EFFECTS OF VAPORIZATION AND CONDENSATION
ON APOLLO 11 GLASS SPHERULES: IMPLICATIONS FOR COOLING RATES

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Fourteen of 40 glass spherules present in a section of the Apollo 11 microbreccia 10019,22 were found to exhibit steep concentration gradients at their rims: the oxides of the relatively volatile elements Na, K, and P increase by, respectively, factors of up to 67, 16, and > 54, at the spherule rims in comparison to the homogeneous centers. These gradients usually extend over $25-30\ \mu$. Furthermore, the natural surfaces of 11 unpolished glass spherules separated from the fines 10084,97, in 60–80% of all cases, show higher concentrations in Na_2O, K_2O, and P_2O_5 than the averages for the central portions of 45 independently analyzed glass spherules. It is suggested that the concentration gradients observed are diffusion gradients and are the result of the impact event which produced the glasses: in the impact melting process, splash drops of melt formed that lost volatiles by vaporization. If the impact-produced vapor cloud surrounding the freely-floating spherules was large enough, then partial condensation of the volatile elements in the vapor cloud should take place upon cooling. These volatile elements condensed on the relatively hot spherules, and thermal diffusion of Na, K and P from the spherule surfaces towards their interiors occurred. Depending upon the temperature, cooling rate, and diffusion coefficient for the particular spherule composition, concentration gradients of different steepness and width should originate. A procedure is described to determine the cooling rate of a spherule from measured concentration gradients, provided the diffusion coefficients are known for the particular glass compositions in question.

1. Introduction

Recently, the presence of small silicate droplets on the surfaces of lunar glass spherules as revealed by scanning electron microscopy [1] and of K-rich rays extending outward from micrometeorite craters on spherules [2]; of opaque coatings on the surfaces of lunar fines that can easily be removed by leaching [3]; and of K-rich areas on external surfaces of lunar rocks [4] has been interpreted to be, at least in part, the result of vaporization of lunar (and meteoritic) material, followed by condensation from the vapor phase. Furthermore, most analyses of glass spherules from Apollo 11 show deficiencies for certain elements such as sodium, potassium, phosphorus, and silicon, when compared to the crystalline rocks and lithic fragments

from which they originated, presumably by impact melting [5]. Impact melting can be sufficiently energetic to produce molten droplets with temperatures high enough to cause vaporization of the more volatile elements and, hence, many of the authors listed [5] have suggested that the observed compositional differences between glass spherules and crystalline rocks are due to loss of volatile elements in the glass forming process. This suggestion is supported by experiments which show that sodium, potassium, and phosphorus are very volatile, and silicon moderately volatile, in basaltic matrices and when heated in inert atmospheres to high temperatures ($2700°-3200°K$) for extended periods of time (up to 3 min) [6].

If vapor fractionation and condensation has indeed been important on the Moon, then glass spherules from Apollo 11 might show evidence to this effect, other than overall element depletion as described above. Since vaporization takes place from the surface of a

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molten spherule, a compositional gradient, for example, might be expected to originate with lower concentrations of comparatively volatile elements at the spherule surface and higher concentrations in the interior, provided very rapid cooling took place which froze in this gradient and prevented it from being destroyed by thermal diffusion. Furthermore, if vaporization occurred, then condensation might also have taken place which would result in a compositional gradient but with high concentrations of comparatively volatile elements at the surface of the spherule (i.e. contrary to the gradient established by vaporization). Thus, a number of processes may affect the concentrations of comparatively volatile elements at or near surfaces of spherules which are related to such parameters as temperature, duration of vaporization and condensation, and density and size of the vapor cloud produced by the impact process and associated vaporization. The following cases might be expected to occur in lunar glass spherules:

(i) Depletion of comparatively volatile elements at or near the spherule surface due to fractional loss of those elements via vaporization.

(ii) Overall depletion of comparatively volatile elements by vapor fractionation without retention of a pronounced compositional gradient.

(iii) Formation of a complex gradient resulting from two competing processes, namely vaporization followed by condensation of relatively volatile elements (analogous to what has been observed for certain meteoritic chondrules [7]).

(iv) Enrichment of relatively volatile elements at or near the spherule surface, solely as the result of condensation or of case (ii), followed by an enrichment at the surface due to condensation.

It is the purpose of this paper to present results of a study of glass spherules from Apollo 11 which was undertaken in an attempt to evaluate whether vaporization and condensation have been important in the process of glass formation, and to what extent such processes have affected the composition of lunar glasses.

2. Experimental techniques

A total of 40 optically homogeneous glass spherules of different colors were analyzed in a polished thin

section of microbreccia 10019,22, using an Applied Research Laboratories EMX-SM electron microprobe X-ray analyzer. Emphasis was placed on a detailed study of the distribution of Na_2O, K_2O, and P_2O_5 in the central portions in comparison to the rims of the spherules, and CaO was determined to serve as a reference; however, for a number of spherules SiO_2, TiO_2, Cr_2O_3, FeO, MgO and MnO were also determined. Tests were made to determine the best-suited experimental conditions to prevent volatilization of the alkalis when under the electron beam and to provide sufficiently high counting rates. It was found that when using an accelerating potential of 15 kV, a sample current of approximately 0.01 μA, a beam of approximately 0.5 μ in diameter, and 10 sec counting time per analytical point, neither the alkalis nor phosphorus vaporized measurably, and the counting rates were sufficient. Using the same experimental conditions, the surfaces of ten unpolished spherules separated from the loose fines 10084,97 were analyzed for Na_2O, K_2O, P_2O_5, and CaO.

Wet-chemically analyzed homogeneous minerals and glasses of compositions similar to those of the spherules studied here were used as standards. Corrections were made for drift, background, mass absorption, secondary fluorescence, and atomic number. Mass absorption corrections were made using Philibert's [9] equation as modified by Duncumb and Shields [10], and Frazer's [11] mass absorption coefficients. The formula of Wittry [12] was applied to correct for secondary fluorescence by characteristic X-ray radiation, and atomic number corrections were made following the procedures of Duncumb and Reed [13].

3. Results

3.1. Glass spherules in microbreccia 10019,22

Of the 40 optically homogeneous glass spherules studied in a polished thin section of microbreccia 10019,22, eleven were found to be inhomogeneous when studied with the electron microprobe. The patterns of compositional variation observed are irregular, show no relation to spherule morphology, and are apparently the result of incomplete mixing and inhomogenization in the vitrification process; these spherules were therefore eliminated from further study. Fifteen of the remaining 29 spherules were found to be homogeneous with-
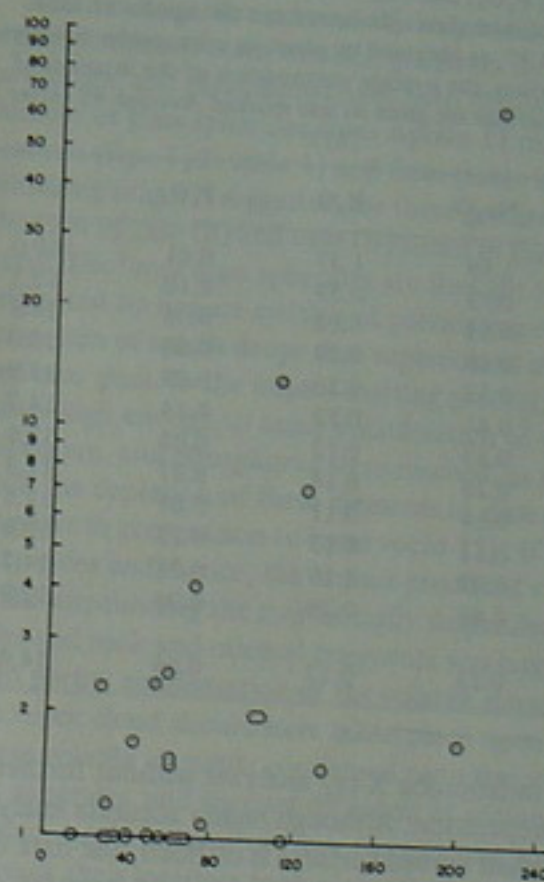
Fig. 1. Ratio of Na contents in outermost rims of glass spherules (C_{Na}^{rim}) to Na contents in spherule centers (C_{Na}^{center}) (logarithmic scale) plotted as a function of apparent spherule diameter (in microns), for 29 glass spherules in a polished thin section of microbreccia 10019,22. Fifteen spherules show essentially no enrichment at their rims, whereas 14 others show enrichments by factors of 1.5 to 67.
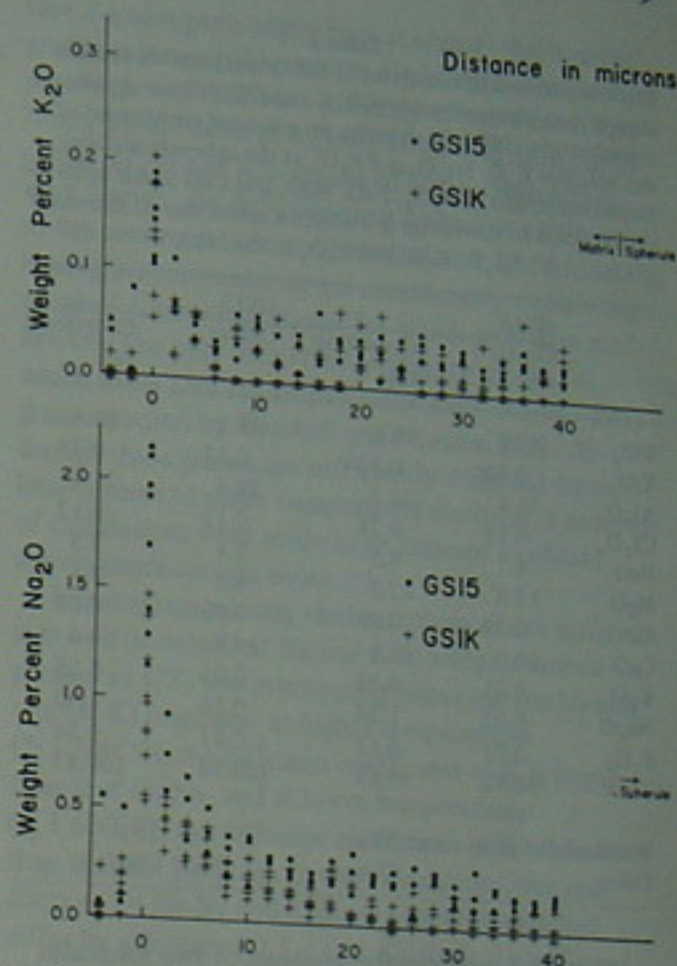

Fig. 2. Quantitative electron microprobe point analyses of Na_2O and K_2O across the rims of spherules GS1K (apparent diameter in thin section is 220 μ) and GS15 (apparent diameter in thin section is 110 μ). Individual analyses are spaced 2 μ apart and represent 5 runs on spherule GS1K and three runs on spherule GS15, each of which was taken at a different location on the spherule rim. However, at the very spherule edge, several additional individual point analyses were made.

in the experimental error and show no compositional gradients for sodium, potassium, and phosphorus; they are uniformly low in these elements. The remaining 14 spherules, although perfectly homogeneous in their interiors, show a pronounced increase in Na_2O and, to a lesser degree, K_2O and P_2O_5, towards their rims (fig. 1). Four of these spherules show an increase in Na_2O at the spherule rims that exceeds by more than a factor of three their interior Na_2O contents. Two examples are given in detail in fig. 2 and table 1 to illustrate this effect. In fig. 2, quantitative point analyses (2 μ apart) of two spherules (GS15 and GS1K) for Na_2O and K_2O are plotted as a function of distance from the interiors of the spherules towards their

rims. Three facts are apparent from that figure: (i) Na_2O and K_2O increase by more than an order of magnitude when comparing the spherule centers to the rims. (ii) The concentration gradients are nearly the same in any direction from the rims towards the centers, as is indicated by the nearly identical concentrations for the different runs plotted in fig. 2 (5 for Na_2O and K_2O in GS1K; 3 each for Na_2O and K_2O in GS15). (iii) The increase in Na_2O and K_2O, although very steep near the rim, extends over approximately 30 μ in case of Na_2O and approximately 10 μ in case of K_2O. In this respect, the curves resemble diffusion gradients and their shapes are probably diffusion controlled.

Table 1

Electron microprobe analyses of the centers and outermost rims of two glass spherules (GS1K and GS15) from Apollo 11 microbreccia 10019,22 showing pronounced enrichment of the volatiles K_2O, Na_2O, and P_2O_5 at the spherule surfaces. Depletion of SiO_2, Al_2O_3, FeO, MgO, and CaO in the spherule rims relative to the center is a dilution effect due to increased Na_2O, K_2O, and P_2O_5 in the rims.

	GS1K		GS15	
	Center	Outermost rim	Center	Outermost rim
SiO_2	45.0	44.6	45.2	44.4
TiO_2	0.44	0.43	0.23	0.23
Al_2O_3	23.1	22.3	28.4	27.7
Cr_2O_3	0.19	0.24	0.12	0.12
FeO	4.7	4.5	3.4	3.3
MgO	12.8	12.2	8.6	8.4
MnO	0.09	0.09	0.03	0.03
CaO	14.0	13.6	14.4	14.0
K_2O	0.01	0.16	0.01	0.15
Na_2O	0.02	1.34	0.15	2.00
P_2O_5	0.01	0.15	< 0.01	0.54
Total	100.45	99.61	100.54	100.87

Width of diffusion zone: 30 μ 25 μ
Color: Clear   Clear

In table 1, quantitative analyses of two spherules (GS1K and GS15) for 11 elements are presented. The pronounced changes in concentration of the relatively volatile elements sodium, potassium, and phosphorus are evident. The data given are the average values measured for the centers and the highest values measured for the rims. In the case of spherule GS1K, increases by factors of 67, 16 and 15, respectively, are found for Na_2O, K_2O, and P_2O_5 when comparing the center to the rim. For spherule GS15, these factors are 14, 15 and > 54. Whereas Na_2O, K_2O, and P_2O_5 increase at the rims of the spherules, most other elements decrease by about 1–2% relative (table 1) which is simply the result of dilution caused by the addition of sodium, potassium, and phosphorus.

3.2. Glass spherules from loose fines 10084, 97

Eleven glass spherules were picked at random from the loose fines 10084,97 and mounted on a glass slide using conductive silver paint in such a way that the surfaces of the spherules were exposed. After vacuum depositing a thin layer of carbon onto the surface, the natural spherule surfaces were analyzed in the

Table 2

Na_2O, K_2O, P_2O_5, and CaO concentrations at the surfaces of eleven unpolished glass spherules from the Apollo 11 loose fines 10084,97, as obtained by electron microprobe techniques. For comparison, the average composition of the interiors of 45 glass spherules are given in line marked Average 45 (after [8]).

Spherule	Na_2O	K_2O	P_2O_5	CaO
1	1.59	1.37	0.01	10.0
2	0.73	0.59	0.10	12.2
3	0.62	0.12	0.06	14.6
4	0.56	0.20	0.03	13.0
5	0.53	0.20	0.08	13.9
6	0.41	0.12	0.14	14.2
7	0.33	0.13	0.02	12.6
8	0.26	0.14	0.07	11.8
9	0.14	0.11	0.09	12.5
10	0.11	0.12	0.13	12.0
11	0.09	0.10	0.08	14.7
Average	0.49	0.29	0.06	12.9
Average 45	0.23	0.12	0.06	14.0

electron microprobe X-ray analyzer without further sample preparation. Although highly accurate analysis of unpolished curved surfaces is difficult, the data obtained are considered to be accurate within ± 10% of the amounts present. The purpose of this study is to determine the volatile element contents at the very surface of the spherules which is difficult to achieve in thin section because of interference from the surrounding matrix at the spherule—matrix interface. The results of this analysis are shown in table 2, where the spherules are listed in order of decreasing Na_2O content and are compared to the average composition of 45 spherule interiors [8]. It is apparent from this table that the amounts of Na_2O, K_2O, and P_2O_5 are usually higher for the spherule surfaces than for the average of 45 spherule interiors. In fact, of the eleven spherule surfaces analyzed, eight are higher in Na_2O, six are higher in K_2O, and 7 are higher in P_2O_5 than the average for 45 spherule interiors. Furthermore, Na_2O and K_2O usually vary sympathetically with each other, whereas no clear relationships can be recognized between these oxides and P_2O_5.

4. Discussion

The most significant result of the present study is that pronounced concentration gradients for sodium, potassium, and phosphorus have been discovered in a number of glass spherules from Apollo 11 microbreccias (figs. 1, 2; table 1) and fines (table 2). The following origin is suggested for these gradients (combination of case (ii) and case (iv) listed in the introduction): The lunar glass spherules are thought to have originated by impact melting of preexisting rocks and formation of splash drops that supercooled and solidified into glass. In the impact melting process, temperatures high enough to cause volatilization of sodium, potassium, and phosphorus were reached, as is evident from the depletion of these elements in glass spherule interiors in comparison to lunar rocks [5]. If the impact event and, hence, the impact-produced vapor cloud surrounding the momentarily suspended spherules and rock and mineral fragments was large enough, then partial condensation of the volatile elements in the vapor cloud should have taken place upon cooling. These volatile elements condensed onto the relatively hot spherules, and thermal diffusion of sodium, potassium, and phosphorus from the spherule surfaces towards their interiors took place. Depending upon the temperature, the cooling rate, and the diffusion coefficient for the particular spherule composition, concentration gradients of different steepness and width should originate. We therefore propose in this model that the concentration gradients observed in the surface regions of lunar glass spherules are diffusion controlled (i.e. they are diffusion gradients), and should allow one to estimate, at least qualitatively, the cooling rates of lunar glass spherules.

The product Dt of the diffusion coefficient D and the diffusion time t (i.e. the time required for a certain concentration gradient to be established at a given temperature) can be calculated from the measured concentrations of Na and K at the spherule surface (C_s); the concentration inside the spherule before diffusion started (C_o; concentration at spherule center); and the concentration C_x at point x, using the diffusion equation for diffusion from a thin surface layer [14]. For the two spherules shown in fig. 2 (GS15 and GS1K, identical average Dt values are calculated, and these are 1×10^{-7} (cm^2) for Na and 4×10^{-8} (cm^2) for K (note that D is strongly dependent on tempera-

ture T and is particularly high at high T; the 'average' gradients measured here were established over a certain range of T but were probably affected most drastically by diffusion at high T). If the diffusion coefficients for Na and K in glasses of lunar composition were known, the diffusion time t which is a measure of the cooling rate, could be calculated. Unfortunately, lunar glass compositions are considerably outside the range of commercial glasses for which such data are known. The only alkali-free refractory glasses for which some data are available, are $CaO-Al_2O_3-SiO_2$ glasses studied by Winchell and Norman [15]. Although these glasses are sufficiently different from lunar glasses to make comparisons doubtful, a number of calculations were made in an attempt to obtain approximate cooling times.

In a diagram relating the logarithms of the diffusion coefficients D of Na and K to temperature expressed as $1/T$, two intersecting lines (one for Na and one for K) originate: at higher temperatures ($\gtrsim 1,600°C$), the diffusion coefficient of K is larger than that for Na, and at lower temperatures ($\lesssim 1,600°C$), the diffusion coefficient of K is smaller than that for Na [15]. In our calculations, the products of Dt for Na and K for the spherules studied differ by a factor of 2.5, i.e. the diffusion coefficient of Na is 2.5 times greater than that for K (making the reasonable assumption that for one spherule, t for Na and K is the same). In the log D vs. $1/T$ plots made from the data given by Winchell and Norman [15], the factor 2.5 determines the temperature and diffusion coefficients for alkali-free glasses in the system $CaO-Al_2O_3-SiO_2$ to be $T = 1460°C$; $D_{Na} = 2 \times 10^{-6}$ $(cm^2 sec^{-1})$; $D_K = 8 \times 10^{-7}$ $(cm^2 sec^{-1})$; and a diffusion time $t = 5 \times 10^{-2}$ sec is then calculated. This diffusion time is unreasonably short, and the temperature T and diffusion coefficients D_{Na} and D_K are unreasonably large (e.g. at that temperature, alkalis, because of high vapor pressures of alkali oxides and silicates, would tend to vaporize rather than to condense [16]). It appears, therefore, that the glasses of Winchell and Norman [15] are too different in composition from the lunar glasses to determine reliable cooling rates for lunar glass spherules. However, the method proposed here can be applied and cooling rates of reasonable accuracies can be obtained once experimental data for the dependence of the diffusion coefficient D on temperature T are available for glasses of lunar composition.

The fact that some spherules show enrichment of volatile elements at their surfaces and others do not may be related, at least in part, to the magnitude of the particular impact event and the size of the vapor cloud that formed as a result of it. It appears that a rather dense vapor cloud of reasonable size would be required in order to retain part of the vapor phase and to allow condensation to take place onto spherules at or above 1000°C. Vapors produced in a very small impact event, on the other hand, are likely to escape and to condense as finely dispersed material on cool rocks in the vicinity. It is therefore suggested that lunar glass spherules with high volatile element contents at their surfaces formed in relatively large impact events. Further research, both experimental and theoretical, on the behavior of volatiles should allow one to characterize more clearly impact events on the moon and, at least to some extent, the physical conditions under which these processes took place.

Acknowledgment

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