

**REDOX CONDITIONS AMONG THE TERRESTRIAL PLANETS.** J.H. Jones, SR, NASA/JSC, Houston, TX 77058 (john.h.jones1@jsc.nasa.gov).

**The Solar Nebula:** Early solar system conditions should have been extremely reducing. The redox state of the early solar nebula was determined by the  $H_2O/H_2$  of the gas, which is calculated (based on solar composition) to have been about IW-5 [1]. At high temperature under such conditions, ferrous iron would exist only as a trace element in silicates and the most common type of chondritic material should have been enstatite chondrites. The observation that E-chondrites form only a subset of the chondrite suite and that the terrestrial planets (Earth, Moon, Mars, Venus, 4 Vesta) contain ferrous and ferric iron as major and minor elements, respectively, implies that either most chondritic materials formed under conditions that were not “solar” or that early-formed metals oxidized at low temperature [2], producing FeO. For example, equilibrated ordinary chondrites (by definition, common chondritic materials), by their phase assemblage of olivine, orthopyroxene and metal, must fall not far from the QFI (Quartz-Fayalite-Iron) oxygen buffer. The QFI buffer is about IW-0.5 and, as we shall see below, this  $f_{O_2}$  is close to that inferred for many materials in the inner solar system.

**The Eucrite Parent Body (4 Vesta).** The eucrites are basalts that contain ~18 wt% FeO and contain trace metal. The eucrites are very depleted in siderophile elements, so it appears that the source regions of these basalts contained (or once contained) Fe-Ni metal [3]. Therefore, it is of interest to ask what  $f_{O_2}$  is required to precipitate metal from a liquid of eucrite composition. Or in other words, what  $f_{O_2}$  did eucrites form under? This  $f_{O_2}$  has been determined experimentally by [4] and was found to be IW-1. Therefore, eucrites formed at about IW-1. In addition, it is interesting to note that assuming  $X_{FeO} = a_{FeO}$  allows calculation of eucrite  $f_{O_2}$  (assuming equilibrium with Fe metal). This calculation yields the same result as the experiments to within ~0.25 log units, reinforcing this result.

**The Moon.** Lunar basalts also contain about 18 wt% FeO and may also contain trace metal. Therefore, we might guess that, by analogy to eucrites, lunar basalts also formed at about IW-1 and this turns out to be correct. Like eucrites, lunar mare basalts are in equilibrium or close to being in equilibrium with Fe metal. This is demonstrated by experiments on real lunar basalts (15555 and 15565) that are shown to experience no Fe gain or loss when encapsulated at liquidus temperatures in pure Fe-metal capsules [5].

Thus, from our experience with eucrites, mare basalts and ordinary chondrites, a picture starts to emerge

that chondritic materials containing Fe metal will, upon partial melting produce basalts that contain ~18 wt% FeO and that this process will take place at oxygen fugacities near IW-1.

**Mars.** Mars, being a much larger body than the Moon or 4 Vesta, might be expected to have more complex variations in redox state, and this turns out to be the case. Originally, it was thought that the martian interior was very “Earthlike” [6]. However, this was because the original investigation focussed on two SNC meteorites, Shergotty and Zagami, which we now know are the oxidized endmembers of a continuum(?) of redox states that span at least the range of IW to IW+2.5 [7]. One interpretation, based on Sr and Nd isotopes, is that primitive, reduced magmas from the martian interior have been contaminated by oxidized crust [7]. Because Mars does not have subduction-driven plate tectonics, which could transport oxidized crustal materials to the mantle, it may be that the martian mantle remembers the redox state imposed by the presence of Fe metal. If so, the martian interior probably also has an  $f_{O_2}$  of IW-1, because martian basalts have FeO contents of ~18 wt% [6]. Therefore, Mars appears to be an interesting example of a planet whose interior is Moon-like and its crust is Earth-like, in terms of redox state.

**Venus.** Little is known about the redox state of Venus. It is not even known whether Venus has a core. This is because Venus rotates so slowly that it is difficult to measure its moment of inertia. However, x-ray fluorescence analysis of basaltic rocks by Veneras 13 and 14 yield FeO contents of 8-10 wt% [8], similar to terrestrial mid-ocean ridge basalts (MORB). Therefore, it is possible that the redox states of the venusian and terrestrial mantles are similar.

**Mercury.** Even less is known about the redox state of Mercury. Spectral imaging of the mercurian surface reveals little (if any) absorption features that can be attributed to ferrous iron [9]. Therefore, some have speculated that Mercury is very reduced, much like an E-chondrite [10]. Alternatively, it may be that the surface of Mercury has had most of its ferrous iron component reduced by hypervelocity micrometeorite impacts, a process that is known to occur on the Moon [11].

**The Earth.** The Earth is clearly not equilibrated with respect to redox state. There is a reduced metallic core overlain both by a relatively oxidized mantle and a highly oxidizing crust/atmosphere/hydrosphere. This situation has apparently evolved over geologic time.

At some point about 2 b.y. ago, the oxygen content of the atmosphere began to rise, presumably due to the production of oxygen by photosynthetic cyanobacteria [12].

The mantle redox state (near QFM), though, has been relatively unchanged over much of geologic time. Chromium and vanadium have multiple valence states. Therefore, abundances of these elements in terrestrial basalts are controlled by both redox state and the presence of spinel in the mantle source region. Therefore, concentrations of these elements in basalts are sensitive indicators of mantle redox state. However, a detailed investigation of these elements in terrestrial basalts reveals no change in their MgO-normalized concentrations over geologic time [13]. Presumably this means that the mantle has been near QFM since very early times (3-3.5 b.y.) — the oldest basalts in the geologic record.

However, that redox state must have changed sometime in the first billion years of Earth history. Using the same kind of calculation that was performed for the eucrites, the redox state at the time of core formation must have been IW-2 to IW-3, significantly more reducing than Vesta, the Moon, or Mars. And the similarity of FeO contents between MORB and venusian basalts suggests that the  $f_{O_2}$  at the time of venusian core formation was similar [8].

Why did the mantle redox state change? One possibility (because both Venus and the Earth can generate megabars of internal pressure) is that 3 FeO disproportionates into Fe metal and  $Fe_2O_3$ , a reaction that can occur at high pressures because of its negative  $\Delta V$ . Over time, this type of reaction could both lower the FeO content of the mantle and raise the  $Fe^{3+}/Fe^{2+}$  ratio. This reaction (if it occurred) would cause calculations of the  $f_{O_2}$  during core formation to appear artificially low. It is not known if disproportionation reactions have affected mantle FeO. However, it seems very unlikely that the differences in FeO contents between terrestrial and (for example) lunar basalts were caused by disproportionation. To lower the bulk FeO by ~10 wt.% by this mechanism would mean that all or nearly all of the Fe in the Earth's mantle would have to be ferric and this is not the case. At QFM only about 15% of the total Fe is ferric.

Another possibility is that subduction of oxidized materials began to occur during the first billion years of Earth history. The initiation of this tectonic style therefore may be responsible for the ~6 log unit change in  $f_{O_2}$ . If so, though, why has the mantle not grown continually more oxidizing over time, as subduction proceeds?

Therefore, in some ways the Earth is the most mysterious of the terrestrial planets, in terms of redox state.

The Moon, Mars, and Vesta all fit into fairly simple pictures but the Earth and, perhaps, Venus do not. Because of the size difference between the Earth these smaller bodies, it is tempting to attribute the complexities associated with the Earth to a high pressure process, but this is speculation.

**Other Redox Reservoirs.** Not all chondrites and asteroids are as reduced as ordinary and (of course) enstatite chondrites. This is emphasized by the observation that some asteroids have a small  $Fe^{3+}$  absorption feature [14]. Do we see any igneous meteorites that appear to have come from more oxidized bodies. As a matter of fact we do.

A class of igneous meteorites that does not easily fit into normal categories is the angrites. They are silica undersaturated and have unusual mineralogies. Experimental melts of Allende (CV) performed at IW+1 and IW+2 are the best matches to the most primitive angrites [15]. So it appears that we now have samples from oxidized mantles other than the Earth's.

**References:** [1] Jurewicz S.R. (1995) *Earth Planet Sci. Lett.* **132**, 183-198. [2] Grossman L. and Larimer J.W. (1974) *Rev. Geophys. Space Phys.* **12**, 71-101. [3] Mittlefehldt D.W. and Lindstrom M.M. (2003) *GCA* **67**, 1911-1934. [4] Stolper E.M. (1977) *GCA* **41**, 587-611. [5] Walker D. et al. (1977) *PLSC 8<sup>th</sup>*, 1521-1547. [6] Stolper E.M. and McSween H.Y. Jr. (1979) *GCA* **43**, 1475-1498. [7] Herd C.D.K. et al. (2002) *GCA* **66**, 2025-2036. [8] Moroz V.I. (1983) In *Venus*. U. Arizona Press. pp.45-68. [9] Vilas F. (1988) In *Mercury*. U. Arizona Press. pp. 59-76. [10] Wasson J.T. (1988) In *Mercury*. U. Arizona Press. pp. 622-650. [11] Cintala M.J. (1992) *JGR Planets* **97**, 947-973. [12] Cloud P. (1968) *Science* **160**, 729-736. [13] Delano J. W. (2001) *Origin Life Evol. Biosphere* **31**, 311-341. [14] Rivkin A.S. et al. (2002) In *Asteroids III*. U. Arizona Press. pp. 325-253. [15] Jurewicz A.J. et al. (2004) *Lunar Planet Sci. XXXV*.