Reports

Heating of Basalts with a Carbon Dioxide Laser

Abstract. *Basalts heated strongly with focused infrared laser radiation vaporized and splattered. Electron microprobe analyses of condensate, ejecta, and residue show strong vapor fractionation trends which, for some elements, are different from what would be expected theoretically and from previously reported data on more siliceous materials. It appears that solution effects can account for these differences. Heating of materials by a powerful focused laser beam for the purpose of study of vapor fractionation is a convenient technique that is more versatile than previous methods such as heating in solar or arc image furnaces.*

This study was originally undertaken in an attempt to explain the high titanium and low sodium contents of the lunar surface layers: analyses obtained by the Surveyor 5 spacecraft indicated basaltic compositions for the surface of the moon at Mare Tranquillitatis but showed anomalously high contents of titanium and low contents of sodium (*1*). We hypothesized that heating of the parent rocks to high temperatures by meteorite bombardment or other processes and resulting vapor fractionation could possibly account for the observed high content of relatively involatile titanium and the low content of relatively volatile sodium. Work on returned lunar samples indicates, however, that not only the impact-produced lunar regolith (loose surface material) but also the basalts are rich in titanium and low in sodium (*2, 3*). Hence, other processes must be responsible for the bulk of the observed elemental abundances (unless large-scale vapor fractionation occurred before or during the formation of the basalts at least 3.6 billion years ago, this being the age of the rock).

Although the experimental results of this study apparently are of little help in interpreting the origin and history of the lunar surface layer, they are of general interest because of several novel approaches to the study of vapor fractionation. In the past, much of the experimental work dealing with vapor fractionation of geologically important systems was carried out with materials comparatively rich in silica and under oxidizing conditions. In particular, significant work was done with starting materials of tektite composition (SiO_2 ~ 75 percent by weight) in solar furnaces (*4*). We report here the results of volatilization from molten basalts (SiO_2 ~ 40 to 50 percent by weight) heated strongly with a focused infrared laser beam. It is the purpose of this work (i) to study vapor fractionation of comparatively SiO_2-poor materials in inert atmospheres rather than under oxidizing conditions (air) at temperatures higher than previously attained; (ii) to investigate vapor fractionation of mineralogically and chemically complex materials such as basalts, and to study possible solution effects in the melt which may influence vaporization; (iii) to study the chemistry and, hence, fractionation trends in all materials produced in these experiments, namely, highly volatile condensate, ejected material, and residual glass; and (iv) to explore the feasibility of a focused, continuous laser beam to heat materials to high temperatures for the purpose of studying vapor fractionation.

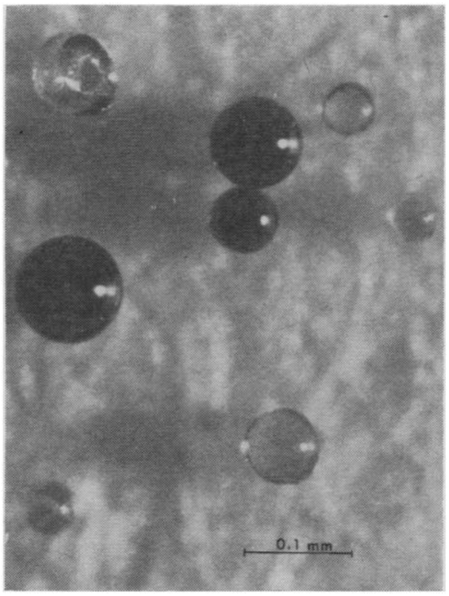

Fig. 1. Ejected glass spherules produced by laser heating of Hawaiian basalt (*5*). Although spherules pictured were made from one and the same rock, their colors range from almost colorless to brown and almost black.

In the study reported here two well-characterized Hawaiian basalts (grain sizes seldom exceeded 300 μm) (*5*) were heated by a continuous CO_2 laser (*6*) ($\lambda = 10.6\ \mu$m) focused to a ~ 1-mm spot with a beam power of approximately 200 watts. The beam was directed perpendicular to the surface of the sample. Basalt slabs about 3 by 1.5 by 0.2 cm were placed vertically on a plate and an inverted petri dish was suspended about 3 cm above the sample to catch some of the condensed vapor. The entire assembly was placed inside a plastic bag which also enclosed the front window of the laser. As much air as possible was squeezed out of the bag which was then purged with a strong continuous stream of pure helium. The laser was not turned on until the enclosure had been flushed for at least 30 minutes.

When heating began, a pool of homogenized molten basalt 2 to 3 mm in diameter formed. The initial volatilization at any one spot on the slab was vigorous, forming a horizontal plume 3 to 5 cm long. After about 1 minute the volatilization slowed significantly, giving a shorter plume which was bent to the vertical by convective currents. After about 3 minutes a very marked decrease in the rate of volatilization occurred. The slabs were moved horizontally in the beam in order to volatilize the top portion. Successive volumes were volatilized until most of the original slab had been heated. Pyrometric measurements indicated apparent initial temperatures at the focus in the range of 3200° to 3300°K; the apparent temperature decreased later to approximately 2700°K.

Three kinds of materials were recovered: (i) a white fluffy powder which condensed on both the upper dish and the lower plate (x-ray powder patterns of this material indicate that it is amorphous); (ii) a black glass, an essentially involatile residue; and (iii) glass spherules which splattered from the basalt and which collected on the bottom plate during the early vigorous vaporization. Most of the spherules range in size from 10 to 100 μm (Fig. 1) and, in one and the same experiment, vary from almost colorless to a very dark golden brown. Morphologically and in color they are remarkably similar to spherules found in the lunar fines and breccias [see figure 12 in (*2*)].

Polished sections of the ejected glass

spherules and the residual glass were prepared. The condensate was pressed into pills with flat and comparatively smooth surfaces and analyzed without further preparation. We then made electron microprobe analyses for ten elements in the condensate, glass spherules, and residual glass, using an electron microscope x-ray analyzer (*7*) and employing chemically analyzed homogeneous basalt glasses as standards. Corrections were made for drift, dead time, and background. Because the chemical compositions of the standards and samples were similar, corrections for mass absorption, secondary fluorescence, and atomic number were found to be unnecessary. Further details of the analytical technique are given in (*8*).

Analyses expressed as oxides (iron was arbitrarily calculated as ferrous iron) are plotted in Fig. 2 and are compared to the bulk chemical analyses of the respective original basalts (*5*). Data are presented for two different starting materials, namely, basalt C-135 (Fig. 2a) and basalt C-141 (Fig. 2b), which differ in composition: C-135 is lower in SiO_2, Al_2O_3, Na_2O, and K_2O but higher in TiO_2, FeO, MgO, and CaO. Electron microprobe data presented in Fig. 2 are averages of the following numbers of spot analyses: 30 analyses of three spherules from C-135, and 170 analyses of 11 spherules from C-141; 50 analyses of residual glass from C-135 and 70 analyses of residual glass from C-141. Analysis of the alkali-rich condensate was difficult; even at low currents, volatilization was caused by the electron beam. We therefore analyzed this material by using a low current (~ 0.01 μa), a large beam (~ 200 μm in diameter), and an exposure time of the sample to the electron beam limited to 1 second. In spite of these precautions, the sums of the individual analyses of condensate were ~ 94 percent by weight. Therefore, for presentation in Fig. 2, all analyses of condensate were recalculated to 100 percent.

Table 1. Calculated partial pressures of species vaporized from a basalt at 3000°K.

p_s (atm)	Species
>1	Na, NaO, K, KO, PO
10^{-2}–1	SiO, SiO_2, Fe, FeO, Mg($p_{O_2} = 0.1$ atm)
$<10^{-2}$	Al, AlO, Al_2O, Ca, CaO, Mg($p_{O_2} = 1.0$ atm), MgO, Ti, TiO, TiO_2, Zr, ZrO, ZrO_2

Variations in composition between individual spherules ejected from a given parent material, and variations from spot to spot on the condensate, residual glass, and glass spherules are small. For example, standard deviations for averages of 15 spot analyses each on 11 spherules made from C-141 are as follows (in percentage of amounts present): SiO_2, ± 0.6; Al_2O_3, ± 0.5; TiO_2, ± 5; FeO, ± 2.6; MgO, ± 0.8; CaO, ± 5; Na_2O, ± 2; and K_2O, ± 7.

Figure 2 indicates that fractionation trends for the different starting materials C-135 and C-141 are similar. In comparison to the original basalt composition, the condensate is enriched in the relatively volatile oxides SiO_2, Na_2O, K_2O, and P_2O_5 and depleted in the relatively nonvolatile oxides Al_2O_3, FeO, CaO, MgO, and TiO_2. The amounts of Al_2O_3, CaO, and MgO are sometimes lowered 10- to 100-fold. On the other hand, the ejected glass spherules are depleted in the relatively volatile oxides SiO_2, Na_2O, K_2O, and P_2O_5 and enriched in the relatively nonvolatile oxides Al_2O_3, FeO, CaO, MgO, and TiO_2 (*9*). Similar trends are found for the residual glass, but the changes in composition are not as pronounced (*10*). In short, the data indicate that the oxides of Na, K, and P are very volatile, the oxides of Si and Fe are moderately volatile, and the oxides of Al, Ti, Ca, and Mg are relatively involatile.

These relative volatilities reflect the interplay of several factors. The primary factor is the relative volatility of the pure unmixed oxides. When the vapor species have a different stoichiom-

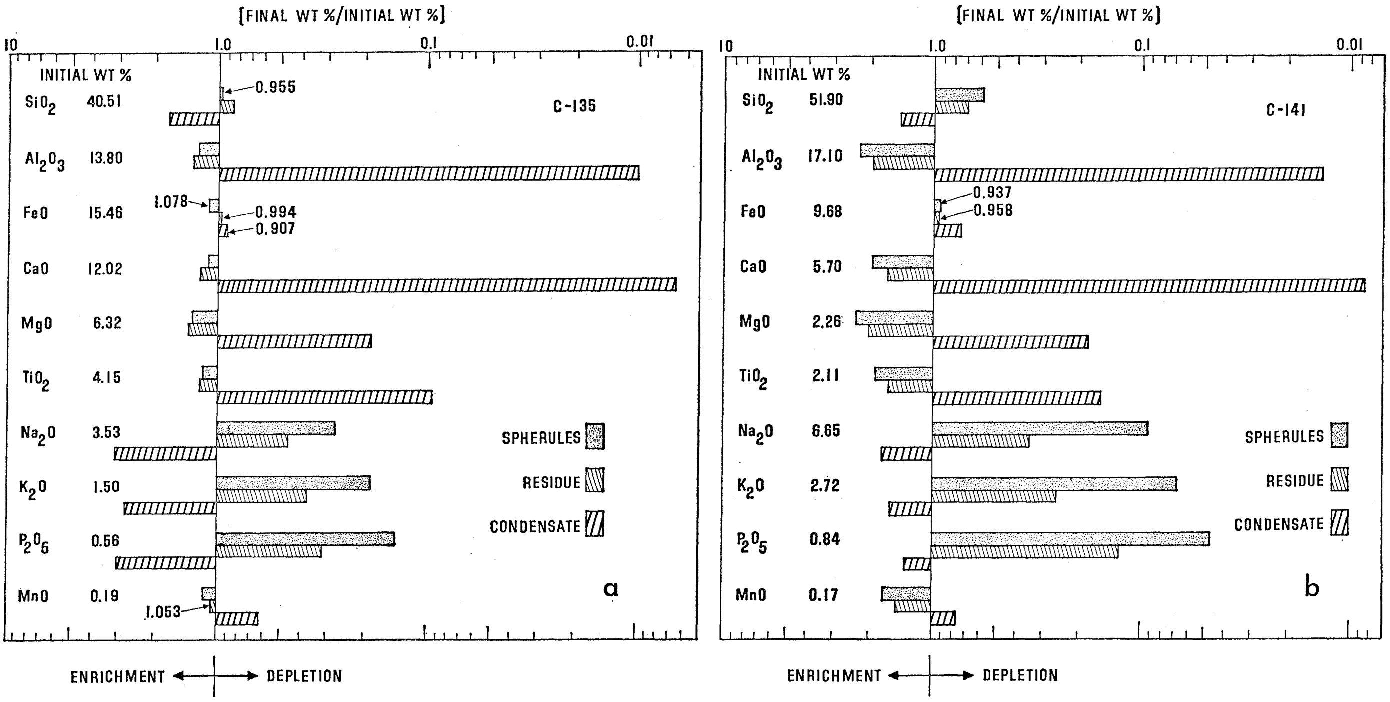

Fig. 2. Ratios of weight percentages of ten elements in condensate, ejected glass spherules, and residual glass produced by laser heating to the weight percentages of the same ten elements in the original Hawaiian basalts (a) C-135 and (b) C-141; SiO_2, Na_2O, K_2O, and P_2O_5 are comparatively volatile and are enriched in the powdery condensate and depleted in the ejected glass spherules and the residual glass; Al_2O_3, FeO, CaO, MgO, and TiO_2 are relatively involatile and are depleted in the condensate and enriched in the ejected glass spherules and the residual glass (*9*).

etry from that of the compound being volatilized, the volatility is influenced by the ambient partial pressures of oxygen which are set by the materials being volatilized. If the solutions were ideal, knowledge of these pressures would permit calculations of relative volatilities. However, a second important factor, namely, the interactions of compounds with the solution (these interactions are characterized by the individual activity coefficients γ), also influences relative volatilities. The stronger the interaction (that is, the lower the activity coefficient), the lower the relative volatility of a given component.

Equilibrium thermodynamic data (*11*) indicate that the partial pressure of oxygen, p_{O_2}, above a typical basalt at 3000°K is initially greater than 1 atm and is set by the volatilization of alkali oxides and the incongruent decomposition of TiO_2 which reduces the average valence state of Ti from +4. As volatilization proceeds, p_{O_2} decreases as the alkali content of the melt decreases and as the melt becomes more reduced. The lower limit of p_{O_2} is fixed by dissociations involving SiO_2, which is a major constituent. If the activity coefficient of SiO_2 is about 0.5, then $p_{O_2} \cong 0.1$ atm. Consequently, the ambient partial pressure of oxygen for the volatilization of the basalt lies largely between 0.1 and 1.0 atm. The partial pressures of the important species, p_s, produced in the vaporization of the pure components of the basalt at 3000°K exposed to oxygen at partial pressures of 0.1 to 1.0 atm are calculated from available data (*11*) and presented in Table 1.

If all components exhibited ideal solution behavior, then relative volatilities from solution would be governed by the partial pressures of these species. Thus the volatilities of Al_2O_3, CaO, TiO_2, and ZrO_2 are low; constituents such as Na_2O and K_2O are very volatile (unless solution effects predominate, as will be discussed below); and SiO_2, FeO, and MgO are moderately volatile. The calculated volatilities of all these oxides except MgO, which is only slightly less volatile than FeO, are in consonance with our experimental results. These conclusions depend, of course, on the accuracy and completeness of available thermodynamic data and on the validity of extrapolating from these equilibrium data to the transient and presumably nonequilibrium processes encountered in the present laser vaporization experiments.

The relative involatility of MgO that we observed as well as the surprisingly low volatilities of Na_2O in glasses of tektite composition under oxidizing conditions (*4*) can be rationalized in terms of solution chemistry. The relative deviations from ideal solution behavior can be gauged from simpler systems. For example, at 1900°K FeO behaves almost ideally (that is, $\gamma \cong 1$) in FeO-SiO_2 binary mixtures, whereas MgO interacts strongly (that is, $\gamma \ll 1$) with SiO_2. The interactions of MgO with the solvent increase as the concentration of "acidic" components such as SiO_2, Al_2O_3, and TiO_2 (*11*) increases; consequently, the relative activity and volatility of MgO decrease in more "acidic" media. However, "acidic" components have a relatively weak interaction with FeO. Thus, solution effects lower the volatility of MgO somewhat and increase the small difference in volatility between MgO and FeO.

The importance of solution effects is further illustrated in the case of Na_2O, which is less volatile in air than SiO_2 in glasses of tektite composition (*4*). This striking phenomenon is a result of the very strong interactions of Na_2O with "acidic" melts. The free energy of solution of Na_2O in SiO_2 at the eutectic between $Na_2Si_2O_5$ and SiO_2 at 1062°K and 74 percent (by weight) SiO_2 is −57 kcal/mole. Even at 3000°K such a negative free energy of solution corresponds to a decrease in the volatility of sodium by a factor of 100. This factor indicates that the relative volatility of sodium is close to that of silica at this composition. The relative volatility of Na_2O would be expected to increase at lower SiO_2 contents, as is apparent from measurements depicted in Fig. 2. At higher SiO_2 contents the relative volatility of Na_2O would be expected to decrease, as shown in earlier measurements (*4*). Likewise, similar but stronger solution interactions decrease the relative volatilities of K_2O. Other involatile constituents such as CaO, SrO, and BaO interact strongly in "acidic" melts, and this interaction reduces their already low volatility below expectations for an ideal solution.

The results of the study reported here may be summarized as follows. (i) Vapor fractionation trends observed involving inert atmospheres, very high temperatures, and relatively SiO_2-poor materials such as basalts are in general agreement with calculated volatilities and data obtained previously at lower temperatures, in air, and for more SiO_2-rich materials of textite composition (*4*). Notable exceptions are the higher volatility of sodium and the lower volatility of magnesium observed in our experiments. It is suggested that solution effects are responsible for these differences. (ii) Three types of materials were produced, thus making possible a study of vapor fractionation trends in the highly volatile, condensed material, the spalled glass spherules, and the residual glass. (iii) We have shown that a focused high-energy continuous laser beam used in the experimental configuration described herein is a valuable new tool in the study of vapor fractionation and high-temperature chemistry (*12*). (iv) Since Apollo 11 lunar glass spherules and fragments do not show pronounced vapor fractionation trends for the elements measured (*3*), we concluded that these glasses were heated either very briefly or at much lower temperatures (or both) than the basalts in our experiments.

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9. Contents of FeO in all materials derived from C-141 are low. This discrepancy is probably due to analytical error, either in the electron microprobe or, possibly, the wet chemical analysis.
10. It should be noted from Fig. 2, a and b, that in C-135 the oxides of Al, Ca, Mg, and Ti are more enriched in the residual glass than in the spherules, whereas in C-141 the reverse is true; that is, these same oxides are more enriched in the spherules than in the residue. This inversion of the order of enrichment does not seem to be due to analytical errors. It is likely that the two sets of spherules splattered from the parent melts after volatilization had progressed to differing degrees; however, there is the possibility that the relatively small number of spherules analyzed, particularly in C-135, were not truly representative of the ejected material.
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Where Was the Moon Formed?

Abstract. *Volatile substances have a low abundance in lunar surface rocks as compared to terrestrial rocks. If this depletion is explained in terms of a late accretion of volatile materials from a solar nebula with falling temperature, then the conclusion can be drawn that the moon accumulated not in earth orbit but as a separate planet, and that it was later captured by the earth.*

Anders and his colleagues (*1*) have proposed an interesting and far-reaching idea, namely, that the depletion of volatile substances (such as lead, bismuth, and thallium) in lunar rocks relative to terrestrial basalts might be due to the process of accretion rather than to a local heating and evaporation of these elements. One can postulate an inhomogeneous accretion process, which proceeds as the solar nebula is cooling so that the most volatile elements are condensed and accreted as a thin veneer on a nearly completed planet.

The first compounds to condense would be those of the refractory metals Ti, Mo, Nb, and Zr; then iron at about 1500°K, later nickel at about 1350°K, followed by various silicates. By the time a temperature of about 1000°K had been reached, all major elements and compounds would have condensed and the accumulation of planetary bodies could have proceeded toward completion. In the terminal stage of accretion, when the temperature had dropped below 600°K, volatile substances such as Pb, Bi, Tl, and In would have condensed (*2*).

Anders and his colleagues further suggested that the 10- to 100-fold depletion of volatile materials in lunar rocks can be explained in terms of the dynamics of the accretion process, and that the accretion rate of the moon would depend very much on the earth-moon distance (*1*).

From the point of view of theories of lunar origin, it is then important to know whether the accretion of the moon, including the final accretion of volatile substances, took place well outside of the earth's gravitational field or whether this accretion took place while the moon was in orbit around the earth. According to the first possibility, the moon would have to be captured subsequent to its formation. According to the second possibility, the moon formed from material in earth orbit and therefore never underwent capture.

We shall therefore calculate the ratio of the accretion rate for the earth to the accretion rate for the moon, ratio (earth : moon), as a function of the earth-moon distance, and compare this ratio with the experimentally observed ratio of 10 to 100.

Table 1. Ratio of specific accretion rates of earth and moon Z_E/Z_M as a function of earth-moon distance.

Geocentric velocity	Earth-moon distance d (earth radii)					
	1*	5	10	50	100	∞
$c << w_M$:	(0.83)	3.6	6.2	14.6	17.6	22
$c = w_E$:	(0.905)	1.56	1.71	1.86	1.88	1.9

* Calculated for a transparent earth. With a solid earth the distribution of accreting particles near the earth's surface is semi-isotropic, and the ratios at $d = 1$ should be multiplied by a correction factor $F = 2$. The correction becomes rapidly negligible with increasing distance (*4*), being < 10 percent at $d = 3$.

We assume an isotropic gaussian velocity distribution for the particles (containing volatile materials) relative to a circular orbit (at 1 astronomical unit) around the sun. The most probable speed in that reference frame is c, and the concentration of particles is N. The earth then accretes the volatile substances at a rate

$$A_E = 2\sqrt{\pi} R_E^2 \; N \; c \left(1 + \frac{w_E^2}{c^2}\right) \tag{1}$$

where w_E is the escape velocity from the earth's surface and R_E is the earth's radius. A moon in a circular orbit around the earth at a distance of d earth radii accretes this dust at a rate

$$A_M = 2\sqrt{\pi}\, R_M^2\, N\, c \left(1 + \frac{w_M^2}{c^2} + \frac{7}{6}\frac{1}{d}\frac{w_E^2}{c^2}\right) \tag{2}$$

where R_M is the moon's radius and w_M is the escape velocity from the moon's surface.

These expressions for accretion rates are derived as follows (*3*). We assume that far from the earth the phase space density of the dust is given by

$$f_\infty(\mathbf{v}_\infty) = \frac{N}{(c\sqrt{\pi})^3} \exp\left(\frac{-v_\infty^2}{c^2}\right) \tag{3}$$

This equation describes an isotropic gaussian velocity distribution of geocentric speeds v_∞ and some most probable speed c, and a number concentration N. By Liouville's theorem, the phase space density at finite distances d from the earth's center is for a transparent earth exactly equal to that given in Eq. 3, since the gravitational field is conservative of energy (*4*); that is,

$$f_d(\mathbf{v}) = f_\infty(\mathbf{v}_\infty) \tag{4}$$

where

$$v^2 = v_\infty^2 + 2GM_E/d \tag{5}$$

and G is the gravitational constant and M_E is the mass of the earth. Let the selenocentric velocity vector be $\mathbf{u}$. The moon's dust accretion rate can then formally be written as

$$A_M = \iiint f_d(\mathbf{v}) u \; S_v \; d^3v \tag{6}$$

where S_v is the effective accretion cross section of the moon for a given (geocentric) velocity $\mathbf{v}$, and d^3v is an element of volume in velocity space. If r_b is the radius of the moon's sphere of gravitational influence, then from the laws of conservation of energy and angular momentum one easily finds

$$S_v = \pi R_M^2 \left[1 + \left(\frac{w_M^2}{u^2}\right)\left(1 - \frac{R_M}{r_b}\right)\right] \tag{7}$$