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Cooling rates of lunar orange glass beads

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ABSTRACT

It is widely accepted that the Apollo 17 orange glass beads are of volcanic origin. The degree of degassing of the glass beads depends on their cooling rates, so the estimation of volatile contents in the parental magmas of these lunar pyroclastic glasses also depends on the cooling rates. The cooling rate can be estimated using the calorimetric properties of the glass across the glass transition. In this study, a series of heat capacity measurements were carried out on hand-picked lunar volcanic orange glass beads during several cycles of heating to temperatures above their glass transition using a differential scanning calorimeter. The cooling rate of orange glass beads (sample 74220,867) was calculated to be 101 K/min using the correlation between glass cooling rates and fictive temperatures estimated from their heat capacity–temperature paths. This cooling rate is close to the lower end of the range that best fits the diffusion profiles of several volatile species in the glass beads, and at the upper end of the cooling-rate range recorded in glasses quenched subaerially on Earth. The cooling rate is likely to be controlled by the cooling environment (cooling medium) such that the lunar volcanic glass beads could have been cooled in a gaseous medium released from volcanic eruptions on the Moon, but not during "free flight" in vacuum. The existence of a gas medium suggests, in turn, that there may have been at least a short-lived or episodic atmosphere on the early Moon at around 3.5 Ga.

1. Introduction

Mare magmas erupted ~3.2–3.8 Ga ago on the Moon's surface as large flood basalts and/or fire fountaining (e.g., Shearer et al., 2006), the latter evidenced by the presence of volcanic glass beads resulting from rapid cooling of lunar magma. Magma cooling rate is a major factor controlling the solidification process, and one that could also affect its final volatile contents. The analyses of some of Apollo glass beads provided evidence that lunar mantle does contain water (e.g., Saal et al., 2008; Füri et al., 2014; Chen et al., 2015). The best estimates of water contents in the magma before eruption have been recalculated by fitting diffusion profiles in the lunar volcanic green (Apollo 15) and orange (Apollo 17) glass beads with cooling rates between 120 to 180 K/min used in the modeling (Saal et al., 2008). However, cooling rates of lunar volcanic glasses estimated from laboratory simulations and theoretical calculations can differ by several orders of magnitude from <60 to >6000 K/min (Arndt et al., 1979; Uhlmann et al., 1981; Fang et al., 1983; Arndt et al., 1984; Birnie and Dyar, 1986; Ni et al., 2017). This large range partially stems from the different cooling environments considered in the studies. Laboratory experiments have demonstrated that cooling environment (ambient temperature, cooling media, etc.) can affect the cooling rate dramatically (Xu and Zhang, 2002). However, it is difficult to infer the exact volcanic environment on the lunar surface when the volcanic glass beads formed with our current knowledge. It is very possible that the environments used for estimating cooling rates of lunar volcanic glass beads are different from the real situation on the early Moon (Uhlmann et al., 1974; Arndt et al., 1979; Needham and Kring, 2017; Saxena et al., 2017). Therefore, it is important to estimate the cooling rates directly from the volcanic glass beads returned by the Apollo missions.

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The cooling rates of glasses can be inferred from their heat capacity (C_p) curves measured during heating (e.g., Moynihan et al., 1976). This method does not require the knowledge of the environment in which the glass formed. The formation of glass via cooling from a silicate melt occurs at the glass transition, across which the structure of the melt is frozen into that of the glass. The glass transition is a kinetic process and the glass transition temperature depends on the cooling rate (Dingwell and Webb, 1990). The glass records the kinetics of the glass transition during cooling and this can be used to infer the cooling rate of the melt across the glass transition. The enthalpy relaxation geospeedometer, involving measuring the heat capacity as a function of temperature (when the quenched glass is heated in a differential scanning calorimeter to a temperature above its glass transition), is often used to determine the glass cooling rate (Wilding et al., 1995). Uhlmann et al. (1974) carried out heat capacity measurements on Apollo 17 orange glass beads and determined their cooling rate to be >320 K/min. However, each heat capacity curve in the glass transition interval (~890–980 K) was modeled with only 10 data points obtained from calorimeter during heating (Uhlmann et al., 1974). Now, in a state-of-the-art differential scanning calorimeter, heat capacities can be continuously measured. Furthermore, no quantitative method was applied to calculate the cooling rate of orange glass beads, and thus the previously measured cooling rate of >320 K/min was only semi-quantitative at best (Uhlmann et al., 1974).

The enthalpy relaxation geospeedometer has been widely used to calculate the cooling rates of natural silicate glasses that formed in different terrestrial environments, such as submarine (Wilding et al., 2000; Potuzak et al., 2008; Nichols et al., 2009), subglacial (Wilding et al., 2004), subaerial (Wilding et al., 1995, 1996a; Gottsmann and Dingwell, 2001, 2002), and even during impact events (Wilding et al., 1996b). The cooling rates of these natural glasses vary from $\sim 10^{-3}$ up to 10^{7} K/min (Gottsmann and Dingwell, 2002; Potuzak et al., 2008). Two methods have been developed to infer glass cooling rates from the heat capacity curves determined during heating using a differential scanning calorimeter: The Tool–Narayanaswamy enthalpy relaxation (T–N) geospeedometer (e.g., Tool, 1946; Narayanaswamy, 1971, 1988; DeBolt et al., 1976; Wilding et al., 1995), and the combined Moynihan–Yue area-matching approach (e.g., Moynihan et al., 1976; Yue et al., 2002; Potuzak et al., 2008; Nichols et al., 2009). The latter method can be applied to glass that cooled at any rate, but the T–N geospeedometer may be unable to fit heating C_p curves of rapidly quenched glasses (e.g., Potuzak et al., 2008; Nichols et al., 2009).

In this study, we report heat capacity measurements on the Apollo 17 orange glass beads. The results will be used to estimate the cooling rate of glass beads using the combined Moynihan–Yue area-matching approach (e.g., Moynihan et al., 1976). The calculated cooling rate of the glass beads is a key parameter in estimating the initial water contents of the glass-forming melts prior to eruption based on water concentration profiles in glass beads (Saal et al., 2008), which has an influence over the lunar mantle melting temperature, magma crystallization temperature and the style of volcanic eruption. Furthermore, the data can allow us to make some inferences about the lunar surface environment during the volcanic eruptions and to understand post-depositional processes such as welding, vesiculation, degassing and crystallization, which are in large part controlled by the thermal evolution of the glass within the volcanic deposit. Finally, the atmospheric conditions on the early Moon may have been influenced by volcanic eruptions (e.g., Needham and Kring, 2017; Neal, 2017) and our results have implications for the lunar atmosphere at the time of volcanic eruption.

Table 1
Chemical compositions of different groups of the Apollo 15 green glass beads (15421) and the Apollo 17 orange glass beads (74220).

	Green A	Green B	Green C	Green D	Green E	74220
SiO_2	45.5	46.0	48.0	45.1	45.2	38.5
TiO_2	0.38	0.40	0.26	0.41	0.43	9.12
Al_2O_3	7.75	7.92	7.74	7.43	7.4	5.8
FeO	19.7	19.1	16.5	20.3	19.8	22.9
MnO	0.22	n.a.	0.19	0.22	0.22	n.a.
MgO	17.2	17.2	18.2	17.6	18.3	14.9
CaO	8.65	8.75	8.57	8.43	8.15	7.40
Na_2O	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
K_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr_2O_3	0.56	0.55	0.57	0.55	0.54	0.69
total	99.96	99.92	100.03	100.04	100.08	99.68

n.a. = not analyzed; n.d. = not detected. The compositions starting with "Green" are for different groups of the Apollo 15 green glass beads. The data presented here were compiled by Delano (1986).

2. Lunar volcanic glass beads

Lunar volcanic glass beads from Apollo 17 orange soil sample 74220,867 were used in this study. Various scenarios have been proposed to explain the formation of these glass beads (Roedder and Weiblen, 1973; Heiken et al., 1974; Meyer et al., 1975). The surfaces of the glass beads are coated by thin films composed of Zn, Ga, Pb, Cu, Tl, S, F, Cl, and other volatile elements (Meyer et al., 1975). It has been proposed that these elements were condensed as a sublimate on the bead surfaces during lava fountain eruptions (e.g., Meyer et al., 1975; Heiken and McKay, 1977; Reed et al., 1977; Clanton et al., 1978). This suggests that the Apollo 17 orange glass beads were produced by gas-charged fire fountain volcanic eruptions (Heiken et al., 1974; Meyer et al., 1975; Delano, 1986; Rutherford and Papale, 2009). A brief summary of sample characterization of 74220, from which sample 74220,867 was separated, is presented here.

Orange soil 74220, collected from the rim of Shorty Crater in the Taurus–Littrow region during the Apollo 17 mission, contains mainly orange glass spherules ranging from <1 μm to ~1 mm and broken fragments of the spherules, with minor amounts of basalt fragments (Heiken et al., 1974). Some of the orange glass beads are partially crystallized. The chemical compositions of the 74220 orange glass beads are homogeneous (Table 1, Heiken et al., 1974; Delano, 1986), as are their textures (Heiken et al., 1974). Compared with the Apollo 15 green glass beads, the 74220 orange glass beads have higher TiO_2 and FeO contents, but lower SiO_2, Al_2O_3, MgO, and CaO contents (Table 1; Delano, 1986). The ^{40}Ar–^{39}Ar age has been measured on five single orange glass beads from soil 74220, which gave a preferred age of 3.60 ± 0.04 Ga for their formation (Huneke, 1978). This is at the lower end of ^{87}Rb–^{87}Sr age range of 3.64–3.84 Ga measured in the Apollo 17 mare basalts (Nyquist, 1977). However, it is older than the ^{207}Pb–^{206}Pb age of 3.48 ± 0.03 Ga for 74220 (Tera and Wasserburg, 1976). The ages of orange glass beads are within error of the Apollo 15 green glass beads, which also resulted from lava fountain eruption (e.g., Chou et al., 1975; Heiken et al., 1974). A ^{207}Pb–^{206}Pb age for the interior of the green glass beads is 3.41 ± 0.33 Ga (Tatsumoto et al., 1987), and ^{40}Ar–^{39}Ar ages for the Groups A and D green glass beads are 3.41 ± 0.12 Ga and 3.35 ± 0.18 Ga respectively (Spangler et al., 1984).

3. Heat capacity measurements

Samples of the lunar soil 74220,867 were immersed in ethanol and individual intact and broken transparent glass beads were hand-picked under a binocular microscope. The selected grains are typically larger than 40 μm as these could be handled with tweezers. Consequently, the coarse fraction of the glass grains is overrep-