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Volatile loss during homogenization of lunar melt inclusions

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ABSTRACT

Volatile abundances in lunar mantle are critical factors to consider for constraining the model of Moon formation. Recently, the earlier understanding of a "dry" Moon has shifted to a fairly "wet" Moon due to the detection of measurable amount of H_2O in lunar volcanic glass beads, mineral grains, and olivine-hosted melt inclusions. The ongoing debate on a "dry" or "wet" Moon requires further studies on lunar melt inclusions to obtain a broader understanding of volatile abundances in the lunar mantle. One important uncertainty for lunar melt inclusion studies, however, is whether the homogenization of melt inclusions would cause volatile loss. In this study, a series of homogenization experiments were conducted on olivine-hosted melt inclusions from the sample 74220 to evaluate the possible loss of volatiles during homogenization of lunar melt inclusions. Our results suggest that significant loss of H_2O could occur even during minutes of homogenization, while F, Cl and S in the inclusions remain unaffected.

We model the trend of H_2O loss in homogenized melt inclusions by a diffusive hydrogen loss model. The model can reconcile the observed experimental data well, with a best-fit H diffusivity in accordance with diffusion data explained by the "slow" mechanism for hydrogen diffusion in olivine. Surprisingly, no significant effect for the low oxygen fugacity on the Moon is observed on the diffusive loss of hydrogen during homogenization of lunar melt inclusions under reducing conditions. Our experimental and modeling results show that diffusive H loss is negligible for melt inclusions of >25 μm radius. As our results mitigate the concern of H_2O loss during homogenization for crystalline lunar melt inclusions, we found that H_2O/Ce ratios in melt inclusions from different lunar samples vary with degree of crystallization. Such a variation is more likely due to H_2O loss on the lunar surface, while heterogeneity in their lunar mantle source is also a possibility. A similar size-dependence trend of H_2O concentrations was also observed in natural unheated melt inclusions in 74220. By comparing the trend of diffusive H loss in the natural MIs and in our homogenized MIs, the cooling rate for 74220 was estimated to be ~1 °C/s or slower.

1. Introduction

Volatile content in the primitive lunar mantle is a fundamental factor to consider for the origin of the Moon, but remains unsolved. The most widely accepted model for Moon formation is the giant impact hypothesis, in which the Moon formed by the collision between a Martian size planetesimal and the proto-earth (e.g. Canup and Asphaug, 2001). Early studies suggest strong depletion of volatile elements on the Moon, with H_2O concentration typically below detection limit, leading authors to conclude that Moon is dry (e.g. <1 ppb H_2O, Taylor et al., 2006), which was thought to be consistent with the giant impact hypothesis. Recently, however, the view of a dry Moon has been challenged by the detection of magmatic water in lunar volcanic glass beads (Saal et al., 2008, 2013; Hauri et al., 2015; Chen et al., 2015), lunar apatite (Boyce et al., 2010, 2014; McCubbin et al., 2010a, 2010b; Greenwood et al., 2011; Barnes et al., 2014; Tartese et al., 2014), olivine-hosted melt inclusions (Hauri et al., 2011, 2015; Chen et al., 2015), and lunar plagioclase from highland anorthosites (Hui et al., 2013, 2017). Olivine-hosted melt inclusions (will be referred as "MIs" hereafter) are pockets of magma trapped in olivine that provides protection on the pre-eruptive volatile content of the magma (Anderson, 1974; Sobolev, 1996; Danyushevsky et al., 2002). They are also the lunar samples where the highest H_2O concentrations were detected (up to ~1400 ppm, Hauri et al., 2011). Although the high H_2O/Ce ratios measured in 74220 indicate a mantle source containing at least 110 ppm

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H_2O (Chen et al., 2015), some authors argue that 74220 is a local anomaly unrepresentative of the entire lunar interior (Paniello et al., 2012; Albarede et al., 2013, 2015; Kato et al., 2015). Therefore, melt inclusion studies on a larger collection of lunar volcanic rocks are necessary before reaching a conclusion on volatile contents of the lunar interior. A major complication is that most lunar olivine-hosted melt inclusions are at least partially crystalline, making it necessary to homogenize the melt inclusions for precise electron microprobe (EMP) or secondary ion mass spectrometry (SIMS) analyses (e.g. Roedder and Weiblen, 1970; Bombardieri et al., 2005; Chen et al., 2015). Homogenization of the melt inclusions, however, involves heating up the olivine to 1267 to 1330 °C for at least several minutes, which might cause volatile loss from the melt inclusions, especially H_2O. One uncertainty in Chen et al. (2015), for example, is whether the relatively low H_2O/Ce ratios in the homogenized lunar MIs are due to H_2O loss during homogenization.

Loss of H_2O from olivine-hosted melt inclusions has been experimentally examined previously using terrestrial samples (e.g. Hauri, 2002; Massare et al., 2002; Portnyagin et al., 2008; Chen et al., 2011; Gaetani et al., 2012 and Bucholz et al., 2013). Hydration and homogenization experiments in these studies show that, H_2O in olivine-hosted melt inclusions can exchange with the surrounding melt in time scales of ten minutes to days. Controversy occurs, however, in terms of the apparent hydrogen diffusivities in olivine suggested by these experiments. For example, the results of Hauri (2002) and Massare et al. (2002) suggest high hydrogen diffusivities, which are in accordance with H diffusion data from Kohlstedt and Mackwell (1998). On the other hand, experiments by Portnyagin et al. (2008), Chen et al. (2011), Gaetani et al. (2012) and Bucholz et al. (2013) are supportive of the lower H diffusivities reported in Demouchy and Mackwell (2006). The range of H diffusivities in olivine hinder accurate estimation of possible H_2O loss from lunar melt inclusions during homogenization experiments. In addition, the more reducing conditions on the Moon (~IW-1, Sato, 1976; Weitz et al., 1997) mean a lower concentration of defects in olivine leading to lower diffusivity (e.g., Dohmen et al., 2007) and a higher proportion of molecular hydrogen among all hydrogen species in the melt leading to higher diffusivity (e.g. Zhang and Ni, 2010; Zhang, 2011; Hirschmann et al., 2012), which further complicate the diffusive loss rate of H_2O through olivine. In order to constrain the effect of homogenization experiments on concentrations of H_2O and other volatiles in lunar melt inclusions, we use lunar melt inclusions as the starting material. In this study, olivine-hosted melt inclusions from 74220 were homogenized under reducing conditions and compared with the un-heated ones from the same batch of samples in terms of their H_2O, F, Cl and S concentrations. The results provide crucial guidance to understand and make best use of the volatile data of homogenized lunar MIs.

2. Experimental and analytical methods

The lunar soil sample 74220, discovered at Shorty Crater during Apollo 17, was famous for its high-Ti orange glass beads. High concentrations of H_2O (up to 1410 ppm) were also first detected in olivine-hosted melt inclusions from this sample (Hauri et al., 2011). Since volatile concentrations (e.g. H_2O, F, Cl and S) in melt inclusions from 74220 are relatively well known (Hauri et al., 2011, 2015; Chen et al., 2015), olivine grains from 74220 are used in this study to experimentally understand the possible loss of volatiles during homogenization. Here we want to emphasize that melt inclusions found in 74220 are naturally glassy or mostly glassy. The purpose of the homogenization experiments are not to produce a glassy and homogenized phase for precise EMP or SIMS analyses, but to study the possible loss of volatiles during the homogenization process. Most of the olivine samples in this study are

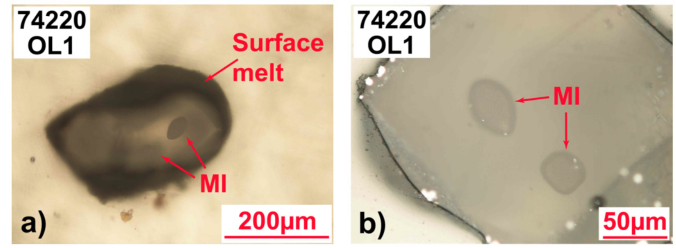

Fig. 1. Optical microscope images of an olivine with melt inclusions from 74220 a) before homogenization and b) after homogenization. The olivine grain was covered by a layer of basaltic glass when picked from 74220. Melt inclusions inside the olivine were discovered when the surface glass on one side of the olivine was carefully removed, as shown in a).

from 74220, 892, except for 74220 OldOL1 and OldOL2, which are from 74220, 871.

The 74220 soil sample was placed in a pan with ethanol, and olivine grains with melt inclusions were manually picked under an optical microscope. These olivine grains are typically ~100 µm in radius and often have a layer of basaltic glass on the surface (Fig. 1a). In order to minimize the reaction between the surface melt with the olivine during homogenization, olivine grains were gently polished before experiment to remove most of the surface glass. Melt inclusions in each olivine grain were homogenized by an individual experiment in a one-atmosphere furnace. Graphite crucibles were used for the homogenization experiments. The graphite crucible for each homogenization experiment was machined from a high-purity graphite rod (with less than 50 ppm impurities) to minimize the possibility of contamination. During homogenization, a graphite crucible containing one olivine grain was gradually inserted into the hot spot of the furnace and kept at 1330 °C for about 2 min under a constant flow of 99.9999% N_2. Oxygen fugacity in the 99.9999% N_2 gas is equivalent to NNO+1.7 at 1330 °C according to direct measurement. Inside the graphite crucible, however, measured oxygen fugacity is IW-1.9 to IW-2.6, which is slightly more reducing than the conditions on Moon (~IW-1, Sato, 1976; Weitz et al., 1997). Oxidation state in the graphite crucible is slightly below the stability field for Fo80 olivines at 1330 °C (IW-1.4, Nitsan, 1974). However, no significant reduction of the olivine grains was observed after heating due to the short experimental duration. Heating rate of the sample was constrained below 200 °C/min to prevent olivine from cracking. The gradual heating means that the effective heating duration is longer than 2 min (discussed later). Then, the graphite crucible was taken out of the furnace and quenched in water. During quench, water was kept out of the graphite crucible to avoid cracking the olivine crystal. The quench process typically took 10 to 15 seconds, except for sample 74220 OldOL1, for which a thick graphite crucible was used. The selection of experimental temperature was based on the experimentally determined liquidus of 74220 orange glasses at one bar (~1323 °C, Green et al., 1975), whereas the homogenization duration was chosen to be similar with previous studies (e.g. Chen et al., 2015). One example of the olivine-hosted melt inclusions after experiment is shown in Fig. 1b. After homogenization, each olivine grain was polished separately to expose the melt inclusions inside and loaded into an indium mount for EMP and SIMS analyses. Besides the homogenized melt inclusions from 74220, four unheated MIs from the same batch of sample were also analyzed for a comparison.

Major element compositions of olivines and melt inclusions were analyzed by a CAMECA SX-100 electron microprobe at the University of Michigan, with a 15 kV and 10 nA focused beam. Counting times are 40 s for Si, Al, Ca and Cr, 30 s for Na, Mg, Fe and K, and 20 s for Ti and Mn. Na was the first element an-