Oxidation of iron *sans* oxygen fugacity: Fresh insights from lower mantle mineral chemistry

A. V. Sankaran

Geophysical, geochemical and experimental investigations conducted since the 1980s on the structure and composition of earth's interior have enlarged our conception of this region but at the same time, they have also generated fresh issues necessitating further explanations. One such issue that has spurred several innovative experimental studies is about the oxygen or the redox state of the earth's mantle and how this has come to be in the state it is observed today. Knowledge about this feature of the mantle is essential to our understanding about earth's geochemical evolution, generation of mantle melts, evolution of the atmosphere and its influence on climate and geomorphology – in short, about the early history of earth itself.

Presently, there are two models describing the redox state of the earth's mantle. One of them considers that the oxidation-state of upper mantle has not changed since 3.9 b.y. ago[1–4]. This model is based on the evaluation of the MgO content in Archaean komatiitic lavas as well as abundance of Cr, V, from the composition of Cr-rich spinels in ancient volcanics, and also from the unchanged composition of mantle volatiles and volcanic gases. An opposite view argues that the upper mantle was in a very reduced state during early geological times (pre-2.0 b.y. period) but progressively became oxidized in subsequent periods. This view stems from several investigations on the sensitive relationship of Fe to oxygen, particularly in spinels which can accommodate large amounts of Fe^{3+} and through chemical and isotopic variations of iron in several Fe-bearing minerals such as spinel, Al-perovskite, garnet, ortho- and clino-pyroxenes from mantle-derived ultramafic rocks[4–8].

The differentiation of early molten earth to metal and silicate phases leading ultimately to the development of a metallic core and a silicate mantle had wielded considerable sway on the mantle's oxidation state[9]. When earth was just about 50 million years old, iron along with iron-loving or the siderophile elements (e.g. Fe, Cu, Ni, noble metals) separated from the molten earth and formed the earth's core leaving a silicate-rich residual portion which became the mantle. At the time of formation of core, the whole mantle was in chemical equilibrium with metallic iron but subsequently the upper mantle became more oxidized due to progressive changes in the composition of earth's interior arising from episodes of massive exhalation of reduced volcanic gases (H, CO, SO_2), subduction of hydrated oxidized seafloor, subduction of ferric iron[4,7] and increased plume activity during the Archaean-Proterozoic transition[10].

The oxidation-state of the mantle is usually estimated in terms of relative oxygen content or the oxygen fugacities of iron-bearing minerals like spinel $(Mg, Fe)Al_2O_4$ through measurement of the ratio between Fe^{3+} and Fe^{2+} in them or from the geochemical abundance of Cr, V in spinel, and also through estimation of Fe-isotope ($\delta^{57}Fe/^{54}Fe$) fractionation in spinel[1,2,9,11,12]. Spinel occurring in the upper mantle records high Fe^{3+}/Fe^{2+} ratio implying that this region is highly oxidized and not in chemical equilibrium with metallic iron[13]. In spite of several studies on mantle fO_2 their results have not been assertive about its state and its homogeneity both vertically and laterally. For example, even between the top and bottom of the upper mantle itself, the oxidation-state varies – above 200 km it is more oxidized relative to its deeper portions[14] and also it is controlled by the melting regime and source mineralogy[12].

With regard to the lower mantle, because of lack of direct samples, its fO_2 is not clearly understood, though this region is believed to be relatively reduced. This is inferred from high-pressure experiments on synthetic mineral phases, from inclusions of $(Mg, Fe, Al) (Si, Al)O_3$ and $(Mg, Fe)O$ phases, and from the narrow distribution of C-isotopes in diamonds of definite lower mantle origin[13,15]. According to the established notions about the connection between oxygen partial pressure and oxidation of Fe to Fe^{3+}, the low oxygen content that prevails in the lower mantle should naturally suppress this

oxidation. But a few years back, this notion was disproved by the finding of an unexpectedly high Fe^{3+}/Fe^{2+} ratio, independent of oxygen fugacity requirement. The ratio, which was much higher than what is generally observed in well-oxidized upper mantle spinels, was recorded in experimental studies[16] on synthetic aluminous Mg–Fe perovskite wherein 50% of Fe was present as Fe^{3+}. This typical lower mantle spinel, though compositionally similar to its upper mantle counterpart, differs from it in having a denser perovskite structure developed due to phase transition in the high-pressure lower mantle zone.

Explanations for this seemingly anomalous Fe^{3+}/Fe^{2+} ratio have now come from the work of Frost and colleagues[11] who conducted high-pressure experimental synthesis of this aluminous silicate perovskite (Mg, Fe, Al) (Si, Al)O_3. The investigators considered some of the possible chemical routes which can provide the oxygen required for producing the high Fe^{3+}/Fe^{2+} ratio. They reasoned that the reduction of Fe^{2+} to metallic iron and Fe^{3+} thus: $3Fe^{2+}O \rightarrow Fe + 2 Fe^{3+}O_{1.5}$, could yield the required extra oxygen. Since magnesian perovskite (Fe here is present as Fe^{2+}) is known to have a great affinity for oxygen to form Fe^{3+}, they carried out suitable experiments under P–T conditions that prevail just below the transition zone (uppermost lower mantle) in very poor oxygen conditions and successfully synthesized aluminous magnesian perovskite having very high Fe^{3+}/Fe^{2+} ratio. Their experiments thus confirmed that oxidized Fe-rich mineral can exist independent of oxygen fugacity condition of the lower mantle through 'auto-reduction' of FeO.

The reaction envisaged by Frost and others leading to generation of free metallic iron in the lower mantle is believed to have supplemented as much as 10% iron to the core during core–mantle segregation that took place within 50 million years after earth's accretion. They believe that the transport of iron into the core was aided by the deep magma-ocean of early earth, which also helped in the

crystallization of Al-perovskite, thereby promoting net oxygen content of lower mantle. Subsequent mantle convection processes are supposed to have increased the bulk O-content of the mantle, thus making the present day upper mantle more oxidized. According to the authors, this co-precipitation of metallic iron resulted in the retention of the iron-loving siderophile elements in the mantle. The presence of high amounts of these elements in the mantle is considered an anomaly and this aspect had earlier invited lengthy discussions. Quite a few explanations have been advanced to account for their excess in the mantle[17], one of which attributes the anomalous presence of these siderophiles to additions from chondrites accreting as a 'late veneer'[18]. However, Frost et al.[11] feel that if a solid lower mantle had already formed before the completion of the core, the retention of metallic iron in the mantle, instead of entering into the core, could inevitably augment these elements in the upper mantle and hence there is no need to invoke additions through a late veneer of chondrites.

A recent contribution[9] has described how FeO content and oxygen distribution is influenced by the size of the growing planet and the depth of the magma-ocean generated during its formative stages by energy released by the impacting bodies and other heat generating reactions early in the planet's development. Experimental studies have shown that while higher temperature favours dissolution of oxygen into molten iron at the time of metal–silicate differentiation in molten-planet scenario, this affinity of oxygen decreases under higher pressure[8,19–21]. This will imply that the overall abundance of FeO or oxygen in the planet's mantle is much controlled by whether pressure was dominant or temperature, in the differentiating magma-ocean.

Earth had a larger magma-ocean (depth of 1800 km) exerting higher pressure and temperature (3500 K) at the bottom of its ocean. It is therefore claimed that greater amount of oxygen dissolved in the molten iron, the latter ultimately segregating to form the massive core (incidentally,

entry of oxygen into earth's core in this manner along with iron could also account for core's density deficit[9,22]) leaving a relatively reduced mantle, poor in Fe-oxides. In the smaller sized Mars, the pressure and temperature of such a magma-ocean were too low, thereby impeding the dissolution of oxygen into iron. Consequently, its magma-ocean remained rich in iron oxide leading to development of Fe-rich silicate mantle.

The above hypothesis, however, assumes that the composition and source reservoir for the accreting materials in the early solar system were the same for both the planets during their formation[21]. But clues from isotopes and other studies indicate a hybrid parentage for earth since its prolonged accretionary phase accumulated compositionally distinct classes of chondrites (heterogeneous accretion) with differing oxidation-states and iron content[23–25]. Besides, the source for the accreting bodies for Earth and Mars were also not the same but known to be well separated[26].

Surfeit of studies about the mantle have undoubtedly stressed the fact that fO_2 is high in the upper mantle in spite of low concentration of ferric iron and contrastingly this is low in the lower mantle despite high abundance of ferric iron, an odd feature now explained through studies of aluminous silicate-perovskite[11]. The key to evaluate the present status of fO_2 in the lower mantle, which still remains unclear, no doubt rests with further studies on minerals of definite lower mantle origin though new constraints that have emerged from several geophysical studies in recent years, emphasizing mixing of mantle zones and penetration by subducting crustal slabs deep into lower mantle, will have to be overcome before arriving at the state of fO_2.

1. Canil, D., Nature, 1997, **389**, 842–845.
2. Canil, D., Geochim. Cosmochim. Acta, 1999, **63**, 557–572; ibid. Earth Planet. Sci. Lett., 2002, **195**, 75–90.
3. Delano, J. W., Lunar Planet. Sci., 1993, **24**, 395–396; ibid. Origin Life Evol.. Biosph., 2001, **31**, 311–341.

4. Kasting, J. F., Eggler, D. H. and Raeburn, S. P., J. Geol., 1993, **101**, 245–257.
5. Kadik, A., Goldschmidt Conf., Oxford, 2000, **5**, 563.
6. Arculus, R. J., Annu. Rev. Earth Planet. Sci., 1985, **13**, 75–95.
7. Lécuyer, C. and Ricard, Y., Earth Planet. Sci. Lett., 1999, **165**, 197–211.
8. Ballhaus, C., Berry, R. F. and Green D. H., Contrib. Mineral. Petrol., 1991, **107**, 27–40.
9. Rubie, D. C., Gessmann, C. K. and Frost, D. J., Nature, 2004, **429**, 58–61.
10. Kump, L. R. and Kasting, J. F., Geochem. Geophys. Geosys., 2001, **2**, 2000GC00114.
11. Frost, D. J., Liebske, C., Langenhorst, F., McCammon, C. A., Trennes, R. G. and Rubie, D. C., Nature, 2004, **428**, 409–412.
12. Williams, H. M., Mcammon, C. A., Peslier, A. N., Halliday, A. N., Teutsch, N., Levasseur, S. and Burg, J. P., Science, 2004, **304**, 1656–1659.
13. O'Neill, H. St. C. and Wall, J. V., J. Petrol., 1987, **28**, 1169–1191.
14. McCammon, C. A., Geophys. Res. Abs., 2003, **5**, 05443.
15. McCammon, C. A., Hutchison, M. and Harris, J., Science, 1997, **278**, 434–436.
16. McCammon, C. A., Nature, 1997, **387**, 694–696.
17. Sankaran, A. V., Curr. Sci., 2001, **80**, 120–122.
18. Holzheid, A., Sylvester, P., O'Neill, H. St. C., Rubie, D. C. and Palme, H., Nature, 2000, **406**, 396–399.
19. Li, J. and Agee, C. B., Geophys. Res. Lett., 2001, **28**, 81–84.
20. O'Neill, H. St. C., Canil, D. and Rubie, D. C., J. Geophys. Res., 1998, **103**, 12239–12260.
21. Agee, C. B., Nature, 2004, **429**, 32–33.
22. Sankaran, A. V., Curr. Sci., 1998, **74**, 726–728.
23. Drake, M. J. and Righter, K., Nature, 2002, **416**, 39–43.
24. Wanke, H., Philos. Trans. R. Soc. London, 1981, **303**, 287–302.
25. Sankaran, A. V., Curr. Sci., 2002, **82**, 1202–1204.
26. Delsemme, A. H., Am. Sci., 2001, **89**, 432–442.

A. V. Sankaran lives at No. 10, P and T Colony, I Cross, II Block, RT Nagar, Bangalore 560 032, India.
e-mail: sankaran@bgl.vsnl.net.in