A hydrogen-based oxidation mechanism relevant to planetary formation

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A B S T R A C T

It is now generally accepted that the Moon formed by collision of a Mars-sized impactor with the Earth (Hartmann and Davis, 1975), a process termed "the Giant Impact". The oxygen isotope compositions of both bodies are indistinguishable (Wiechert et al., 2001), a result that would require extensive chemical homogenization. Recent simulations have been developed that predict intimate mixing immediately following the impact (Canup, 2012; Ćuk and Stewart, 2012; Pahlevan and Stevenson, 2007), minimizing the oxygen isotope problem. Nevertheless, striking chemical differences remain. We propose that the process of hydrogen degassing and loss to space during magma cooling can explain differences in the water content, oxygen fugacity ($f(O_2)$), and isotopic composition of Cl and H in the Earth–Moon system. At low $f(O_2)$, H_2 gas is the stable O–H phase in basalts. The low solubility and rapid diffusivity of H_2 explain the presently dry character of most lunar samples. Many of the apparently discrepant observations regarding the hydrous character of the Moon are reconciled by H_2 degassing. Early H_2 degassing also explains the high $f(O_2)$ of Earth's mantle. A loss of only 1/3 'ocean equivalent' water from Earth by hydrodynamic escape of H_2 would shift the $f(O_2)$ of the upper mantle from the very low oxidation state equivalent to the Moon and other primitive differentiated bodies to its present oxidized state (near the fayalite–magnetite–quartz buffer). No other processes, such as late addition of material to Earth or injection of Fe^{3+}-rich deep mantle materials to the upper mantle are required to explain the early elevated oxidation state of Earth's upper mantle.

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1. Introduction

The return of Apollo samples brought the recognition that the Moon was dry (Shearer et al., 2006 and references therein). No hydrous phases were identified and the H from soils and breccias was attributed to solar wind, meteorite contamination or terrestrial contamination (Epstein and Taylor, 1970; Friedman et al., 1970; Merlivat et al., 1972). This paradigm was overturned when measurable H was found in lunar glass beads that extrapolated to pre-degassed water contents of 745 ppm H_2O (Saal et al., 2008). Follow up studies have also found measurable water (as hydroxyl) in apatites (Barnes et al., 2013; Boyce et al., 2010; Greenwood et al., 2011; McCubbin et al., 2010b, 2010c), in melt inclusions (Hauri et al., 2011), and in nominally anhydrous minerals (Hui et al., 2013). It is clear that this water is not related to frozen water found at the lunar surface (Colaprete et al., 2010), but the source and abundance of the mineral-bound lunar water is still in doubt.

1.1. Current ideas concerning lunar water

Recent ideas concerning the water content of the Moon are summarized in Table 1, from which the following observations can been made. Following the return of the Apollo samples, all petrographic and geochemical evidence supported the view of a 'bone dry' Moon (Taylor, 1994). No hydrous phases were found and geochemical analyses indicated very low volatile contents (Ringwood, 1979) and virtually no indigenous water. Excluding micrometeorite and terrestrial contamination, the hydrogen isotope composition of lunar soils and breccias indicated a predominantly solar-wind implanted component (Epstein and Taylor, 1970; Friedman et al., 1970; Merlivat et al., 1974; Fegley and Swindle, 1993).

Measurable indigenous H contents were detected by ion microprobe analyses of rapidly quenched fire-fountain erupted low- and very low-Ti glasses (sample 15427,41) (Saal et al., 2008). The hydrogen content of the glass beads, along with later analyses of glass inclusions in olivine crystals (sample 74220) (Hauri et al., 2011) were used to argue that parts of the lunar interior had as much water as the Earth's depleted upper mantle ($\sim$100 ppm H_2O).

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Table 1

Current ideas regarding the water content of the Moon. The conclusions that have been made appear to be contradictory, but are reconciled when considered in light of H_2 degassing at low $f(O_2)$.

Original conclusion (ref)	Reasoning	Present explanation
Moon is anhydrous (petrography)	No recognizable hydrous minerals in thin sections and lack of ferric iron-bearing phases and aqueous alteration textures	The rapid diffusion rate and low solubility of H_2 in silicate melts should lead to near-total degassing as predominantly H_2, and H_2 alteration features are observed in lunar samples.
Lunar mantle is hydrated – glass beads and melt inclusions. (1, 2)	Ion microprobe analyses of glass beads extrapolates to 745 ppm water in melt	Sourced at depth, these unique samples had a high H_2 confining pressure, causing their eruption. Combined with rapid cooling, some H_2 remains.
Water in lunar magmas (apatite) (3, 4)	Measurable H in late-crystallizing apatite	Crystallization enriches trace H in liquid. The last stages of crystallization reaches apatite saturation.
Cometary water input (5)	High δD values (generally 400 to 900‰) in apatites similar to comets	No exogenous source required. H_2 loss by Rayleigh fractionation explains high δD.
Anhydrous volatile degassing (6)	Extreme $\delta^{37}Cl$ values indicate anhydrous degassing	Conclusion not incompatible with hydrous melts if H and Cl diffusion are decoupled.
Lunar magma ocean had low water content (7)	Modeling of moderate initial water contents result in extreme water-rich KREEP	The solubility behavior of the O–H system in silicate melts under reducing conditions coupled with the observation that hydrous silicate phases are nearly absent in the Moon limit the starting water content of the lunar magma ocean to $< \sim 400$ ppm H_2O.

Ref.: (1) Hauri et al. (2011); (2) Saal et al. (2008); (3) Boyce et al. (2010); (4) McCubbin et al. (2010a, 2010b); (5) Greenwood et al. (2011); (6) Sharp et al. (2010); (7) Elkins-Tanton and Grove (2011).

Hydroxyl contents of lunar apatites indicate minimum water contents of source regions between 64 ppb and 5 ppm (McCubbin et al., 2010b), lower than estimates from the volcanic glasses. The compositions of the apatites also vary between lithologies. Apatites in mare basalts have the highest apparent hydroxyl content, whereas apatite from other rock types have higher Cl^- and low OH^-, indicating distinct source regions (McCubbin et al., 2011). The hydrogen isotope composition (δD value) of lunar apatites is generally very high, mostly falling in a range of 400 to 900‰ (Greenwood et al., 2011), which was interpreted as indicating a significant cometary input of water post Giant Impact.

Elkins-Tanton and Grove (2011) estimated water contents for various lithologic source regions on the Moon using a magma ocean fractional solidification model. They concluded that the lunar magma ocean likely had less than 10 ppm H_2O, and further that hydrogen, rather than water or hydroxyl, must have been a significant component in the melt due to the low oxygen fugacity. Chlorine isotope data for lunar samples also suggests low water contents. The extraordinarily high $^{37}Cl/^{35}Cl$ ratios measured for a number of Apollo samples were interpreted as evidence of Cl degassing from anhydrous magmas (Sharp et al., 2010).

It is clear from the above studies that the abundance, source, distribution, and speciation of 'water' in lunar samples is not well constrained. Why, for example, is apatite the only known mineral to contain any structural water if the water contents of the Earth and Moon mantles were so similar? How can estimates of high water contents in the lunar magma ocean be reconciled with low water content estimates from modeling?

1.2. The oxygen fugacity of the Moon and Earth mantle

The oxygen fugacity, or $f(O_2)$, of lunar samples are universally low, estimated to be one log unit below the iron–wüstite buffer (IW-1; see Eq. (5)) (Wadhwa, 2008 and references therein). Iron–nickel metal is found as a common late-stage crystallization phase (Jones and Palme, 2000; Reid et al., 1970; Wittman and Korotev, 2013), and buffers the samples to a low $f(O_2)$. The $f(O_2)$ of the Earth's upper mantle is near the fayalite–magnetite–quartz buffer (FMQ; see Eq. (4)) (Canil et al., 1994; Kelley and Cottrell, 2009; Mattioli and Wood, 1986; Wood et al., 1990), over four orders of magnitude higher than for the Moon. The Earth's mantle must have had a low oxygen fugacity after the Giant Impact event re-

sponsible for creation of our Earth–Moon binary planet system (Canil et al., 1994; Frost et al., 2008; Frost and McCammon, 2008; Kelley and Cottrell, 2009). Nevertheless, it appears that the high oxidation state of the outer part of Earth existed at least since 4350 Ma (Trail et al., 2011), suggesting that the high $f(O_2)$ of the Earth's upper mantle was a feature acquired shortly after the Giant Impact event.

Several hypotheses have been proposed to explain the relatively oxidized state of Earth's (upper) mantle. Numerous authors have suggested that oxidation of the lower mantle could occur by disproportionation of FeO at high pressures to Fe metal and Fe_2O_3 components in post-spinel and perovskite form (Frost et al., 2004, 2008; Mao, 1974; Righter, 2003; Wade and Wood, 2005). The metal would sink to the core and the ferric oxide-bearing minerals would convect to the upper mantle. An alternative idea is that addition of late oxidized material, the so-called 'late accretion' model, could raise the $f(O_2)$ of the upper mantle (O'Neill, 1991; Wood et al., 2006). However as explained in Section 5.1, both of the actual processes for oxidation are not well described and are most likely ineffective.

Dreibus and Wänke (1987) proposed an Fe-enrichment model for the martian mantle in which H_2O from the volatile rich silicate portion of Mars reacted with Fe-metal, following the reaction

$$H_2O + 0.947Fe^o = H_2 + Fe_{0.947}O \qquad (1)$$
$$\text{iron metal} \qquad \text{wüstite}$$

to explain Mars' anomalously high mantle FeO content (Bertka and Fei, 1997; Dreibus and Wanke, 1985; Wanke and Dreibus, 1994). The H_2 formed from this reaction was reported to be lost by hydrodynamic escape. Others have suggested that hydrodynamic escape of H_2 could play a role in oxidation of Earth's mantle (e.g., Hamano et al., 2013; Ringwood, 1979; Wade and Wood, 2005), but the importance of this mechanism is usually minimized (Wood et al., 2006).

2. Phase relations in the O–H system relevant to terrestrial planetary formation

2.1. Oxygen fugacity and speciation in the O–H system

The stability of water is governed by the reaction

$$H_2O = H_2 + 1/2\,O_2 \qquad (2)$$