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# Oxygen-rich melt in deep magma oceans

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**High pressures may have enabled ferric iron-rich silicate melts to coexist with iron metal near the base of magma oceans early in the history of large rocky planets like Earth. This suggests a relatively oxygen-rich atmosphere after core formation on these planets.**

Earth has had an oxygen-rich surface for the past 2.5 billion years (Gyr). This is related to oxygen photosynthesis and possibly Earth's mantle being more oxidized than other known mantles of smaller terrestrial planetary bodies, such as Mars<sup>1</sup>. Yet Earth, like most terrestrial planetary bodies, is thought to have formed with a highly reduced primordial mantle. Internal oxidation has thus taken place in Earth's mantle, but it remains unclear when and how this occurred. Writing in *Nature Geoscience*, Kuwahara et al.<sup>2</sup> propose that mantle oxidation occurred very early on, when Earth had a magma ocean more than 1000 km deep, because the pressures near the magma ocean floor were sufficiently high that oxygen-rich silicate melts coexisted with reduced iron metal. Mixing the deep silicate melts into the rest of the magma ocean may have supported more oxidized surface conditions than the present-day.

The oxidation state of mantle rocks, magma and volcanic gases is gauged by their oxygen fugacity,  $fO_2$ , the thermodynamic expression of the minute  $O_2$ -pressure ( $\ll 10^{-7}$  bar) prevailing in the planet's interior. Substantial spatial variations in the  $fO_2$  of Earth's mantle have been reported, highlighting the ongoing interplay between pressure, temperature and mixing of deep and surficial components due to plate tectonics<sup>3</sup>. Nevertheless, the cause of Earth's relatively oxidized mantle must be very persistent, as reconstruction of the mantle's paleo- $fO_2$  using mineralogical proxies indicates only marginal temporal variability back to 4.4 Gyr<sup>4</sup>. Before then, during the first 100 million years of our solar system, magma oceans prevailed on terrestrial planetesimals, planetary embryos and planets<sup>5</sup>. This state led to planetary differentiation, with dense metals segregating inwards forming a core<sup>5</sup>, molten silicate solidification forming a mantle<sup>6</sup> and outgassing creating an atmosphere<sup>7</sup> (Fig. 1). The presence of iron metal in magma oceans implies reduced conditions, involving  $fO_2$  values 4 to 8 orders of magnitude lower than that of Earth's present-day mantle<sup>1</sup>.

Several models have been proposed to explain the increase in the  $fO_2$  of Earth's mantle from core formation to the present. Firstly, it has been argued that complete crystallization of the magma ocean at upper mantle conditions and a constant ratio of ferric ( $Fe^{3+}$ ) to ferrous ( $Fe^{2+}$ ) iron should

increase mantle  $fO_2$ <sup>8</sup>, though this alone is insufficient to account for the magnitude of the  $fO_2$  increase. Secondly, crystallization of the lower mantle deep in the magma ocean could produce ferric iron-rich silicate minerals, such as perovskite, together with iron metal<sup>9</sup>. If this metal were to migrate into the core, the overall mantle would become more oxidized proportionally, however it is unclear whether dispersed iron metal could travel through a solid mantle. Thirdly, a recent numerical modelling study<sup>6</sup> proposed that degassing accompanying magma ocean crystallization could increase mantle  $fO_2$ , but it is uncertain whether the solid-liquid partitioning behaviour of iron supports this.

Experiments have shown enhanced ferric iron stability in andesitic melts at high pressure<sup>10</sup>, which could bridge the  $fO_2$  gap between Earth's magma ocean and its present-day mantle. Kuwahara et al.<sup>2</sup> also propose this based on the results of very high-pressure (up to 28 GPa) experiments on peridotite melts. The composition and pressures used are directly relevant to the magma ocean and to the lower mantle, respectively. The results show much greater stability of ferric iron under high pressures than previously suggested<sup>10,11</sup>. Some technical issues remain, however, in particular that the experimental melts did not quench as glass because of the ultrafast crystallization of dendritic minerals upon freezing, which introduce uncertainty into the measured  $Fe^{3+}:Fe^{2+}$  ratios.

Assuming the results of Kuwahara et al.<sup>2</sup> are correct, the source of the oxygen required for a ferric iron-rich silicate magma ocean should be considered. If the source was dissolved CO or CO<sub>2</sub>, this would cause deep diamond sequestration<sup>10</sup> (Fig. 1). Since the amount of carbon species in a magma ocean is probably small and might occur at depth as CH<sub>4</sub> instead<sup>12</sup>, this scenario is questionable. Incorporation of some magma ocean oxides (e.g., FeO or SiO<sub>2</sub>) into the core (as Fe or Si)<sup>5,13</sup> might be a more plausible oxygen source. However, this process could incorporate oxygen in the core<sup>13</sup>, which would counteract the magma ocean self-oxidation model of Kuwahara et al.<sup>2</sup>. Further work is necessary to address this early oxygen question.

Kuwahara et al.<sup>2</sup> suggest that the  $fO_2$  of the Earth's magma ocean was very high, potentially higher than that of the present-day mantle. The atmosphere derived from such an oxidized magma ocean would be dry and dominated by CO<sub>2</sub>, N<sub>2</sub> and SO<sub>2</sub><sup>7</sup>. High sulfur volatility under such oxygen-rich conditions may explain Earth's non-chondritic sulfur isotopic composition<sup>14</sup>, provided that early atmospheres are dispersed by processes such as impacts. The magma ocean and the resulting mantle would be sulfur-poor under these conditions, so a process is required to return sulfur to the mantle to account for its present-day sulfur content<sup>7</sup>. The potential relationship between the size of terrestrial planets and their mantle  $fO_2$  and thus atmospheric composition (Fig. 1) may enable new insights on rocky exoplanets from measurements of their atmospheric compositions. Notably, this relationship implies that very large terrestrial exoplanets may have oxygen-rich atmospheres that are not indicative of photosynthesis.

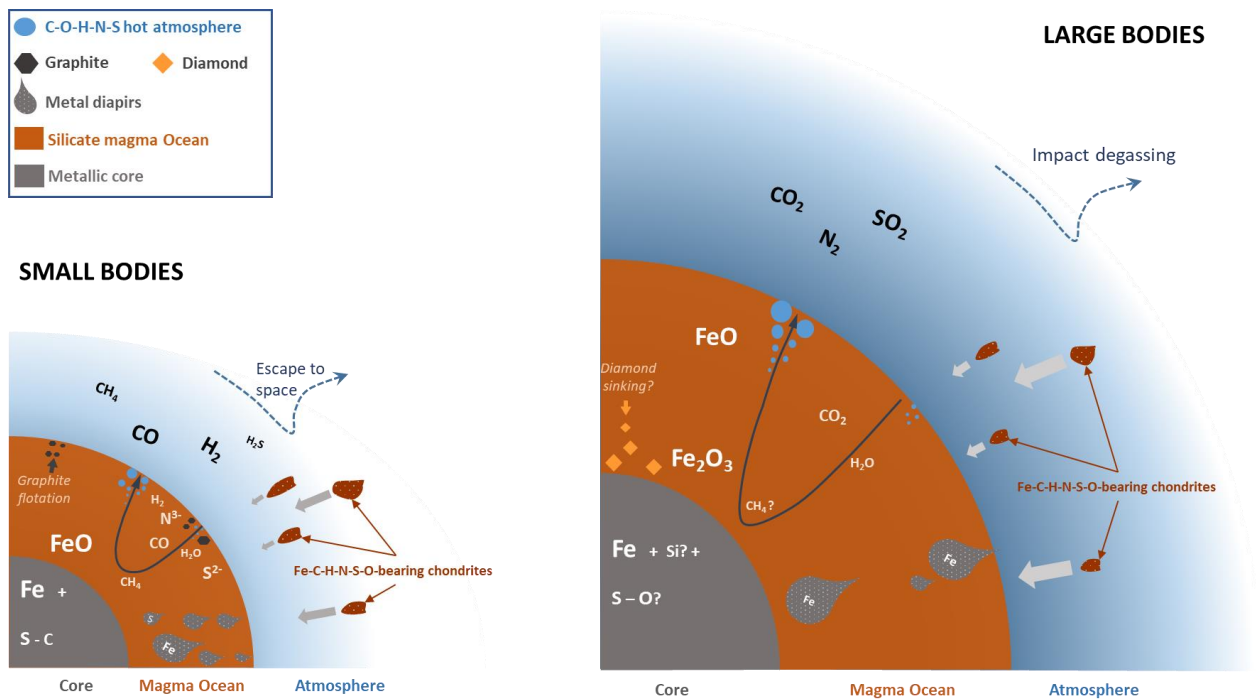
Kuwahara et al.<sup>2</sup> propose that planetary magma oceans are born reduced and can become oxidized for planets approaching or exceeding Earth's size. Therefore, Earth and possibly Venus were oxidized

when their mantle formed, whereas rocky bodies the size of Mars or smaller remained reduced. This implies fundamental differences between these two groups for properties influenced by mantle  $fO_2$ , such as mantle convection regime, melting and degassing.

### Competing interests

The author declares no competing interests.

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**Figure 1 - Effects of magma ocean size on planetary oxidation state and atmospheric composition.** Small planetary bodies (*left*) remain reduced through their magma ocean stage, with an atmosphere comprising predominantly CO and H<sub>2</sub>. Kuwahara et al.<sup>2</sup> suggest that the high pressures near the base of deep magma oceans on large bodies (*right*) may enable a relatively oxidized mantle, which would result in an atmosphere primarily composed of CO<sub>2</sub>, N<sub>2</sub> and SO<sub>2</sub><sup>7</sup>.