increasing pressure.



**Figure 2** Redox state of Fe probed by X-ray absorption spectroscopy. The pre-edge centroid energy (PCE, Fig. S-4) of our samples (orange and purple dots; see Table S-1) are plotted together with our ferropiclasite (red dots, dominantly  $\text{Fe}^{2+}$ ) and bridgmanite (blue dots, 27 %  $\text{Fe}^{3+}$ ) reference compounds. Horizontal grey stripes correspond to PCE values generally found for  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ -bearing minerals at ambient P-T conditions (Wilke *et al.*, 2001). PCEs of our samples plot slightly higher than the reference compounds. Also, they increase regularly with pressure, which suggests significant  $\text{Fe}^{3+}$  contents and excludes a decrease of their bulk  $\#\text{Fe}^{3+}$  up to more than 120 GPa.

**SMS measurements.** Previous studies present detailed analyses of the main SMS parameters of Fe species located in Bg and Fp (Kantor *et al.*, 2009; Kuppenko *et al.*, 2015; Figs. S-7 and S-8). In our sample, which contains a mixture of both phases, we observe an increase in the FeO component in Fp up to ~80 GPa (Fig. 3a), which could be related to the  $\text{Fe}^{2+}$  spin transition in Fp (Badro *et al.*, 2004). We find a low  $\#\text{Fe}^{3+}$  in our samples synthesised below 30–35 GPa, with  $\#\text{Fe}^{3+}$  similar to those previously reported for Al-free or low-Al Bg phases (Fig. 3b). In this pressure range, Al-rich garnet remains stable (*e.g.*, Irifune *et al.*, 1996), thus inducing a low Al content in Bg. On the other hand, previous SMS measurements performed on a Bg sample containing 6 % Al *per* formula unit suggest  $\#\text{Fe}^{3+}$  of 30–35 % in this pressure range (Kuppenko *et al.*, 2015).

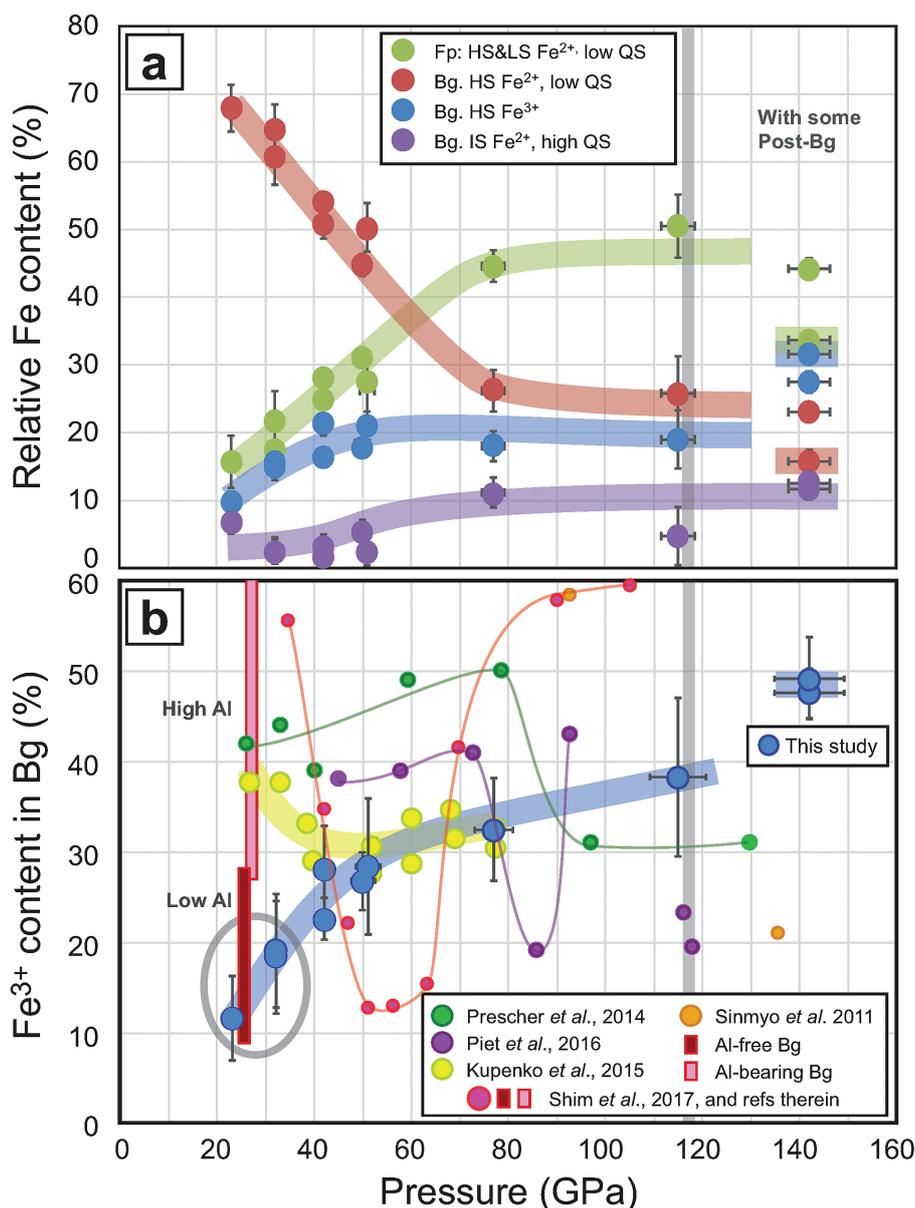
Increasing pressure up to ~120 GPa produces a weak and continuous increase in  $\#\text{Fe}^{3+}$  in Bg up to ~40 %. Our measurements are overall compatible with previous work (see Shim *et al.*, 2017 and references therein). At the highest lower mantle pressures, when post-Bg becomes a major component, the bulk mantle  $\#\text{Fe}^{3+}$  becomes 25–30 %, which corresponds to an  $\#\text{Fe}^{3+}$  in the mixture of Bg plus post-Bg of 45–50 %.

Our XANES and SMS analyses are consistent with each other. The more quantitative SMS results yield an average mantle  $\#\text{Fe}^{3+}$  of ~20 % (Fig. 3a). It corresponds to  $\sim 2 \cdot 10^{23}$  mol of  $\text{Fe}^{3+}$  in the lower mantle and an excess of  $\sim 10^{23}$  mol of oxygen compared to a predominantly  $\text{Fe}^{2+}$ -bearing silicate mantle.

Today, this oxygen excess is compensated by the presence of  $\sim 10^{23}$  mol of  $\text{Fe}^0$  (as in Fig. 1).

### An Oxygen Excess Stored in the Primordial Lower Mantle

As mentioned in the introduction, the redox state of the primitive mantle was largely different from that prevailing today, because  $\text{Fe}^0$  droplets drained down from the magma ocean into the core. The removal of  $\text{Fe}^0$  left the primitive lower mantle with a relative  $\text{Fe}^{3+}$  excess (Frost *et al.*, 2008), and thus a relative excess of oxygen, compared to the present day mantle. The true oxygen excess in the primitive lower mantle was controlled by two main parameters: (i) the amount of Bg present in the lower mantle when the  $\text{Fe}^0$  segregation stopped. Since the magma ocean would have undergone a steep increase in viscosity at 60–70 % fractional crystallisation (Abe, 1997), a transition that would stop the descent of  $\text{Fe}^0$  droplets by gravity, we use a Bg fraction of 50 % of the total lower mantle mass to estimate the  $\text{Fe}^{3+}$  content of the primitive lower mantle at the chemical closure; (ii) the efficiency of  $\text{Fe}^0$  droplet segregation. This depends on complex parameters, such as the level of turbulence in the magma ocean. We consider that 50 % of the  $\text{Fe}^0$  droplets produced by Bg crystallisation (which induces partial  $\text{Fe}^{2+}$  disproportionation into  $\text{Fe}^{3+}$  and  $\text{Fe}^0$ ) were efficiently segregated into the core.



**Figure 3** The mantle #Fe<sup>3+</sup> refined from SMS measurements. (a) Major Fe contributions found in our sample are high spin and low spin Fe<sup>2+</sup> in Fp (Kantor *et al.*, 2009) (both added to each other, green dots), high spin Fe<sup>2+</sup> with low QS (red), intermediate spin Fe<sup>2+</sup> (purple) and high spin Fe<sup>3+</sup> (blue) in Bg (Kupenko *et al.*, 2015). Above ~40 GPa, corresponding to mantle depths greater than ~1000 km, the #Fe<sup>3+</sup> in the bulk sample is almost constant at ~20 %. In the pressure field of post-Bg (~142 GPa), we performed two syntheses at ~2500 K (dot with a coloured trend superimposed) and ~3500 K. (b) When focusing on Bg properties, we observe a continuous increase of its #Fe<sup>3+</sup> with pressure. At low pressure, our two samples plot in the field of previous Al-free (low Al) Bg compounds (see Shim *et al.*, 2017 and references therein). It could be associated with the remaining presence of Al-bearing garnet in our samples. On the other hand, Kupenko *et al.* (2015) found higher #Fe<sup>3+</sup> in Bg in this pressure range (yellow dots). Above ~40 GPa, our data set produces a smooth trend which lies between the previous findings (Sinmyo *et al.*, 2011; Prescher *et al.*, 2014; Kupenko *et al.*, 2015; Piet *et al.*, 2016; Shim *et al.*, 2017).

Based on these assumptions, we calculate that 1/4 of the total amount of Fe<sup>3+</sup> stored in the lower mantle Bg phase (with average #Fe<sup>3+</sup> of 20 %) was not counterbalanced by the presence of Fe<sup>0</sup> after core segregation was completed. It corresponds to an O<sub>2</sub> excess of more than ~2.5 × 10<sup>22</sup> mol O<sub>2</sub>, compared to the current predominantly Fe<sup>2+</sup>-bearing bulk mantle. This oxygen excess represents 500 to 1000 times the O<sub>2</sub> content in the Earth's atmosphere today.

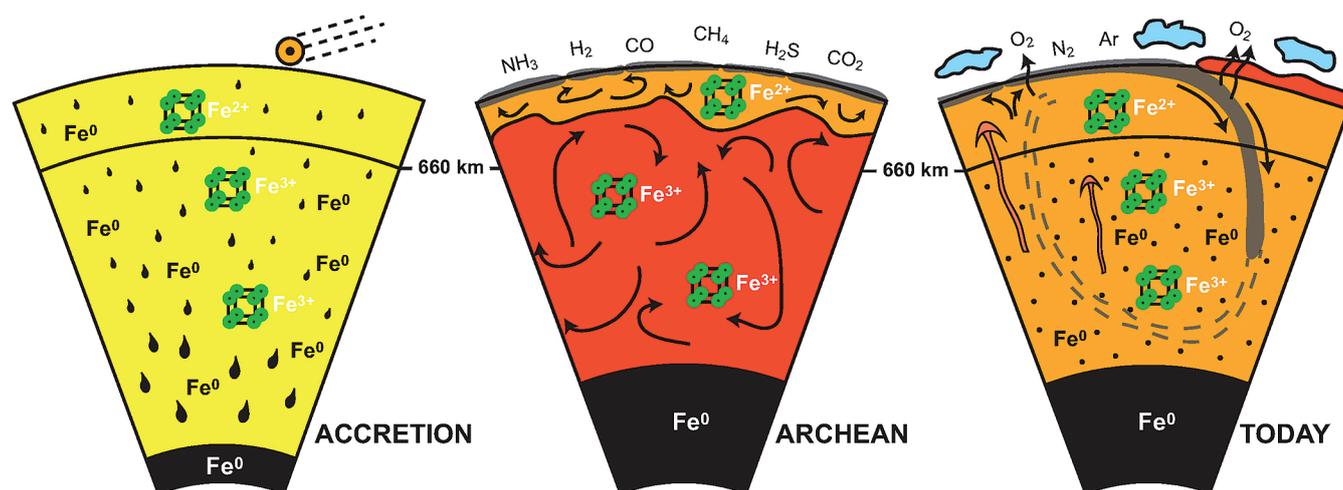
### Geodynamical Changes at the APT Possibly Produced the GOE

The fate of such a large oxygen excess (coupled to Fe<sup>3+</sup> in Bg) trapped in the primordial lower mantle is a major question.

It might have reached the Earth's surface (crust plus atmosphere) through volcanism. Analyses of Archean magma and mantle residues suggest that mantle sources have retained a constant, relatively oxidised, redox state for the last 3.5 Gyr or more (Delano, 2001; Canil, 2002). It is paradoxical that while early volcanic eruptions should have favoured an Earth's atmosphere dominated by oxidised volatile species (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>), the Archean atmosphere remained anoxic (Shaw, 2008). This suggests a limited and/or inefficient mantle degassing during the Archean.

The tectonic regime prevailing during the Archean was dominated by microplates floating at the Earth's surface with a limited amount of subducted material (Condie and Kröner, 2013; Kamber, 2015). In such a regime, the lower mantle





**Figure 4** Change in the redox state of the deep mantle. During the Earth's accretion (left), the descending iron droplets equilibrated chemically in a partially molten mantle, which contained a major amount of Bg below the 660 km discontinuity. After loss of the  $\text{Fe}^0$ , the lower mantle was left with a  $\# \text{Fe}^{3+}$  of ~20 % (Fig. 3a). During the Archean (centre), the oxidised deep mantle remained relatively isolated from the Earth's surface with a tectonic regime characterised by almost no subduction. At that time, the atmosphere was anoxic. The progressive transition to modern plate tectonics around the Archean to Proterozoic Transition greatly enhanced mantle mixing (right). Subduction became the dominant mechanism, which associated to global mantle convection brought deeper material and then fresh lavas to the Earth's surface. Large amounts of oxygen were potentially degassed, due to the increase in volcanic fluxes and other sub-surface exchange processes. In this scheme, " $\text{Fe}^{2+}$ " and " $\text{Fe}^{3+}$ " indicate mantle fractions where the  $\text{Fe}^{3+}/\Sigma \text{Fe}$  ratios are 2–3 % and ~20 %, respectively. Yellow, orange and red colours indicate the Earth's envelopes of Oxygen/ $\Sigma$ Cations ratios that are lower (due to a  $\text{Fe}^0$  excess), similar and higher (due to a  $\text{Fe}^{3+}$  excess), respectively, than the current mantle value.

material could have remained relatively isolated from shallow mantle processes, with only sporadic volcanism associated to deep mantle sources. Another argument in favour of a deep mantle which remained isolated for a long period of time is the relatively constant Lu/Hf ratio reported in rising plumes, suggesting that continents grew from nearly primordial unfractionated material (Guitreau *et al.*, 2012).

Around the APT, the early no subduction regime was progressively replaced by a modern style subduction regime (Fig. 4). This evolution could have been fairly chaotic, because episodic subductions have been identified during the late Archean (van Hunen and Moyen, 2012). Nevertheless, the transition resulted in major ultramafic volcanic events, greatly increasing the amount of fresh lava rising to the Earth's surface (Arndt and Davaille, 2013). We can estimate the flux of lower mantle material carried up by convection by assuming that it was equivalent to the slab volume subducting into the deep mantle today (Wen and Anderson, 1995). An upwelling flux of  $\sim 2.5 \times 10^{11} \text{ m}^3/\text{year}$  of primitive, oxidised, lower mantle material would correspond to the rise in excess of oxygen of  $\sim 1.5 \times 10^{13} \text{ mol}/\text{year}$  of  $\text{O}_2$ . With such a flux, it would take  $\sim 2.5 \times 10^6$  years for the ascent of an amount of oxygen "equivalent" to the current oxygen content of the Earth's atmosphere (Shaw, 2008).

Oscillations and overshoots in atmospheric oxygen pressure have been reported for a few 100 Myr around the APT (Bekker and Holland, 2012). They could be related to the chaotic transition between the two tectonic regimes, which might have resulted in an irregular rate of mantle mixing. In addition, the geological processes that could have accommodated the transfer of oxygen from a deep mantle source to the Earth's surface are multiple and complex. Partial melting is obviously a major component, because  $\text{Fe}^{3+}$  is an incompatible element. Fluids might also have played a role, because the nature of molecular components changes with the redox state (Gaillard *et al.*, 2011). At the time of the GOE, the increased  $f_{\text{O}_2}$  at the Earth's surface led to the precipitation of a large variety of minerals containing more oxidised ionic species, including carbonates, phosphates, sulphates, *etc.* (Sverjensky and Lee,

2010). Consequently, the amount of oxygen needed to induce the GOE must have far exceeded the current oxygen content of the Earth's atmosphere. The massive amount of oxygen that can be stored in  $\text{Fe}^{3+}$ -bearing Bg appears to be a unique redox source which can meet these requirements.

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## Author Contributions

GP and DA prepared the DACs. MM, IK, DA, GP, SP performed XANES measurements, which were subsequently treated by MM. VC, DA, GP, AC, RR performed SMS measurements, which were subsequently treated by DA. DA and MM wrote the manuscript. All authors participated to discussions.

## Additional Information

Supplementary Information accompanies this letter at [www.geochemicalperspectivesletters.org/article1801](http://www.geochemicalperspectivesletters.org/article1801).



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