

Constraints on volatile concentrations of pre-eruptive lunar magma



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ABSTRACT

Until recently, the Moon had long been thought to be depleted of volatiles such as H₂O, S, CO_x and Cl₂. Researchers have recently measured volatile concentrations in the minerals, glasses and inclusions of lunar samples, and the results show that lunar rocks contain volatiles that are more similar to terrestrial materials than was previously thought. Mare basalts are located on the Earth-facing hemisphere in large impact basins, and they are not representative of the feldspathic highlands. Thus, it is likely that the density of lunar mafic magma exceeds that of the highland rocks based on buoyancy alone. According to this observational fact, we calculate the density of mare basalt to give a constraint for the maximum amount of water mare basalt can contain because water can effectively decrease the density of mare magma. Our result shows that water contained in the pre-eruptive magma could not have been more than 1000 ppm; otherwise, the density of very-low-Ti basaltic magma would be less than that of the highland rocks. Additionally, if magma contains other species of volatiles such as C–O, S, F, or Cl₂, the water in the pre-eruptive magma would have to be much less than 1000 ppm because volatiles such as CO₂ can effectively decrease the solubility of water in silicate melts. Based on these calculations on densities and a comparison with water in MORB, we conclude that the moon's water is not as great as has been recently suggested.

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1. Introduction

The lunar surface is divided into mare regions and highlands which correlate with elevation. The mare regions are wide meteorite impact basins that occupy 17% of the area of the lunar surface and are covered by lunar basalts. The highlands are regions that are topographically higher in elevation than the mare regions. The typical characteristic feature of the highlands is an absence of basaltic volcanism (Kaula et al., 1973). The current theory of the moon's early evolution is the magma ocean hypothesis (Elkins et al., 2011; Warren, 1985), which suggests that different spheres within the inner moon are formed by the solidifying process of a magma ocean in a progressive pattern. Earlier theories and a significant amount of work proposed that during the early period of the magma ocean's cooling, the primary magmatic minerals (olivine and pyroxene) were enriched in iron and magnesium, crystallized and sank to form the lunar mantle cumulates. Plagioclase began to develop in the late stages of the magma solidification, forming anorthosite, which led to the formation of a flotation crust. The mare basalts erupted mainly during 4.0–2.0 Ga (Hiesinger et al., 2000). These basalts were mostly distributed in crating basins and may have been derived from different depths in the lunar

mantle (Beard et al., 1998). Based on the concentration of titanium, the mare basalts are classified into three subclasses as (i) high-Ti (TiO₂ > 6 wt.%), (ii) low-Ti (1.5 < TiO₂ < 6 wt.%) and (iii) very-low-Ti (TiO₂ < 1.5 wt.%) basalts (Neal and Taylor, 1992).

Previous studies of lunar samples show that these basalts lack hydrous minerals such as amphibole, mica, and clay minerals (such as kaolinite, smectite, and montmorillonite) (Staid and Pieters, 2001; Warren, 1985) and have a depleted *K/U* ratio compared with Earth samples (Tera et al., 1974). These characteristics imply a general depletion in volatiles, which is consistent with the moon-forming giant impact hypothesis (Albarede, 2009). Present studies indicate that the volatile concentrations in the minerals, glasses and inclusions of the lunar samples are similar to terrestrial materials. For example, H⁺ ion-bearing water content can be up to thousands of ppm (Boyce et al., 2010; Greenwood et al., 2011; Hauri et al., 2011; McCubbin et al., 2010; Saal et al., 2008), much higher than previously thought.

It has been proposed that volatile exsolution from magmatic melt drives eruptions on Earth (Zhang et al., 2007). The whole process of an eruption could be divided into several dynamic stages. Initially, volatile components dissolve in magma. As the magma ascends, the volatiles become supersaturated and bubbles form and grow. Bubbles keep growing until the critical point at which they break up. Once this happens, a nonexplosive magma will transform into an explosive magma and eruption will occur. The key part of

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this process is the reduction in bulk density of the ascending magma through bubble nucleation. We suppose the same dynamic drove the mare magma eruptions on the moon.

During the decade of Apollo missions, the information gathered using seismic data from the four mission stations was used to decipher the structure of moon. This structure includes a 60-km-thick lunar crust and a discontinuous wave interface (approximately 20 km deep), which divides the entire crust into upper and lower layers (Toksöz et al., 1974). The present day research has indicated a thinner crust ranging from 30 to 40 km (Gagnepain-Beyneix et al., 2006; Khan and Mosegaard, 2002; Khan et al., 2000; Lognonne et al., 2003). In this paper, we adopt the dual-layer crust model (Jolliff et al., 2006). The density is 2820 kg/m³ for the upper crust and 3040 kg/m³ for the lower crust. An average 20-km-thick upper crust is supposed for the highland areas, although local regions may be thinner or thicker because of impact events.

The goal of our work is to use mare basalt composition and a model to calculate the density of magma with various water contents, compare the magma density with that of the upper crust and give an upper limit of water in the pre-eruptive magma to ensure that magma could not have erupted on the highlands.

2. Methodology

2.1. Driving force for magma eruption

It is well established that mare basalts on the moon are preferentially located both on the Earth-facing hemisphere and within large impact basins. Several theories suggest a relation between crust thickness and the distribution of basaltic eruptions (Kaula et al., 1973; Solomon, 1975; Wieczorek et al., 2001). Advances in understanding the magmatic processes suggest that magma buoyancy plays a vital role in the dynamics of magma transport and emplacement. Earlier studies have proven that the Earth's crust acts as a density filter that allows less-dense magma to erupt on the surface (Herzberg et al., 1983; Stolper and Walker, 1980).

Besides the buoyancy, other factors such as viscosity of the magma, fractures of overlying crust may also play some roles and possibility exist that light magma may be “stuck”. In this paper, we ascribe the lack of mare basalts on the highlands to the driving force (i.e. buoyancy). The reasons for this assumption are listed as follows: (1) Using the same methods in our paper, we calculate the density of the KREEP (KREEP rocks are high in concentration of incompatible elements such as **K**, **Rare Earth Elements**, **P**), which is a typical rock from the feldspathic highlands (Heiken et al., 1991). The densities of the dry KREEP melt at the base of the upper lunar crust are 2.54–2.76 g/cm³, much less dense than the upper lunar crust (2.82 g/cm³), thus they can erupt at the feldspathic highlands. This indicates that the “access” for light magma erupting exist. (2) Based on the origin of the mare basalts (decompression melting of primitive lunar mantle caused by the overturn of the magma ocean ilmenite cumulate layer) (Elkins et al., 2000; Hess and Parmentier, 1995; Zhong et al., 2000), we can know that they are global-scale magmatism, and can be generated beneath the feldspathic highlands. If the mare basalts were less dense than the feldspathic highlands, it is inexplicable that why the feldspathic highlands only inhibit the eruption of the mare basalts and not the KREEP, because the absence of mare basalts from the feldspathic highlands is also a global-scale feature. Therefore, we believe the absence of basalts on highlands is the result of negative buoyancy.

The driving force is in terms of pressure differences for terrestrial magma eruptions was elucidated by Lange (Lange, 2002) and is composed of two terms:

$$\Delta P = [\rho_{\text{rock}}(H) - \rho_{\text{magma}(H)}]gH + \Delta P_{\text{chamber}}, \quad (1)$$

where $\rho_{\text{rock}(H)}$ is the integrated average density of the overlying rock (which varies as a function of depth), $\rho_{\text{magma}(H)}$ is the density of the magma (which also varies with depth), g is the gravitational acceleration, H is the depth from the surface to the magma reservoir, and $\Delta P_{\text{chamber}}$ is the overpressure in the magma chamber. Eq. (1) does not consider the additional force required to open a fracture to the surface.

The first term of Eq. (1) describes the magma buoyancy relative to the overlying rock column. If $\rho_{\text{magma}(H)} > \rho_{\text{rock}(H)}$, the magma buoyancy is negative, and if $\rho_{\text{magma}(H)} < \rho_{\text{rock}(H)}$, the magma buoyancy is positive. The second term, $\Delta P_{\text{chamber}}$, is the magma chamber overpressure against the magma. The typical magma chamber overpressure on the Earth was calculated as approximately 10 MPa (Bower and Woods, 1997). This magnitude of force could push the magma by approximately 400 m in depth past the balanced buoyancy interface. The lunar basalt is mainly located in large impact basins rather than highlands (Wieczorek et al., 2001). Therefore, the density of magma must be more than that of the upper crust. This observation is limited to pre-eruptive volatile (H₂O) concentrations. These limits are obtained by quantitatively comparing the average density of the lunar highland upper crust with the calculated effect of dissolved H₂O or exsolved CO on the density of various mare basalts as a function of depth.

2.2. Calculation details

For the present work, we chose data of 54 representative mare basaltic samples (Papike and Vaniman, 1977; Warren et al., 2003) to cover all types of mare basalts. These samples were obtained by lunar exploration and Apollo projects. The 54 samples contain 15 high-Ti basalts, 19 low-Ti basalts and 20 very-low-Ti basalts.

The pressure at the bottom of the upper crust is obtained by

$$P_{\text{magma}} = \rho_{\text{rock}} * g * H \quad (2)$$

where P_{magma} is the pressure of the magma chamber, ρ_{rock} is the average density of the overlying crust (2820 kg/m³), g is the gravitational acceleration of the moon, which is approximately one-sixth that of Earth, and H is the depth of the upper crust (i.e., 20 km). The calculated pressure at the bottom of the upper crust is 921 bar.

The oxidation state of the moon is QFM-4 log unit (Sato, 1976), relatively reduced compared with that of Earth mantle. We add different amounts of water (i.e., 5000 ppm, 3000 ppm and 1000 ppm) to the basaltic samples and calculate their densities. The Fe²⁺ and Fe³⁺ compositions and the magmatic liquidus are calculated using MELTS (Smith and Asimow, 2005).

The densities of these magmas with additional water are estimated by the calculations of magma volumes and magma weights. The volume of magma at a given temperature and pressure can be described as a linear function of composition (Bottinga and Weill, 1970):

$$V_{\text{liq}}(T, P) = \sum X_i [V_i + dV_i/dT(T - T_{\text{ref}}) + dV_i/dP(P - 1\text{bar})] \quad (3)$$

where $V_{\text{liq}}(T, P)$ is the molar volume of melt at temperature T and pressure P , X_i is the mole fraction of each oxide component, V_i is the partial molar volume of oxide component i at the reference temperature, T_{ref} is the reference temperature, dV_i/dT is the coefficient of thermal expansion, and dV_i/dP is the coefficient of compressibility. The density of a silicate melt is

$$\rho_{\text{liq}}(T, P) = \frac{\sum X_i (M.W.)_i}{V_{\text{liq}}(T, P)} \quad (4)$$

where $(M.W.)_i$ is the molecular weight of oxide component i . All parameters used in the calculation are listed in Table 1 (the parameters of Cr₂O₃ are assumed the same as those of Fe₂O₃ (Lange and Carmichael, 1987)).

Table 1Partial molar volumes, thermal expansions and compressibilities of components used in calculations.^a

	$V_{i1400\text{ °C}} (\text{cm}^{-3}/\text{mole})$	$(dV_i/dT)_{1\text{ bar}} (10^{-3} \text{ cm}^{-3}/\text{mole}\cdot\text{°C})$	$(dV_i/dP)_{1400\text{ °C}} (10^{-4} \text{ cm}^{-3}/\text{mole}\cdot\text{bar})$	$(dV_i/dP)/dT (10^{-7} \text{ cm}^{-3}/\text{mole}\cdot\text{bar}\cdot\text{°C})$
SiO ₂	26.86 ± 0.03 ^a	0 ± 0.50	−1.89 ± 0.02	1.3 ± 0.1
TiO ₂	23.16 ± 0.26	7.24 ± 0.46	−2.31 ± 0.06	0
Al ₂ O ₃	37.42 ± 0.09 ^a	2.62 ± 0.17	−2.26 ± 0.09	2.7 ± 0.5
Fe ₂ O ₃	42.13 ± 0.28	9.09 ± 3.49	−2.53 ± 0.09	3.1 ± 0.5
FeO	13.65 ± 0.15	2.92 ± 1.62	−0.45 ± 0.03	−1.8 ± 0.3
CaO	16.90 ± 0.06 ^a	3.74 ± 0.12 ^a	0.34 ± 0.05	−2.9 ± 0.3
MnO	14.13 ^d	2.13 ^d		
MgO	12.02 ± 0.07 ^a	3.62 ± 0.61 [†]	0.27 ± 0.07	−1.3 ± 0.4
K ₂ O	47.28 ± 0.10 ^a	11.91 ± 0.89 [†]	−6.75 ± 0.14	−14.5 ± 1.5
Na ₂ O	29.65 ± 0.07 ^a	7.41 ± 0.58 [†]	−2.40 ± 0.05	−6.6 ± 0.4
P ₂ O ₅	64.5 ± 0.7 ^b			
H ₂ O	26.70 ^c	9.50 ± 0.8 ^c	−3.20 ± 0.6 ^c	
CO ₂	27.76 ^e	3.41 ^e	−4.61 ^e	−12.7 ^e

^a All partial molar volume are recalculated to $T = 1400\text{ °C}$ and 1 bar. Data without marks are from Lange and Carmichael (1990).^b Lange (1997).^c Toplis et al. (1994).^d Ochs and Lange (1999).^e Bottinga et al. (1983).[†] Estimated using methods proposed by Liu and Lange (2003).

The environment on the moon is under a reduced oxidation state with mostly carbon monoxide as the carbon gas species. The present understanding also suggests that the solubility of CO in silicate melt is negligible and it is presumed that the CO has similarities to the CO₂ in magma (Rutherford and Papale, 2009).

When the magma contains exsolved volatiles, the molar volumes of H₂O and CO at a given T and P are calculated using Eq. (3) in Pitzer and Sterner (1994). Therefore, the density of melt with exsolved volatiles is

$$\rho_{\text{liq}}(T, P) = \frac{X_{\text{exsolved}}(M.W.)_{\text{H}_2\text{O}} + X_{\text{exsolved}}(M.W.)_{\text{CO}} + \sum X_i(M.W.)_i}{V_{\text{liq}}(T, P) + V(T, P)_{\text{exsolved H}_2\text{O}} + V(T, P)_{\text{exsolved CO}}} \quad (5)$$

where $(M.W.)_{\text{H}_2\text{O}}$ and $(M.W.)_{\text{CO}}$ are the molecular weights of H₂O and CO, respectively. The two X_{exsolved} terms are the mole fractions of exsolved H₂O and CO, respectively. $V(T, P)_{\text{exsolved H}_2\text{O}}$ and $V(T, P)_{\text{exsolved CO}}$ are molar volumes of the exsolved H₂O and CO, respectively. In this calculation, we ignore the crystallization and magma viscosity change as magma ascending, because the rising velocity is fast once volatile exsolution occurs (Zhang et al., 2007).

The solubilities of H₂O and CO in basaltic melts are calculated using VolatileCalc (Newman and Lowenstern, 2002). The water is completely dissolved at high pressures, unless there are other types of volatiles in the magma or at some point where the upper crust is thin enough to allow water to be partially exsolved from the magma.

We calculate the magma densities with varying pressures to correspond to the magma ascent process. Here, we considered the possible CO gas species in our calculation because carbon will be oxidized to the CO gas phase at low pressures (Rutherford and Papale, 2009). We assume that 500 ppm CO (a similar quantity to that in Rutherford and Papale 2009) is present when the pressure decreases to 40 MPa at 1350 °C under low $f\text{O}_2$ (QFM-4 log unit).

We also calculate the error propagation to evaluate the reliability of this work based on differences between the magma densities and the lunar upper crust. The error of the molar volume of the magma is expressed as

$$\sigma V_{\text{liq}} = \sum X_i(\sigma V_i + (T - T_{\text{ref}})\sigma(dV_i/dT) + (\sigma(dV_i/dP) - \sigma((dV_i/dP)/dT)(T - T_{\text{ref}}))(P - 1)) \quad (6)$$

where σV , $\sigma(dV_i/dT)$, $\sigma(dV_i/dP)$ and $\sigma((dV_i/dP)/dT)$ are errors of molar volume, coefficient of thermal expansion, coefficient of com-

pressibility and coefficient of compressibility variation with temperature, respectively. The other parameters are the same as Eq. (3).

The error of density, $\sigma\rho_{\text{liq}}(T, P)$, is expressed as

$$\sigma\rho_{\text{liq}}(T, P) = -\frac{\sum X_i(M.W.)_i}{V_{\text{liq}}^2(T, P)}\sigma V_{\text{liq}}(T, P) \quad (7)$$

where X_i , $(M.W.)_i$, $V_{\text{liq}}(T, P)$, and $\sigma V_{\text{liq}}(T, P)$ are the mole fraction of each oxide component, molecular weight, partial molar volume and error of partial molar volume, respectively.

3. Results

3.1. Densities of magma at the bottom of the upper crust

First, the magma density decreases from high-Ti to very low-Ti basalts, with intermediate low-Ti magma densities, and the magma densities decrease as the water concentration increases. For very low-Ti basalts, with 1000 ppm water, the magma densities can be as low as 2.82 g/cm³, corresponding to the upper crust values. With the addition of more water (e.g., 3000 ppm or 5000 ppm), the very low-Ti basaltic densities would be less than 2.82 g/cm³ (Fig. 1). The sample errors range from 10^{−5} to 3×10^{−2}. Lesser errors would be obtained with a more precise database of σV , $\sigma(dV_i/dT)$, $\sigma(dV_i/dP)$ and $\sigma((dV_i/dP)/dT)$.

3.2. Density trend as magma rises to the surface

We simplify the complex magma system containing several volatiles to be silicate melt with only H₂O and CO. The result reveals that three types of basalts with various water concentrations show similar trends. First, when the pressure is more than 400 bar (>8–9 km deep), the magma density decreases gradually as the magma ascends. Once the pressure falls to 400 bar, the density will decrease rapidly as the magma rises (Fig. 2.).

4. Discussion

Our results suggest that the densities of the anhydrous basaltic samples are less than that of the lower crust (i.e., 3.04 g/cm³) and greater than that of the upper crust (i.e., 2.82 g/cm³). This result is consistent with the fact that basaltic magma is absent in the lunar highlands, i.e., it cannot pass through the anorthositic upper crust. The magma density will progressively decrease as increasingly more volatiles are added, and 1000 ppm water may be the

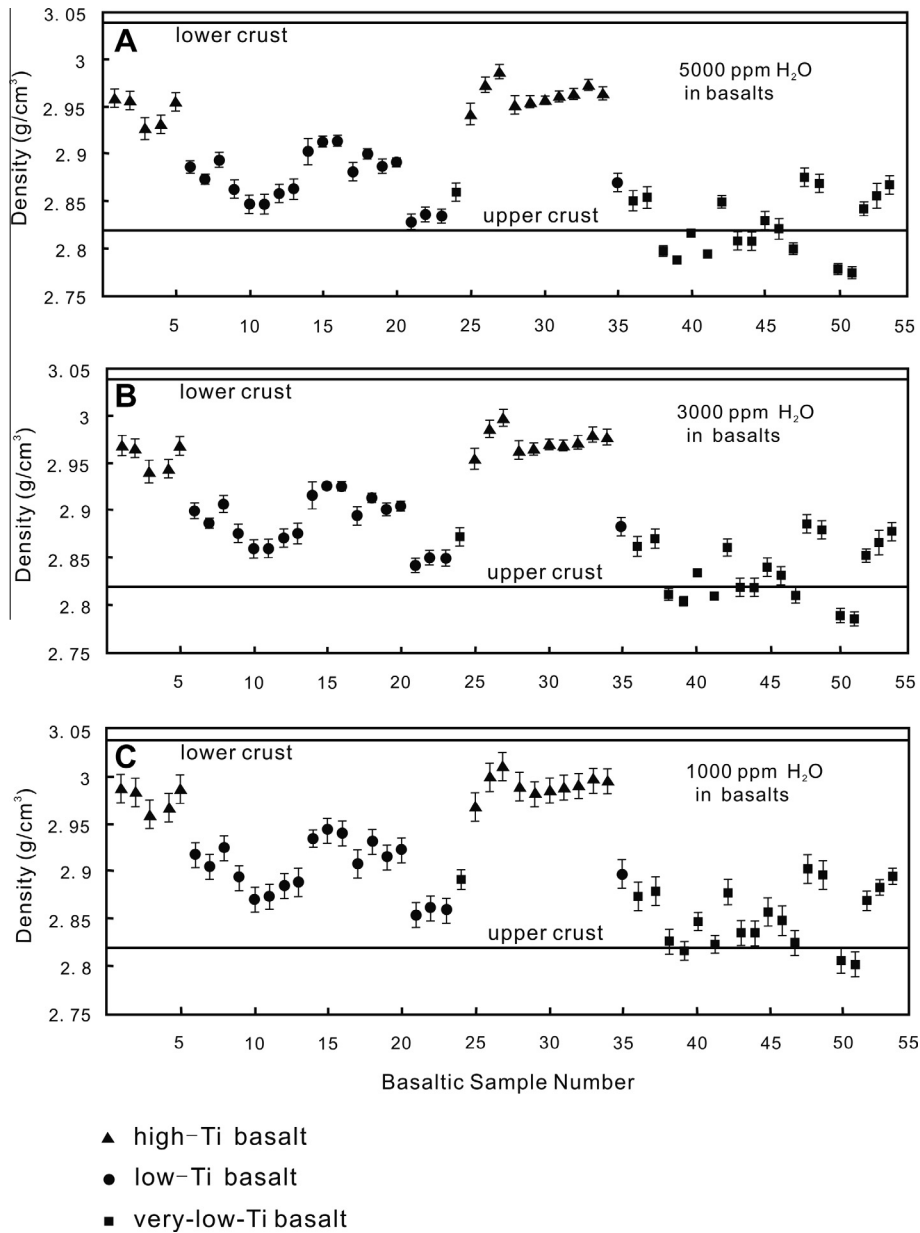


Fig. 1. Plot of liquidus density of mare basaltic magma as a function of composition and water concentration. Horizontal lines denote the density of the moon's upper anorthositic crust and lower noritic crust. (A and B) magma densities with 5000 ppm and 3000 ppm water, respectively. Several VLT basaltic magmas (sample numbers 38, 39, 41, 47, 50, 51) are less dense than the upper crust. (C) All sample densities are between the lower crust and upper crust; only samples 50 and 51 have a density lower than the upper crust.

maximum limit mare basalt can take before their density becomes lower than the upper crustal, anorthositic lid. (Fig. 1). As the results show, the very-low-Ti (VLT) basalts are the lightest, the high-Ti basalts are the heaviest, and the low-Ti basalts are intermediate. Thus, the VLT basalts are the most important for constraining the volatile concentration. In Fig. 1(C), although we note that 1000 ppm H₂O is a suitable maximum value, there are still two samples (sample 50 = 2.805 g/cm³, sample 51 = 2.798 g/cm³) with densities less than the upper crust. However, the errors of the two samples' densities are ± 0.025 g/cm³ and ± 0.026 g/cm³, respectively, so we consider 1000 ppm to be a conservative and acceptable value for what magma can take.

The average thickness of the upper crust is approximately 20 km, and the magmatic density is calculated at a 20-km pressure. However, the thickness of the upper crust varies laterally on the

moon. In a theoretical sense, by considering that magma has a unique property of ascending and abruptly stopping at any depth, our studies suggest a series of magma densities at different pressures to correspond with the magma ascent process. Our results suggest a 400 bar (8–9 km depth) pressure transition point where the density will decrease abruptly. In the model proposed Rutherford and Papale (2009), the fire-fountain eruptive process of lunar basaltic magma indicates that carbon is stable at depth and can be oxidized to C–O volatile species during their ascent to the surface. Their conclusions were insufficient and did not include water; therefore the interplay between H₂O and CO was overlooked. The results of the present study indicate that the solubility of H₂O or CO will be less in a binary system of H₂O and CO than that of a system containing one volatile species. The apparent density decline point that divides the density curve into two sections can be determined

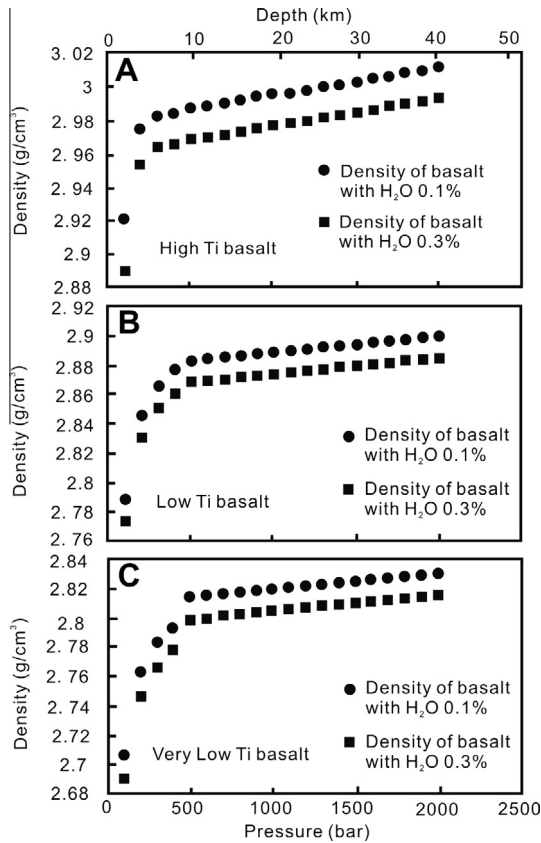


Fig. 2. Plot of liquidus density of mare basaltic magma as a function of pressure. 500 ppm C–O is supposed to occur when the magma pressure decreases to 400 bar because carbon would be oxidized at this pressure (discussed above). Three typical mare basalts, (A) high-Ti basalt (No. 1 in Fig. 1), (B) low-Ti basalt (No. 12 in Fig. 1) and (C) very-low-Ti basalt (No. 39 in Fig. 1), are calculated, and the results show that exsolved gas (mainly CO) would reduce the magma density by a large degree.

(Fig. 2). In the first section, the magma density decreases gradually, corresponding to a gradual increase in the molar volume of melt, and H₂O is dissolved in the melt under a high-pressure range (>9 km). In the second section, the magma density decreases rapidly after it breaks through a depth of approximately 9 km. The cause of this decrease is CO exsolving partially from melt, which leads to a rapid expansion in magma volume. The calculated result suggests that if H₂O and CO exist in magma at the same time, the density of the magma can be lowered to a small value. If the local crust is only 9 km or thinner, magma would have erupted on these highlands with a thin upper crust. However, lunar highlands, even some where the upper crust may be thin due to impacts, lack basalts. Thus, the most likely scenario is that the water concentration in magma melt is less than 1000 ppm, especially for other volatile species, e.g., CO.

According to Elkins and Grove (2011), hydrogen is an important volatile species in wet pre-eruptive magma. Their assumptions are based on the reaction relationship of



Which is controlled by an equilibrium constant K ,

$$K = \frac{f_{\text{H}_2\text{O}}}{f_{\text{O}_2}^{1/2} f_{\text{H}_2}} \quad (9)$$

They conclude that to keep water stable in magma, hydrogen would have to be equal to or within one order of magnitude of the abundance of water in magma under low f_{O_2} (QFM–4 log unit).

Under these circumstances, the density of magma decreases further, eventually causing the magma to erupt on the lunar highlands. If it is assumed that this process is operational and exists during magmatic upwelling, the water concentration will be constrained to a much lower value (<1000 ppm) to keep the highlands free of mare basalts.

At these levels, the samples contain high concentrations of the volatiles, which we suggest may be a consequence of deuterium impact events. Large impact objects are likely to carry water, cause mare basalts to remelt, and may bring water to the lunar rocks. Moreover, Elkins-Tanton et al. suggest that water can be held in local regions of low-temperature crust at the end of magma ocean solidification, and upwelling magma with little water could assimilate these regions, causing high water concentrations in some lunar rock samples.

5. Conclusion

- (1) Although the lunar basalts have a higher iron content under low oxygen fugacity conditions than most terrestrial basalts, such as MORB, our calculations give a constraint for the water concentration in pre-eruptive mare magma of less than 1000 ppm.
- (2) If magma contains other species of volatiles, such as C–O, S, F, H₂ or Cl₂, the water in the pre-eruptive magma would be much less than 1000 ppm due to volatiles such as CO effectively decreasing the solubility of water in silicate melt.
- (3) Other processes, e.g., large impacts or crust condensation (Elkins and Grove, 2011; Greenwood et al., 2011), may influence the water content in lunar samples. Recently, Liu et al. (2012) presented Fourier transform infrared spectroscopy and secondary ion mass spectrometry analyses of Apollo samples that imply the presence of hydroxyl formed by micrometeorite impacts. They also found that the hydrogen isotope composition of glass suggests that some of observed hydroxyl is from a solar wind source. Thus, a high water concentration may not be characteristic of a magma source region.

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