Earth science: Redox state of early magmas

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A study of cerium in zircon minerals has allowed an assessment of the redox conditions that prevailed when Earth's earliest magmas formed. The results suggest that the mantle became oxidized sooner than had been thought. See Letter p.79

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A prime goal of petrologists has been to assess the redox conditions of magmas produced throughout Earth's evolution, because magmas are known to affect various major phenomena — such as the composition of volcanic emanations, which are widely believed to affect the composition of the atmosphere[1]. But research efforts have been hampered by the lack of rocks from the Hadean eon, which encompasses nearly the first half-billion years of Earth's existence. On page 79 of this issue, Trail *et al*.[2] report their analysis of the sole mineral survivors of the Hadean, zircon samples more than 4 billion years old. Their findings allowed them to determine the 'fugacity' of oxygen in Hadean magmatic melts, a quantity that acts as a measure of magmatic redox conditions. Unexpectedly, the zircons record oxygen fugacities identical to those in the present-day mantle, leading the authors to conclude that Hadean volcanic gases were as highly oxidized as those emitted today.

The continuous reshaping of the surface and deep interior of our dynamic planet has inevitably resulted in the loss of evidence of Earth's ancient composition. In this respect, Earth contrasts sharply with other planetary objects — particularly the Moon and Mars, which are largely unaffected by large-scale geodynamics. Thanks to the Apollo programme and to meteorites inferred to be of Martian origin, we have rock samples that provide direct testimonies of the Moon and Mars's very early past. But the same cannot be said of Earth. Nevertheless, it is generally assumed that all of these bodies were chemically reduced when they first formed and then underwent either a gradual or stepwise oxidation[3].

One of the main arguments for a reduced start is that, during or soon after accretion, Earth must have entered a magma-ocean stage, when a sizeable part of the planet was molten because of the energy released by accretion processes[3]. A massive segregation process must then have occurred that separated metals from silicates, thus allowing the formation of the metallic core and the silicate-containing mantle. The formation of Earth's core is thought to have occurred 30 million to 60 million years after the beginning of the Solar System. The coexistence of silicate and metal liquids in the magma ocean would have made conditions severely reduced, with oxygen fugacity (f_{O_2}) 5 to 8 log units below the current value for the upper mantle (Fig. 1).

The oxygen fugacity (f_{O_2}, measured in bar) of the mantle — a measure of the mantle's redox state — has varied over time. Here, log f_{O_2} is plotted relative to a standard value (known as the iron-wüstite buffer; IW); the scale on the *x*-axis is logarithmic. At first, the mantle was highly chemically reduced, but it became more oxidized as Earth's accretion proceeded and as core–mantle redox equilibration occurred (blue arrow). Meteorite bombardment may have contributed to oxidation of the mantle[8] (orange dotted arrows) once it had segregated from the core. A 'great oxidation event' in the mantle (black dotted arrow) then occurred, in which f_{O_2} rapidly increased. On the basis of their analysis of 4.4-billion-year-old zircon samples, Trail *et al*.[2] report that the mantle's redox state about 100 million years after core–mantle separation (green box, left) was similar to that of the present-day lithospheric mantle (green box, right). The most highly oxidized mantle melts are the most recent — the arc magmas (red box) that formed as a result of crust–mantle exchanges triggered by subduction. The timing of some key events in Earth's history are indicated, along with the times when the oldest rock and zircon samples were formed; GOE is the Great Oxidation Event.

Assuming that such a reduced starting point is inescapable, how did Earth reach its modern oxidized state, and how fast did this happen? Persistent oxidizing conditions at Earth's surface started when the planet was around 2.3 billion to 2.4 billion years old, a phenomenon known as the Great Oxidation Event[1] (GOE). Rock analyses[4] suggest that the mantle's redox state has been similar to its current state from as early as 3.8 billion years ago. Trail *et al*.[2] wanted to look even further back in time, so they developed a technique for studying Hadean zircons, which are the only solids dating from the first 500 million years of Earth's history that are [5]known to have survived unchanged to the present day. By analysing the cerium content of the zircons and developing a method to calibrate their results, the authors were able to determine f_{O_2} for Hadean magmas.

Their findings extend the mantle's oxidized realm to almost 4.4 billion years ago. Although somewhat tenuous, this is the first direct evidence of the redox state of the earliest Earth. If the zircons analysed by the authors are representative of the Hadean eon, this result shrinks the duration of the reduced era of Earth's mantle to less than 150 million years. It also increases the lag time between the oxidation of the mantle and the subsequent oxidation of the atmosphere (the GOE; Fig. 1), which might seem to make it difficult to establish a direct connection between the two events. However, redox changes upon the release of gas from magmas and changes in the pressure of volcanic degassing[6] could explain why the atmospheric GOE happened so long after the mantle's oxidation. But what was the cause of the mantle's great oxidation event?

Planetary-scale geodynamics is often cited as a mechanism for bringing oxidized material into the deep, reduced mantle, and water is thought to be responsible for oxidation[7]. This concept is deeply entrenched among geologists, although the details of the redox mechanisms involved remain unknown. Although a matter of strong debate[8, 9], Earth's current budget of volatile compounds (including water) seems to have been reached no later than 100 million years after core formation, and so volatiles may have fuelled the mantle's great oxidation at about that time (Fig. 1). However, it is known that terrestrial magmas do not necessarily have a high oxidation state, even if volatiles are abundant[10, 11], and that the Moon's reduced lavas contain a substantial amount of volatiles[12]. Taken together, these facts argue against the existence of an unequivocal relationship between high f_{O_2} and the abundance of volatiles.

But the accretion of volatiles into Earth's bulk is not the only possible mechanism for oxidation of the mantle. Experiments have shown[13] that, at the pressure of the lower mantle, iron(II) oxide is converted into iron metal and iron(III) oxide — which means that large bodies such as Earth can self-oxidize their mantle, whereas smaller ones cannot (or do so to a lesser extent). In other words, a nominally dry mantle can be oxidized. This mechanism, however, would require that wholesale mantle convection and mixing occurred within a short period of time (less than 100 million years).

Alternatively, changes in the mantle's redox state could have occurred if the early magma ocean crystallized and degassed, because of the redox effect of degassing[5] and the greater affinity of iron(III) for liquid relative to minerals[14] (the iron(III) would have become concentrated in the residual liquid, thus increasing the oxidation state of the liquid). Such processes would probably have affected the entire mantle and would not have required large-scale convection.

Clearly, many parts of Earth's early evolution are still obscured by poor preservation of the geological record and by our limited knowledge of the mechanisms that drive magmatic redox patterns. Even so, the zircon record revealed by Trail *et al*.[2] firmly anchors one of the first redox steps of the infant Earth. This extraordinary tale is certainly not finished, and future work will augment the existing data — perhaps the discovery of other zircon samples will allow f_{O_2} to be determined for even more highly reducing conditions at earlier periods of Earth's history, thereby refining our knowledge about what f_{O_2} represents. Also much needed are experimental or modelling studies aimed at understanding the mechanisms of redox processes in magma, and the extent to which redox state reflects either the origins of magmas or later processes that affect them.

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Figure 1: Evolution of the redox state of Earth's mantle.