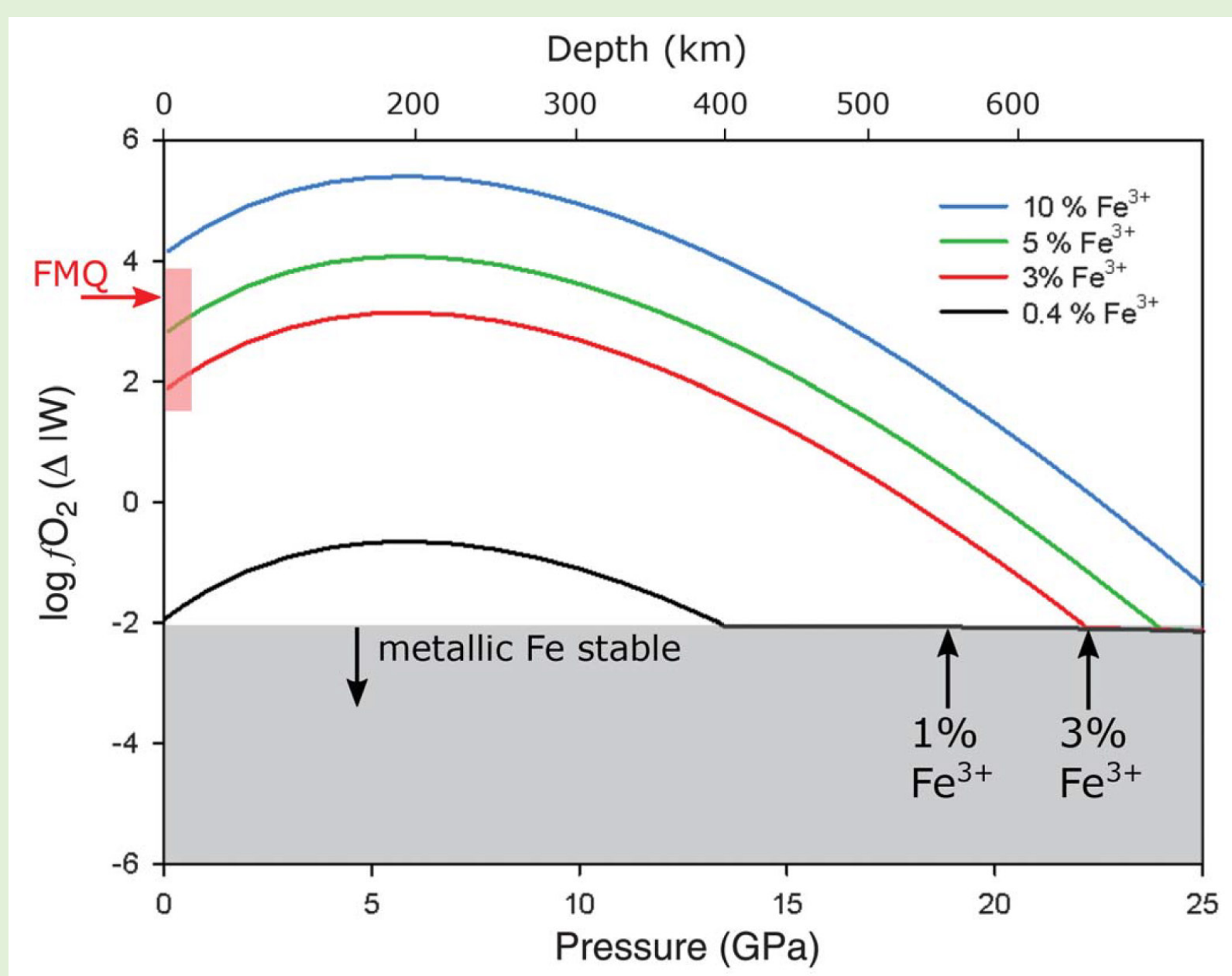
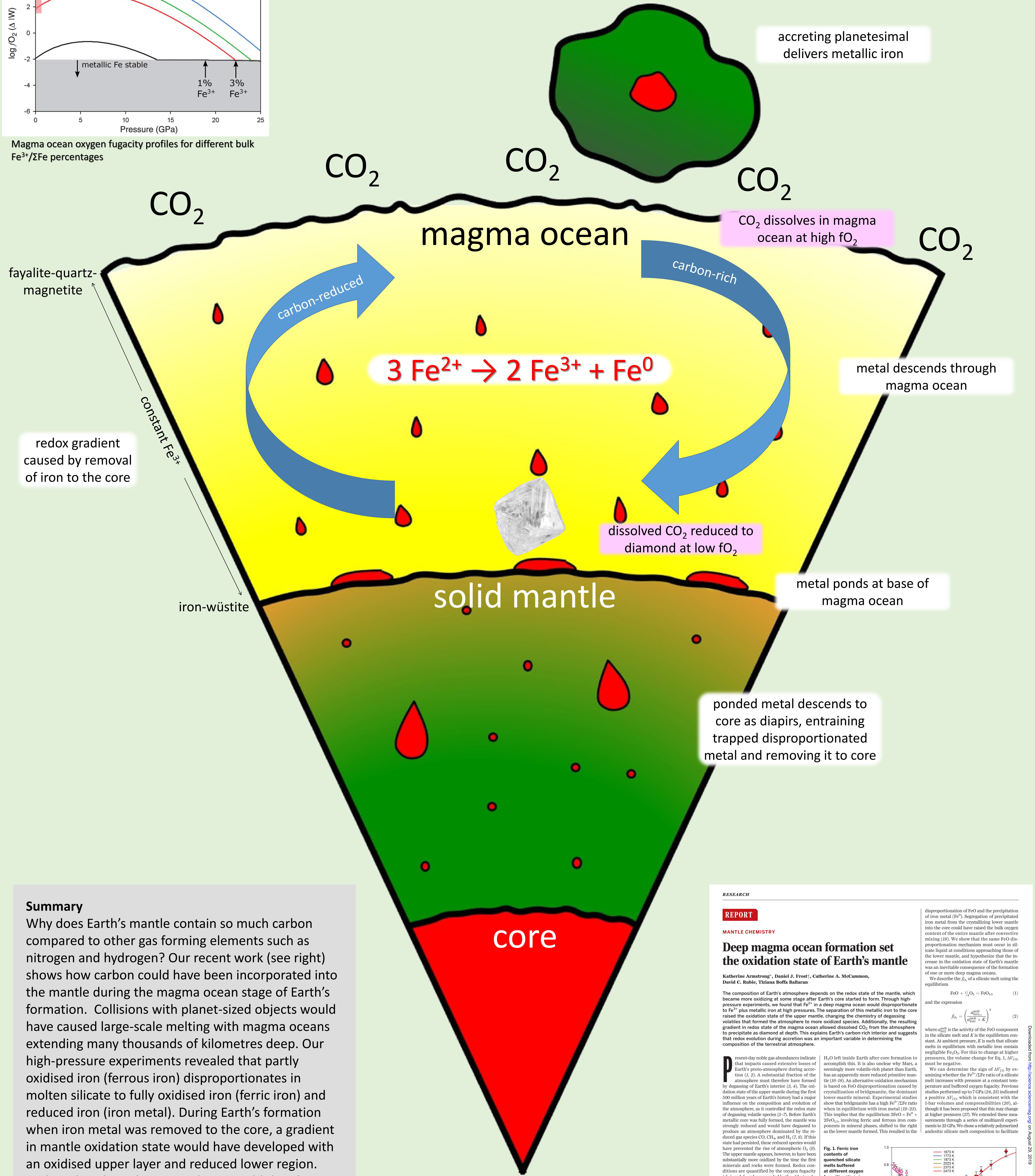


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Magma ocean oxygen fugacity profiles for different bulk Fe<sup>3+</sup>/ΣFe percentages



## Summary

Why does Earth's mantle contain so much carbon compared to other gas forming elements such as nitrogen and hydrogen? Our recent work (see right) shows how carbon could have been incorporated into the mantle during the magma ocean stage of Earth's formation. Collisions with planet-sized objects would have caused large-scale melting with magma oceans extending many thousands of kilometres deep. Our high-pressure experiments revealed that partly oxidised iron (ferrous iron) disproportionates in molten silicate to fully oxidised iron (ferric iron) and reduced iron (iron metal). During Earth's formation when iron metal was removed to the core, a gradient in mantle oxidation state would have developed with an oxidised upper layer and reduced lower region. Carbon dioxide in the atmosphere would then have partly dissolved in the magma ocean and be reduced to diamond as it was convected downwards. This mechanism was probably important for removing carbon dioxide from Earth's early atmosphere and implies that diamonds may still exist that date back to Earth's formation.

**RESEARCH REPORT**

**MANTLE CHEMISTRY**

### Deep magma ocean formation set the oxidation state of Earth's mantle

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The composition of Earth's atmosphere depends on the redox state of the mantle, which became more oxidizing at some stage after Earth's core started to form. Through high-pressure experiments, we found that Fe<sup>2+</sup> in a deep magma ocean would disproportionate to Fe<sup>3+</sup> plus metallic iron at high pressures. The separation of this metallic iron to the core raised the oxidation state of the upper mantle, changing the chemistry of degassing volatiles that formed the atmosphere to more oxidized species. Additionally, the resulting gradient in redox state of the magma ocean allowed dissolved CO<sub>2</sub> from the atmosphere to precipitate as diamond at depth. This explains Earth's carbon-rich interior and suggests that redox evolution during accretion was an important variable in determining the composition of the terrestrial atmosphere.

Present-day noble gas abundances indicate that impacts caused extensive losses of Earth's proto-atmosphere during accretion (1, 2). A substantial fraction of the atmosphere must therefore have formed by degassing of Earth's interior (3, 4). The oxidation state of the upper mantle during the first 500 million years of Earth's history had a major influence on the composition and evolution of the atmosphere, as it controlled the redox state of degassing volatile species (5–7). Before Earth's metallic core was fully formed, the mantle was strongly reduced and would have degassed to produce an atmosphere dominated by the reduced gas species CO, CH<sub>4</sub>, and H<sub>2</sub> (7, 8). If this state had persisted, these reduced species would have prevented the rise of atmospheric O<sub>2</sub> (9). The upper mantle appears, however, to have been substantially more oxidized by the time the first minerals and rocks were formed. Redox conditions are quantified by the oxygen fugacity (f<sub>O<sub>2</sub></sub>) and f<sub>O<sub>2</sub></sub> values recorded by the oldest rocks indicate that the redox state of the upper mantle had increased by about 5 log units by the beginning of the geologic record. Subsequent changes appear to have been relatively minor (10–14). This oxidation event allowed the more oxidized species CO<sub>2</sub> and H<sub>2</sub>O to degas from the mantle.

The main mechanism proposed to explain the increase in mantle redox state in the past has been oxidation by H<sub>2</sub>O accompanied by the loss of H<sub>2</sub> to space (8, 15). Although this almost certainly occurred to some extent, the question remains as to whether there would be sufficient disproportionation of FeO and the precipitation of iron metal (Fe<sup>0</sup>). Segregation of precipitated iron metal from the crystallizing lower mantle into the core could have raised the bulk oxygen content of the entire mantle after convective mixing (16). We show that the same FeO disproportionation mechanism must occur in silicate liquid at conditions approaching those of the lower mantle, and hypothesize that the increase in the oxidation state of Earth's mantle was an inevitable consequence of the formation of one or more deep magma oceans.

We describe the f<sub>O<sub>2</sub></sub> of a silicate melt using the equilibrium

$$\text{FeO} + \frac{1}{2}\text{O}_2 = \text{FeO}_{1.5} \quad (1)$$

and the expression

$$f_{\text{O}_2} = \left( \frac{a_{\text{FeO}_{1.5}}}{a_{\text{FeO}} \times K} \right)^2 \quad (2)$$

where a<sub>FeO<sub>1.5</sub></sub> is the activity of the Fe<sup>3+</sup>/ΣFe component in the silicate melt and K is the equilibrium constant. At ambient pressure, K is such that silicate melts in equilibrium with metallic iron contain negligible Fe<sub>2</sub>O<sub>3</sub>. For this to change at higher pressures, the volume change for Eq. 1, ΔV<sub>1.5</sub>, must be negative.

We can determine the sign of ΔV<sub>1.5</sub> by examining whether the Fe<sup>3+</sup>/ΣFe ratio of a silicate melt increases with pressure at a constant temperature and buffered oxygen fugacity. Previous studies performed up to 7 GPa (24, 25) indicated a positive ΔV<sub>1.5</sub>, which is consistent with the 1-bar volumes and compressibilities (26), although it has been proposed that this may change at higher pressures (27). We extended these measurements through a series of multi-anvil experiments to 23 GPa. We chose relatively polymerized andesitic silicate melt composition to facilitate

H<sub>2</sub>O left inside Earth after core formation to accomplish this. It is also unclear why Mars, a seemingly more volatile-rich planet than Earth, has an apparently more reduced primitive mantle (16–18). An alternative oxidation mechanism is based on FeO disproportionation caused by crystallization of bridgmanite, the dominant lower-mantle mineral. Experimental studies show that bridgmanite has a high Fe<sup>3+</sup>/ΣFe ratio when in equilibrium with iron metal (19–23). This implies that the equilibrium 3FeO = Fe<sup>3+</sup> + 2FeO<sub>1.5</sub>, involving ferric and ferrous iron components in mineral phases, shifted to the right as the lower mantle formed. This resulted in the

Fig. 1. Ferric iron contents of quenched silicate melts buffered at different oxygen fugacities. We buffered the experimental oxygen fugacity of ~ΔIW ± 8, or by equilibrium with Fe metal (gray squares), ~ΔIW – 2. Downward- and upward-pointing triangles indicate initially fully oxidized and fully reduced starting materials, respectively. Results from previous studies are shown as open circles (24, 25). All starting compositions were andesitic except an experiment at 4 GPa that had a MORB melt composition (green diamond). The curves show the fit of our model to the experimental data. The gray curve is calculated for liquid iron metal saturation at 2373 K. The experimental temperature uncertainties are ~50 K.

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