ESCAPE FROM A TRANSIENT ROCK VAPOR ATMOSPHERE AS THE MECHANISM FOR FRACTIONATION OF THE MOON'S MODERATELY VOLATILE ELEMENTS.

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Introduction: Isotope ratios of moderately volatile elements (MVEs, defined as elements with 50% condensation temperatures of 800 to 1290K) are clues to the processes attending the giant impact that formed the Moon and/or its immediate aftermath. Previous studies of MVE isotope ratios, including those for K, Zn, and Rb, have demonstrated that the Moon has distinctive isotope ratios of these elements compared to those of the Earth [e.g., 1-4]. Thus, it has been proposed that MVE fractionation should have occurred shortly before or during crystallization of the near-surface molten rock comprising the lunar magma ocean (LMO) that existed immediately after coalescence of the Moon.

In order to extract additional information about the early history of the Moon, we are investigating the causes of isotopic fractionation of MVEs in mare basalts. We focus here on the evolution of the LMO and rock-vapor atmosphere produced by its evaporation. The formation of a magma ocean subsequent to the accretion of the Moon almost certainly occurred, making the events investigated here inevitable. We use the fractionation of K isotopes as a test case and analyze the chemical and isotopic influences of the rock-vapor atmosphere produced by evaporation of the LMO. Our results show that instead of LMO evaporation alone, the removal of the vapor beyond the sonic point should have produced an atmosphere enriched in heavy isotopes. Vapor-melt isotopic exchange of isotopes can efficiently shift the MVE isotopic composition of the LMO to the present values before complete solidification of the LMO surface.

LMO evaporation: We applied Equation (9) in [5] to estimate the net evaporation isotopic fractionation for MVEs. For potassium in the Moon, the net fractionation factor can be calculated as a function of ambient background pressure. At 1800K with increasing background pressure, the net evaporation fractionation factors for $^{41}K/^{39}K$ ascend rapidly from the value of free evaporation to equilibrium (near unity) where P $>10^{-9}$ bar. The results illustrate that the crucial parameter that controlled MVE isotope fractionation factors attending evaporation was the pressure of the rock vapor atmosphere above the LMO, which can be estimated based on the structure of the atmosphere.

We simulate the composition the rock vapor atmosphere produced from LMO evaporation by modifying the IDL+Fortran code described by [9] to expand the applicable composition space from the reference CMAS system to one that includes MVEs. The evaporative flux of metal M compared to that for Mg is

$$\frac{J_M}{J_{Mg}} = \frac{x_{MO_x}^{melt}\gamma_{MO_x}^{melt}}{x_{MgO}^{melt}\gamma_{MgO}^{melt}} \sqrt{\frac{m_{Mg}}{m_M}} \exp\left(\frac{\Delta\hat{G}_{MgO\to Mg+1/2O_2}^{\circ} - \Delta\hat{G}_{MO_x\to M+1/2xO_2}^{\circ}}{RT}\right) P_{O_2}^{(1/2)(1-x)}$$

where the dependence on the partial pressure of O_2 results in a modest pressure-dependence on the flux of alkalis relative to Mg. Based on this relatively Na-depleted initial composition, Na is the dominant species in the vapor for melt evaporation temperatures from the solidus to $\leq$ 2000K. Together with our model of Moon's thermal history, here we confine our calculations to T_{LMO}=1800K to 2000K where the silicate is largely molten.

By equating the surface-integrated evaporative flux from the surface LMO with the surface-integrated gas loss flux beyond the critical point, we establish plausible *P-T* profiles with altitude for the steady-state atmosphere above the LMO corresponding to different LMO temperatures and Earth-Moon distances. For $a_{Earth-Moon}$ = 20000 km to 70000 km (5.2% to 18.2% of the present Earth-Moon distance), the surface steady-state pressure for LMO evaporation varies from 10^{-8} to ~10^{-7} bar. With such pressures, LMO evaporation cannot generate resolvable isotope fractionation for K (and other MVEs). Thus an alternative to simple evaporation is required to explain the high $^{41}K/^{39}K$ of lunar samples. This mechanism is escape from the atmosphere under the right conditions.

Structure of the rock-vapor atmosphere: We show that the rock-vapor atmosphere above the LMO was optically thin and that the high specific entropy of the hot vapor made it free of condensates. It was composed of a lower adiabatic troposphere, an overlying isothermal stratosphere above the tropopause, and a bounding escape layer where the gas leaves the Moon by hydrodynamic escape [6]. The critical radius defining the threshold for hydrodynamic escape and the influence of the nearby Earth is determined based on the equations of mass and momentum conservation for any point located between Earth and Moon. We find that the critical radius for escape depends on the Earth-Moon distance. As shown in Figure 1A, a short Earth-Moon distance lowers the altitude of the critical radius. The recession of the early Moon would extend the Moon's Hill sphere and therefore diminish the effects from the Earth, causing the critical radius to approach the transonic radius for an isolated Moon.

Isotopic fractionation in the atmosphere: The near equal fluxes of MVE molecules from melt to vapor and from vapor to melt that arises as a result of evaporation into a steady-state rock vapor atmosphere allows for isotopic exchange between melt and vapor. Therefore, if isotope fractionation is present in the atmosphere, this fractionation could have been imparted to the partially molten surface of the Moon by melt-vapor exchange.

In principle two mechanisms may fractionate K isotopes in the rock vapor atmosphere, hydrodynamic escape at the critical radius and gravitational settling inside the isothermal stratosphere. In a Na-rich vapor, hydrodynamic escape cannot result in a resolvable K isotopic fractionation [5]. On the other hand, in an atmosphere in hydrostatic equilibrium, gaseous species above the convective troposphere are distributed according to their scale heights. This leads to the prospect of large isotope fractionations in the isothermal stratosphere below the critical radius. The number density for potassium isotopes in the vapor as a function of altitude in the stratosphere can be estimated using

$$n_{j_K} = n_{j_K}^T \exp\left(-z / H_{j_K}\right)$$

where z is the altitude above the tropopause, n_{jK} is number density for potassium isotope j (39 or 41), and the scale height is evaluated continuously due to the variability in $g(z)$. Our calculated K elemental and isotopic fractionation effects in the escaped vapor due to gravitational settling are shown in Figure 1B and 1C. The escaped vapor enriched in light isotopes results in an isotopically heavy atmosphere.

We estimate the timescale to reproduce the present isotopic composition observed for lunar samples due to exchange between the fractionated atmosphere and the LMO by using a two-box model composed of a well-mixed magma ocean and overlying rock vapor atmosphere. As an example, with $a_{Earth-Moon} = 50000$ km and $T_{LMO} = 1800$ K, the Moon δ^{41}K is raised to the observed value of 0.4 ‰ in about 160 years. The corresponding fractional loss of K is just 2.3 parts per thousand. Similarly, for other MVEs, we can obtain the isotopic value of Rb and Zn observed in lunar samples within ~200 years by our model. This timescale is consistent with the longevity of widespread LMO estimated from our thermal model. In addition, such a short timescale prohibits any resolvable isotopic fractionation of rock-forming elements, such as Mg and Si, which is consistent with previous observations [e.g., 7,8]. The vapor escape mechanism also precludes heavy isotope enrichment for Sn and Cr isotopes.

We propose that vapor escape from a thin rock-vapor atmosphere can be an efficient way to fractionate the isotopes of MVEs in the Moon. Exchange between the fractionated rock-vapor atmosphere and lunar melt resulted in the isotope fractionation observed in lunar samples. Moreover, atmospheric escape caused an apparent decoupling between isotope fractionation and concentrations for MVEs.
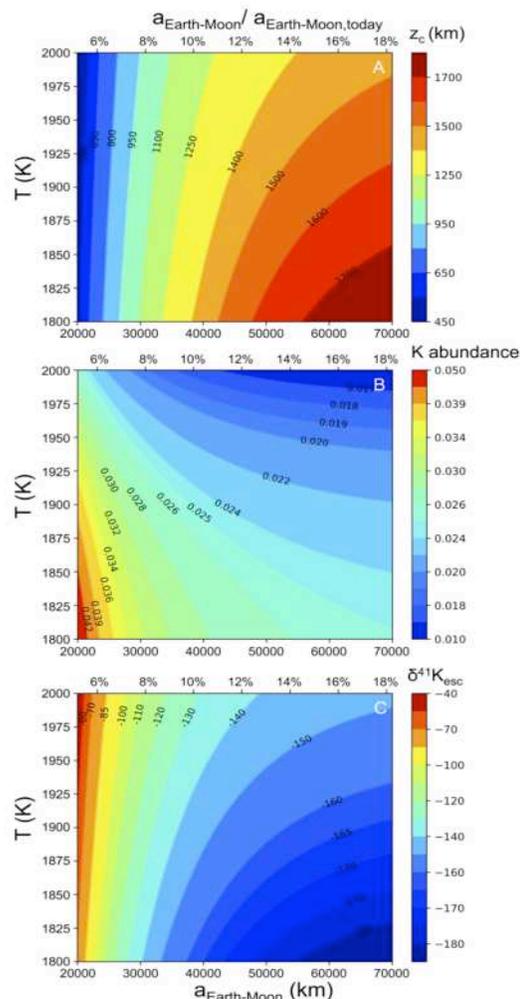

Fig. 1. The altitude of critical point above the surface of the Moon (A) associated with LMO temperature and Earth-Moon distance, and corresponding potassium mixing ratio (B) and isotopic composition (C) of the escaped vapor.

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