

WHY IS THE WHOLE MOON MORE OXIDIZED THAN THE WHOLE EARTH, BUT THE LUNAR MANTLE IS MORE REDUCED THAN EARTH'S UPPER MANTLE? Youxue Zhang, Dept of Earth & Environmental Sciences, the University of Michigan, Ann Arbor, MI 48109-1005, USA <youxue@umich.edu>

Introduction: Earth has a large core, accounting for 32.5% of the mass of Earth [1]. On the other hand, Moon has a small core, accounting for ~1.3% of the mass of Moon [2]. Although there are uncertainties about the composition of Earth's core, the bulk silicate Moon, and Moon's core, clearly Earth has a much higher metal/oxygen ratio compared to Moon. That is, when the whole Earth and whole Moon are compared, Earth is more reduced, and Moon is more oxidized. In the simplest thinking, either Earth's mantle would also be more reduced than Moon's mantle, or if core-mantle equilibrium is imposed, both the terrestrial mantle and lunar mantle would have similar oxygen fugacity slightly below Iron-Wustite (IW) buffer. However, Earth's mantle (at least the upper mantle) has a fairly high oxygen fugacity close to Quartz-fayalite-magnetite buffer (QFM) [3], about 4 orders of magnitude higher than IW. On the other hand, even though Moon has a lower metal/oxygen ratio, lunar mantle has a much lower oxygen fugacity, about IW-1 [4] and the lunar mantle might have more Fe than the terrestrial mantle depending on which compositional model of the bulk silicate Moon one adopts [5-6]. Hence, the question is: Why does Earth have a higher Metal/oxygen ratio but terrestrial basalts are more oxidized compared to Moon?

Because the oxygen fugacity of lunar basalts is consistent with that at the core-mantle boundary [4], one might argue that Moon behaves normally. It is Earth that shows abnormal behavior. There are a number of possible solutions. This contribution addresses the issue and discusses the possible solutions.

Possible solution 1: One possibility is that at the time of core formation, Earth's mantle was roughly in redox equilibrium with the core (assuming the redox equilibrium is not much dependent on pressure) and hence was as reducing as Moon, but the mantle, maybe only the upper mantle, was oxidized by later processes, such as a late veneer [7-8], or O₂ from surface processes such as photochemical decomposition of H₂O to H₂ and O₂ with H₂ being lost to outer space [9] and O₂ being somehow incorporated into the upper mantle. An order of magnitude estimate of the amount of oxygen needed to change the oxygen fugacity from IW-1 to QFM can be made as follows. The oxygen fugacity of the upper upper mantle is calculated by the ferrosilite-spinel-fayalite buffer [10]: $6\text{FeSiO}_3(\text{opx}) +$

$\text{Fe}_3\text{O}_4(\text{sp}) \rightleftharpoons 6\text{Fe}_2\text{SiO}_4(\text{oliv}) + \text{O}_2(\text{gas})$. Calculations show that when the Fe₂O₃ concentration in spinel in a typical spinel peridotite increases from 0.3 wt% to 7.0 wt%, meaning a 6.7 wt% increase in Fe₂O₃ in spinel, meaning $6.7 \times 0.1113 = 0.7457$ wt% of extra oxygen, log_fO₂ would increase from IW-1 to QFM. A typical mantle peridotite contains ~2% spinel (equivalent to a garnet peridotite containing 5.7% garnet because the mass of garnet formed in the spinel lherzolite to garnet lherzolite transition, $\text{MgAl}_2\text{O}_4(\text{sp}) + 4\text{MgSiO}_3(\text{opx}) \rightleftharpoons \text{Mg}_2\text{SiO}_4(\text{ol}) + \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{gt})$, is 2.83 times the mass of spinel consumed). Hence, in the rock, oxygen must increase by $0.7457 \times 0.02 = 0.0149$ wt%, or 149 wt ppm. Total amount of oxygen in a typical peridotite is 44.23 wt%. Hence, the amount of extra oxygen would be within analytical error if one wants to use whole rock analyses. The mass of the upper mantle is 1.09×10^{24} kg [1]. 149 ppm of the upper mantle means 1.62×10^{20} kg oxygen, or 137 times the amount of O₂ in air. Hence, it is not a trivial amount. On the other hand, the amount is equivalent to 13.5% of the amount of oxygen in ocean water. If there was H₂ loss in the magma ocean stage [11], or if about 1/7 of all degassed H₂O (if all ocean water originated from degassing, see discussion in [12]) in the early vigorous magmatism was decomposed with the resulting H₂ being driven off to outer space by hydrodynamic escape and O₂ being incorporated into the upper mantle, that could explain the increase in *f*_{O₂} in the upper mantle. This does not seem to be prohibitively too difficult. On the other hand, if H₂ loss from a magma ocean caused the oxidation of the terrestrial mantle, one would need to explain why the process was more effective on Earth than on Moon, which seems difficult.

Possible solution 2: Another solution is that Earth's core is disproportionately too large, so that most of Earth's metal is in Earth's core, and the mantle (at least the upper mantle) has a low metal to oxygen ratio. On the other hand, Moon's core is disproportionately too small even compared to the lower overall metal/oxygen ratio, leaving the lunar mantle with high metal/oxygen ratio and hence a lower oxygen fugacity, below IW [4]. Hence, the question is: Why did Earth form a disproportionately large core compared to Moon? One possible answer is the pressure effect. Processes on Moon occurred at pressures below 5 GPa, whereas much of Earth has higher pressures.

The high pressure in Earth's mantle and core-mantle boundary has the potential to produce a number of effects. For example, if high pressure favors any of the disproportionation reactions of iron: $3\text{Fe}^{2+} \rightleftharpoons \text{Fe}(\text{metal}) + 2\text{Fe}^{3+}$, then Fe(metal) thus produced at high pressure would sink into the core, leaving behind a more oxidizing mantle. One such reaction is $3\text{FeO}(\text{silicate melt}) \rightleftharpoons \text{Fe}(\text{molten metal}) + \text{Fe}_2\text{O}_3(\text{silicate melt})$. Disappointedly, the volume change for this reaction [13,14] is positive. If the volume change were negative, high pressure would push the reaction to the right-hand side, leading to more molten Fe sinking into the core and leaving a more oxidizing mantle. Although this reaction does not work, there are other reactions that lead to the formation of Fe in the lower mantle [15,16], such as $3\text{FeO}(\text{magnesiowustite}) \rightleftharpoons \text{Fe}(\text{metal}) + \text{Fe}_2\text{O}_3(\text{bridgemanite})$, or $\text{Al}_2\text{O}_3(\text{bridgemanite}) + 3\text{FeSiO}_3(\text{bridgemanite}) \rightleftharpoons \text{Fe}(\text{metal}) + 3\text{SiO}_2(\text{stishovite}) + 2\text{FeAlO}_3(\text{bridgemanite})$, in which Fe metal would sink to the core, and leaving behind a more oxidizing mantle.

Campbell et al. [17] hinted that the pressure effect on the oxygen fugacity buffers might reconcile the high oxygen fugacity in the upper mantle with the low oxygen fugacity and core-mantle boundary. Hu et al. [18] used theoretical calculations and experiments to show that a new Fe oxide, FeO_2 with the structure of pyrite, is stable at 76 GPa and 1800 K. If such a phase is swept up by mantle plumes or other mantle dynamic processes, it would make the upper more oxidizing, and would also create heterogeneity in oxygen fugacity in the mantle.

These pressure effects imply that the size of the core of a planetary body is determined not only by the the metal/oxygen ratio of a planetary body, but also to the size of planetary body. Large planetary bodies would have a more oxidizing mantle.

Possible solution 3: Because Moon has a weaker gravity field, if core formation was through liquid metal segregation from solid silicate minerals, then metal sinking into core might be less effective in Moon, and lunar core formation might be less complete than in Earth. This does not seem to be viable because Moon experienced a deep lunar magma ocean, which arguably post-dated the lunar core formation and would have allowed liquid metal to sink into the core.

Possible solution 4: In the Giant Impact Hypothesis for the origin of the Earth-Moon system, the choice of the impactor may also have consequence on the redox state of Moon. Wade and Wood [19] used simulations and modeling to suggest that a reduced

impactor is able to produce a reduced Moon. In this scenario, the reduced nature of Moon is accidental, rather than having more general significance for planetary bodies.

Summary: There are a number of possible explanations to the question why Earth is overall more reducing but Earth's upper mantle is more oxidizing compared to Moon. It seems that the relative size of the core of a planetary body is controlled not only by the metal/oxygen ratio of the whole body, but also by how reducing or oxidizing the mantle is. The latter might be related to the size of the planetary body. Larger terrestrial planetary bodies may have a more oxidizing mantle.

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