GREEN SPHERULES FROM APOLLO 15: INFERENCES ABOUT THEIR ORIGIN FROM INERT GAS MEASUREMENTS*

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Abstract. Green spherules from the 'clod' 15426 and from fines 15421 contain about 100 times less trapped inert gases than normal bulk fines from Apollo 15. These spherules have apparently never been directly exposed to the solar wind. Spherules from other fines contain about 10 times more trapped gas than those from the 'clod'. The gas in the former is surface correlated. However, spherules from fines 15401 are exceptionally gas-poor. $(He^4/Ne^{20})_T$ in all spherules is commonly less than 10, which implies severe He^4 losses. $(Ne^{20}/Ar^{36})_T$ on the other hand is nearly always greater than 10; and ranges up to 20.3.

The Ne_C^{21} and Ar_C^{38} radiation ages vary from 22 to 750 $\times 10^6$ yr, but most of them lie in the range 200–400 $\times 10^6$ yr. He_C^3 ages are always much younger, owing to He_C^3 losses.

The trapped gases can be of solar-wind origin, but this origin requires a two-stage model for the spherules from the clods. First, solar wind was trapped in a parent material, from which the spherules were formed, presumably by impact melting. When the spherules were formed, some fraction of the original gas was retained by them. Another possibility is that the gases were absorbed from an ambient gas phase.

The trapped gases may also be assumed to represent primordial lunar gas. The composition of this gas is then similar to the 'solar' or 'unfractionated' component of gas-rich meteorites, but unlike that in most of the carbonaceous chondrites.

The Ar^{40}–Ar^{36} systematics show two families of spherules: those from 15426 and 15421 which define a line with slope of about 4–5; and those from the fines which fall near a line with slope of about 1.4–1.9. Both lines have similar Ar^{40}-intercept-values of about 3–9 $\times 10^{-6}$ cm^3 STP g^{-1} of Ar^{40}. The corresponding K–Ar^{40} age can be as old as 4300 or as young as 2500 $\times 10^6$.

The gas content of the spherules from fines suggests strongly that all spherules were at one time in 'clod'-like material. This, in turn, seems to imply that a body or layer of 'cloddy' material like 15426 was, and perhaps still is present in the Apollo 15 landing area. Cone Crater impact has tapped this body, but has probably not produced the 'clods'. The green material may have been transported to the Apollo 15 site from elsewhere either as impact-ejecta or by a volcanic eruption. Our results do not permit a choice between the two possibilities.

1. Introduction

Among others the Apollo 15 crew collected some unusual green material, principally at the rim of Spur Crater. The so-called 'green clods' 15425 and 15426 consist largely of spherules or fragments of spheres. Green glass is abundant in the 'clods'; however, the proportion of glass in spheres is variable. Some spheres are entirely vitreous,

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TABLE I

Inert gas contents (Units: cm^3 STP g^{-1})

Sample	Weight μg	He^3 10^{-7}	He^4 10^{-4}	Ne^{20} 10^{-5}	Ne^{21} 10^{-7}	Ne^{22} 10^{-6}	Ar^{36} 10^{-6}	Ar^{38} 10^{-7}	Ar^{40} 10^{-5}
15426, 500–700 μm	4732	9.4 ± 0.3	0.91 ± 0.06	2.48 ± 0.07	7.4 ± 0.2	2.69 ± 0.06	1.72 ± 0.06	5.67 ± 0.18	1.46 ± 0.06
, 354–500 μm	7750	5.5 ± 0.1	1.33 ± 0.05	2.60 ± 0.06	6.9 ± 0.1	2.75 ± 0.08	1.72 ± 0.06	5.60 ± 0.15	1.52 ± 0.06
, 250–354 μm[a]	1890	2.1 ± 0.2	0.62 ± 0.09	1.06 ± 0.03	6.2 ± 0.2	1.46 ± 0.04	0.72 ± 0.04	3.54 ± 0.10	1.12 ± 0.08
, 105–250 μm	2415	1.3 ± 0.2	0.64 ± 0.07	0.76 ± 0.02	6.0 ± 0.2	1.20 ± 0.05	0.67 ± 0.03	3.34 ± 0.20	1.65 ± 0.10
, 105–250 μm[a]	1645	1.6 ± 0.2	0.40 ± 0.09	1.06 ± 0.03	6.4 ± 0.3	1.48 ± 0.04	0.70 ± 0.03	3.60 ± 0.10	1.09 ± 0.10
, single spherule	1129	17.1 ± 0.8	0.82 ± 0.20	0.35 ± 0.03	6.4 ± 0.4	0.93 ± 0.05	0.54 ± 0.04	3.24 ± 0.12	0.77 ± 0.19
, single spherule	817	94 ± 7	[b]	0.15 ± 0.01	5.1 ± 0.4	0.63 ± 0.06	0.35 ± 0.03	2.7 ± 0.2	0.93 ± 0.19
15301, 354–500 μm	3305	8.6 ± 0.3	4.00 ± 0.12	7.06 ± 0.21	6.4 ± 0.2	6.66 ± 0.20	4.64 ± 0.18	10.3 ± 0.03	0.95 ± 0.05
, 250–354 μm	3410	6.6 ± 0.2	5.7 ± 0.2	11.2 ± 0.03	7.9 ± 0.2	9.32 ± 0.3	5.6 ± 0.2	12.6 ± 0.04	1.21 ± 0.06
, 105–250 μm	2115	10.4 ± 0.3	15.8 ± 0.5	26.1 ± 0.9	12.3 ± 0.4	20.6 ± 0.6	14.4 ± 0.5	29.2 ± 0.9	2.4 ± 0.1
15301, 105–250 μm									
0 pits	375	9.7 ± 0.9	12.6 ± 0.8	16.2 ± 0.5	6.7 ± 0.5	10.6 ± 0.4	8.1 ± 0.3	16.5 ± 0.4	2.2 ± 0.3
1 pit	985	8.9 ± 0.4	9.7 ± 0.3	12.2 ± 0.4	6.8 ± 0.4	9.8 ± 0.3	6.0 ± 0.2	12.5 ± 0.4	1.0 ± 0.2
2 pits	685	10.0 ± 0.9	13.7 ± 0.4	19.5 ± 0.6	9.7 ± 0.5	15.7 ± 0.4	10.2 ± 0.3	20.8 ± 0.8	2.0 ± 0.3
3 pits	470	8.7 ± 0.8	10.3 ± 0.4	16.0 ± 0.6	8.3 ± 0.6	12.8 ± 0.4	8.2 ± 0.2	17.0 ± 0.6	2.5 ± 0.3
15421, 250–354 μm	1540	4.0 ± 0.3	1.03 ± 0.08	0.86 ± 0.03	5.9 ± 0.2	1.25 ± 0.03	0.76 ± 0.03	3.54 ± 0.10	0.59 ± 0.09
15401, 250–354 μm	1900	1.2 ± 0.2	0.40 ± 0.04	0.096 ± 0.008	0.46 ± 0.15	0.11 ± 0.01	0.17 ± 0.09	0.45 ± 0.04	0.60 ± 0.06
15271, 105–500 μm	1660	12.9 ± 0.6	6.8 ± 0.2	12.1 ± 0.3	10.8 ± 0.3	10.1 ± 0.3	6.8 ± 0.2	15.6 ± 0.04	1.08 ± 0.10
15091, single spherule	469	8.8 ± 0.9	20.4 ± 1.5	16.5 ± 0.3	15 ± 1	13.9 ± 0.7	16.6 ± 0.5	34.1 ± 1.3	[b]
, 250–354 μm	220	10 ± 2	14 ± 1	16.3 ± 0.6	12 ± 1	14 ± 1	9.0 ± 0.5	19 ± 1.5	2.4 ± 0.6
, 105–250 μm	440	17.4 ± 1.0	33.9 ± 1.3	33.8 ± 1.3	21 ± 1	27.8 ± 1.0	[c]	[c]	[c]
15601, single spherule	93	9 ± 4	13 ± 2	15 ± 2	8 ± 4	12 ± 2	15 ± 1	28 ± 4	[b]

Table I (continued)

Sample	He^4/He^3	Ne^{20}/Ne^{22}	Ne^{21}/Ne^{22}	Ar^{36}/Ar^{38}	Ar^{40}/Ar^{36}	He^4/Ne^{20}	Ne^{20}/Ar^{36}
15426, 500–700 μm	97	9.2	0.273	3.03	8.72	3.67	14.4
, 354–500 μm	242	9.5	0.250	3.06	8.85	5.12	15.1
, 250–354 μm[a]	295	7.2	0.425	2.05	15.6	5.85	14.7
, 105–250 μm	515	6.4	0.499	2.01	15.5	8.42	11.3
, 105–250 μm[a]	250	7.1	0.428	1.94	15.7	3.77	15.1
, single spherule	48	3.9	0.684	1.66	14.4	23.4	6.51
, single spherule	[b]	2.4	0.810	1.29	26.6	[b]	4.30
15301, 354–500 μm	440	12.1	0.096	4.51	2.04	5.66	15.2
, 250–354 μm	863	12.1	0.085	4.57	1.97	5.08	20.0
, 105–250 μm	1520	12.7	0.060	4.92	1.97	6.05	18.1
15301, 105–250 μm							
0 pits	1300	12.7	0.063	4.93	2.75	7.78	20.0
1 pit	1090	12.5	0.069	4.80	1.00	7.95	20.3
2 pits	1370	12.4	0.062	4.91	1.92	7.03	19.1
3 pits	1180	12.5	0.064	4.80	3.01	6.44	19.5
15421, 250–354 μm	257	6.9	0.472	2.15	7.68	12.0	11.3
15401, 250–354 μm	333	8.5	0.413	3.66	36.3	41.7	5.64
15271, 105–500 μm	527	12.5	0.107	4.35	1.59	5.61	17.8
15091, single spherule	2320	11.9	0.109	4.86	[b]	12.4	9.94
, 250–354 μm	1400	11.8	0.084	4.81	2.61	8.59	18.1
, 105–250 μm	1950	12.2	0.076	[c]	[c]	10.0	[c]
15601, single spherule	1360	12.6	0.072	5.28	[b]	8.6	10.0

[a] Ultrasonic cleaning in acetone for 1 hr, all others for 2 hrs.
[b] Procedural blank too large.
[c] Gas pumped by ion gauge.

others are partially or entirely recrystallized to crystals composed of orthopyroxene or sometimes olivine. The glass has a high refractive index of 1.65 (LSPET, 1972), and a unique composition, i.e. rich in Fe and Mg, but poor in Ti (Ridley *et al.*, 1972). Green spherules are also present in the soils. The largest concentration of spherules or fragments of spherules, or green glass occurs at the base of Hadley Delta (stations 2, 6, and 7), where the green glass content of the soils ranges from 7 to 40% (LSPET, 1972). The soils from the Mare region (LM and ALSEP stations) as well as those from the ridge of Hadley Rille (Stations 9 and 9[a]) are considerably poorer in green glass (LSPET, 1972).

The unusual composition of the green glass, its presence at the landing site nearest to the Imbrian Basin, at the base of the Apennine Mountains, and its absence or paucity at the other landing sites (Ridley *et al.*, 1972) raise questions about its origin, age, and evolution. The significant difference in green glass content of the soils from 'Front' and 'Mare' sites raises additional questions, e.g. how this material was deposited at the Apollo 15 site, its present depth of burial, and the extent of its lateral distribution in the area. Our own work, the measurement of inert gases in spherules from 15426 and from six fines (see Table I) is an attempt to help answer these questions.

The spheres were handpicked with the aid of a binocular microscope from the fines and from a sample of disaggregated 'clod' 15426. The spherules were treated ultrasonically in acetone to remove the fine dust adhering to their surfaces. The clean spherules were weighed and packaged in aluminium foil and these packages were placed in the gas-extraction system. Mr J. L. Jordan has measured the refractive index of the spherules in samples from 15426 and from all of the fines. He found that all the values lie in the range 1.64–1.66.

The inert gases were measured mass-spectrometrically. The procedures have been described in detail elsewhere (Heymann and Yaniv, 1970). The results are given in Table I.

2. Results

A. GAS CONTENTS

In Figure 1 we compare Ar^{36} contents in spherules and bulk fines (data bulk fines from Jordan *et al.*, 1972). Note that the samples fall into four categories: (a) spherules from 15401 which have exceptionally small Ar^{36} contents; (b) spherules from 15426 and 15421 which have Ar^{36} contents between about 3×10^{-7} and 2×10^{-6} cm^3 STP g^{-1}; (c) spherules from fines (except 15421) which have Ar^{36} contents between about 5×10^{-6} and 2×10^{-5} cm^3 STP g^{-1}; and (d) bulk fines which have Ar^{36} contents between about 1.5 and 3×10^{-4} cm^3 STP g^{-1} (except 15401). Similar trends exist for Ne^{20} and He^4.

The trapped gas contents of the bulk fines are normal, i.e. very similar to those seen in fines from other landing sites, including Luna 16. The small gas content of spherules from the 'clod' 15426 can be easily explained by shielding, i.e. only the spherules at the exterior surface of the 'clod' could receive solar wind, those inside could not. Most, if not all the spherules from 15426 which we have measured were

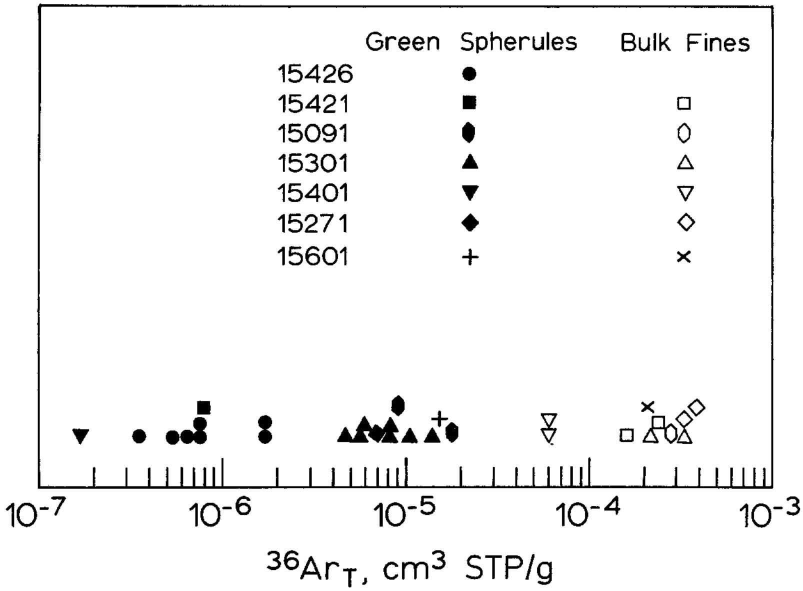

Fig. 1. Contents of trapped Ar_T^{36} in green spherules and bulk fines from Apollo 15. Three groups are seen: (a) spherules from 15401, 15421, and 15426; (b) spherules from 15091, 15271, 15301, and 15601; (c) bulk fines. Spherules from group (a) were not, or only briefly exposed to solar wind; those of groups (b) and (c) were exposed. The systematic difference between groups (b) and (c) is in part due to particle size. Group (b) does not contain spherules smaller than 105 μm; the fines in group (a) contain a considerable proportion of particles smaller than 105 μm.

probably so shielded; that these spherules do contain trapped gas, albeit in small amounts, is interesting because it implies that this gas must have been trapped *before* the formation of the 'clod'.

That the spherules picked out of the fines contain less trapped gas than the fines themselves is, in part a particle size effect. No spherules were measured with diameter less than about 100 μm, but the bulk fines contain a substantial proportion of very gas-rich, smaller particles. The Ar_T^{36} content of the 105–250 μm fraction of 15601 is 4.99×10^{-5} cm^3 STP g^{-1} (Yaniv and Heymann, 1972); of 15091 is 1.08×10^{-4} cm^3 STP g^{-1} (Jordan *et al.*, 1972). The largest Ar_T^{36} content of spherules from fines in this size fraction is 1.44×10^{-5} cm^3 STP g^{-1} (15301). Hence, there may be a systematic difference in gas content of spherules and bulk fines. Two explanations can be considered. One possibility is that the spherules have intrinsically low retentivity for inert gases. The uncommonly small $(He^4/Ne^{20})_T$ ratios speak in favor of this explanation, but the relatively large $(Ne^{20}/Ar^{36})_T$ ratios (see below) speak against it. Another possibility is that nearly all the spherules, now found as individuals in fines, were once inside 'clods' such as 15426; and were removed from them by the gradual disaggregation of 'clods' at the surface of the regolith.

The Ar^{36} contents of bulk fines 15091 and 15601 are inversely proportional to particle size (Jordan *et al.*, 1972). This means that most of the trapped gases were directly implanted from the solar wind into the surfaces of particles in the fines. This anticorrelation of trapped gas content and particle size is clearly present in spherules from fines 15301; those from 15091 show a weak trend. However, the anticorrelation is clearly absent in spherules from 15426, which confirms that these spherules were not, or only very briefly exposed to solar wind bombardment.

B. HELIUM

The striking characteristic of the spherules is that they show very small He^4/Ne^{20} ratios; sixteen of twenty values are ten or smaller. He^4/Ne^{20} ratios in bulk fines from Apollo 15 are nearly always between 40 and 60 (Jordan *et al.*, 1972). This indicates very low He retentivity of the spherules; perhaps not surprising in view of the abundant presence of glass.

Whether the spherules still contain any radiogenic He_R^4 cannot be concluded from the data. U in *bulk* 15426 is reported as 0.41 ppm; Th as 1.89 ppm (LSPET, 1972), which means that about 7×10^{-4} cm^3 STP of He_R^4 were produced per gram during the last 4000×10^6 yr, an amount considerably greater than the amounts of He^4 now present in the spherules. However, the U and Th contents of the spherules are probably much smaller than the *bulk* values of 15426 because the K-content of 15426 spherules is only 113 ppm (Drs J. Huneke and F. Podosek, private communication).

He^4/He^3 is also relatively small in the spherules; this ratio is nearly always greater than 2000 in the bulk fines (Jordan *et al.*, 1972). The small ratios are almost certainly due to the presence of cosmogenic He_C^3.

C. NEON

The neon isotopic data are shown in Figure 2, a three isotope plot Ne^{20}/Ne^{22} vs Ne^{21}/Ne^{22}. The spherules from 15426 fall close to a straight line, which intersects the value of cosmogenic neon in the lower right-hand corner. The trapped component present in these spherules lies on the same line in the upper left-hand portion, but its exact position cannot be determined with the data at hand. An Eberhardt plot (Eberhardt *et al.*, 1970) yields very inaccurate results in this case. If we make the reasonable assumption that $(Ne^{21}/Ne^{22})_T$ is 0.033 (values measured in lunar fines show this value within $\pm10\%$), we find $(Ne^{20}/Ne^{22})_T$ from the line as 12.3. We have adopted these values in our calculations of cosmogenic Ne_C^{21} in 15426 spherules.

An intriguing aspect of Figure 2 is that the data points of spherules from fines as well as those of bulk fines themselves are systematically displaced from the 'clod'-line. We do not know the reasons for the displacement, except that it cannot be due to compositional differences in the case of spherules (cf. Ridley *et al.*, 1972). The following possibilities must be considered: (1) isotopic fractionations and (2) the presence of one or more additional components, e.g. neon produced by solar flare protons; directly implanted solar flare-neon; or neon cycled through the lunar atmosphere, either in 'clod' spherules or 'fines' spherules.

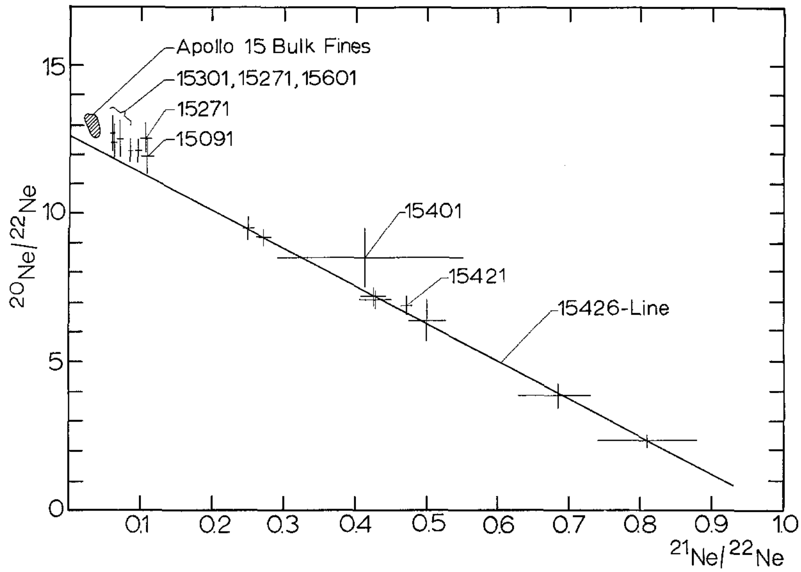

Fig. 2. Ne^{20}/Ne^{22} vs Ne^{21}/Ne^{22}. Spherules from the 'clod' 15426 fall near a straight line. Neon in these spherules is probably a two-component mixture, consisting of trapped Ne_T with $Ne^{20}/Ne^{22} = 12.3$ (on the assumption that $Ne^{21}_T/Ne^{22}_T = 0.033$) and cosmogenic Ne_C with $Ne^{20}/Ne^{22} = 1$. Spherules from fines (not all the data from Table I are shown for the sake of clarity) and the bulk fines themselves (hatched area) are displaced from the line to greater values of Ne^{20}/Ne^{22} or Ne^{21}/Ne^{22} or both. The most likely explanations are: (a) that the Ne_T in bulk fines and spherules from them is richer in Ne^{20}_T or poorer in Ne^{21}_T than Ne_T in 'clod' spherules; (b) that bulk fines and spherules from them contain a third component (see text).

To account for the systematic displacement, we have adopted $(Ne^{21}/Ne^{22})_T = 0.033$ and $(Ne^{20}/Ne^{22})_T = 13.0$ for the calculation of Ne^{21} in spherules from fines.

D. ARGON

The Ar^{36}/Ar^{38} ratios are nearly always much smaller than the ratio in trapped argon, for which we have adopted a value of 5.35 ± 0.05. This means that cosmogenic Ar^{38}_C is clearly detectable, and may be calculated with the assumption that $(Ar^{36}/Ar^{38})_C = 0.6$. The Ar^{40}/Ar^{36} ratios will be discussed separately.

E. $(Ne^{20}/Ar^{36})_T$

We have already noted that this ratio is uncommonly large; sixteen of the nineteen values are greater than 10. In bulk fines from Apollo 15 this ratio ranges from 4.9 to 8.2 (Jordan *et al.*, 1972). The large values are seen to occur in spherules from the 'clod' as well as in spherules from the fines. Since the latter have been exposed directly to the solar wind, one must suspect that the green glass possesses a relatively large trapping efficiency for solar wind neon. In fact, because of the very small $(He^4/Ne^{20})_T$ ratios, one must also suspect that the intrinsic trapping ratio of Ne^{20}/Ar^{36} in the glass is considerably greater than 20; and that the ratios now seen in the spherules are decreased because of Ne^{20} losses.

F. PITTED SPHERULES

We have selected spherules with different numbers of 'pits' from the 105–250 μm fraction of 15301 to investigate whether such spherules would show differences in amounts of trapped gas and cosmogenic gas. A 'pit' is defined as a microcrater observable at 80 times magnification. In some cases we have observed that two pits occurred at diametrically opposed positions on the sphere. It may well be that only one is the primary impact craterlet, while the other is a spall pit, produced by the same impact. Table I shows that there is no clear-cut difference between the gas contents of the four groups of spherules. Spherules with 2 and 3 pits are slightly richer in Ne^{21} and Ar^{38} than those with 0 and 1 pits, suggesting that the former were perhaps exposed at the top of the regolith a little longer.

3. Cosmic Ray Exposure Ages

We have calculated exposure ages for the three principal cosmogenic nuclides He_C^3 Ne_C^{21}, and Ar_C^{38}. The data from Table I were corrected for the trapped components with the following ratios: $(He^3/He^4)_T = 3.7 \times 10^{-4}$; $(Ne^{20}/Ne^{21})_T = 370$ (for spherules from the 'clod'); $(Ne^{20}/Ne^{21})_T = 390$ (for spherules from fines); $(Ar^{36}/Ar^{38})_T = 5.35$; and $(Ar^{36}/Ar^{38})_C = 0.6$. The production rates were calculated with the equations from Yaniv *et al.* (1971). For the composition of the spherules, we have used the data as reported by Ridley *et al.* (1972). The following production rates were obtained: $He_C^3 = 1.09 \times 10^{-8}$; $Ne_C^{21} = 0.169 \times 10^{-8}$; and $Ar_C^{38} = 0.068 \times 10^{-8}$ cm^3 STP g^{-1} per 10^6 yr. These values are valid for 2π irradiation geometry and represent production rates at a depth of about 20–30 g cm^{-2}.

The ages are shown in Table II. The He_C^3 ages are seen to be systematically younger than the Ne_C^{21} and Ar_C^{38} ages, but the latter are nearly always concordant. Because of the He_T^4 losses, one may safely conclude that the spherules have also lost much He_C^3.

The Ne_C^{21} and Ar_C^{38} ages of spherules from 15426, 15301, 15421 and 15601 are essentially equal. The first three samples come from station 7 (Spur Crater), the fourth comes from the Rim station 9[a]. The ages of spherules from 15271 (station 6) and from 15091 (station 2, St. George) are significantly older; spherules from 15401 (station 6[a]) are very much younger than the former.

These ages do not necessarily represent the date at which the spherules or clods were brought from a completely shielded position at depth to the top of the regolith. In fact, it is much more reasonable to assume that there existed, or still exists a layer of green material, perhaps 'cloddy' at some depth, where the production rates are significantly smaller than those given above; hence that the real exposure times of the spherules to cosmic-ray protons may have been considerably longer than the ages given in Table II. We will consider the following simple model. At T_0 years ago the green glass was formed and a blanket of this material was deposited in the Apollo 15

TABLE II

Cosmic ray exposure ages (Units: 10^6 yr)

Sample	Ages		
	He^3_C	Ne^{21}_C	Ar^{38}_C
15426 (500–700 μm)	82	400	400
(354–500 μm)	46	360	390
(250–354 μm)[a]	17	350	360
(105–250 μm)	10	340	350
(105–250 μm)[a]	13	360	380
15426 (single spherule)	150	370	360
(single spherule)		300	330
15301 (354–500 μm)	65	270	270
(250–354 μm)	41	300	350
(105–250 μm)	41	350	380
15301 (105–250 μm)			
0 pits	46	160	220
1 pit	49	220	200
2 pits	45	290	290
3 pits	45	260	280
15421 (250–354 μm)	33	340	350
15401 (250–354 μm)	10	26	22
15271 (105–250 μm)	95	460	480
15091 (single spherule)	11	650	510
(250–354 μm)	44	450	360
(105–250 μm)	44	750	
15601 (single spherule)	51	280	

[a] These samples were cleaned in acetone for only one hour.

landing area on top of whatever regolith was already present at that time. This blanket became covered in turn either gradually or suddenly, by a layer of normal Apollo 15 fines (such as 15021 which is very poor in green glass). The covering layer was essentially complete T_1 years ago. Vertical mixing was always restricted, except at sufficiently large craters, which could penetrate, hence sample the 'green glass layer' underneath. 'Clods' and spherules were ejected by impacts T_2, T_3, etc. years ago. Now, T_0 is about 3000×10^9 yr ago (see Section 5). If T_2, T_3,···, the *true* near-surface residence times should turn out to be always very close to the radiation ages of Table II, the green glass must have been covered by a layer of normal fines of considerable thickness (say a few meters at least) *soon* (i.e. no more than about 300–400×10^6 years at Spur Crater) after T_0. However, if T_2, T_3,..., are always very much younger than the radiation ages (say, the former are a few million or tens of millions of years only), T_1 can have any value between T_0, on the one hand, and T_2, T_3, $\cdots$ on the other; but the covering layer of normal fines cannot have grown too thick (several meters), too soon (times on the order of 10^8 yr) after T_0. Which of these cases is more nearly correct, say for the 'clod' 15426 cannot be decided, because we do not know the age of Spur Crater.

However, some interesting inferences can be drawn from the ages of 15426, 15401, and 15091 spherules. The age of spherules from 15401 suggests that the rate of deposition of normal fines on top of the 'green glass layer' must have been fairly high at about T_0 years ago, because these spherules became wholly shielded almost instantaneously, less than about 25×10^6 yr after T_0 (unless, of course, the green glass layer itself was several meters thick; and 15401 spherules come from deep inside this layer). Spherules from 15091 as well as from 15426 suggest a much slower rate of deposition, or else these spherules come from shallower depths inside the green glass layer. Substantial local variations of deposition rates are to be expected at the base of the Front (from which all these samples come), if the principal process contributing normal fines to the area is that of 'landslides' from slopes above the stations.

4. Origin of the Trapped Gas

A. SOLAR WIND

Lunar fines are nearly always rich in directly implanted solar wind. They show a clear-cut anticorrelation between inert gas content and particle size. Etching experiments have shown that much of the gas is still located near the external surfaces of the particles (cf. Eberhardt *et al.*, 1970). We have seen that the spherules from the 'clod' 15426 do not show the anticorrelation, but a rather irregular pattern. Between 700 and 105 μm the content of trapped gases tends to decrease; however, the two large spherules, which have diameters between 700 and 1000 μm have the smallest gas contents (Table I). This observation does not imply, however, that the gases are not of solar wind origin. A two-stage model can be proposed with solar-wind implantation into some parent material which acts as a 'catcher'. The spherules were formed, presumably by impact-melting from this parent material with retention of some fraction of the originally trapped gas.

One may speculate that the 'catcher' was a regolith itself, but it can hardly have been the local regolith at the Apollo 15 landing site, because its chemical composition is very different from that of the green glass (cf. Ridley *et al.*, 1972). Ridley *et al.* have suggested that the green glass was formed from ultramafic rocks, or from their glassy equivalents somewhere in the Appenine Front. A variant of their hypothesis assumes regolith fines of ultramafic composition as the parent material.

Fines from Apollo 11, 12, 14 and 15, as well as from Luna 16 typically contain between $1\text{–}5 \times 10^{-3}$ cm^3 STP g^{-1} of Ne_T^{20} (Heymann and Yaniv, 1970; Hintenberger *et al.*, 1971; Heymann *et al.*, 1972; Vinogradov, 1971). The Ne_T^{20} content of the spherules in 15426, however, is about two orders of magnitude less. This would seem to imply a very low gas retention of only about 1% in the process by which the spherules were formed from the parent materials. Such a near-quantitative gas loss should cause substantial fractionation of the inert gases. We have seen that the $(He^4/Ne^{20})_T$ ratios in the spherules are much smaller than those in bulk fines from all the Apollo landing sites, which is consistent with the assumption of substantial gas loss. However, the $(Ne^{20}/Ar^{36})_T$ ratios in the spherules are not smaller, but nearly always larger than those seen in bulk fines, and this is somewhat puzzling.

Near-quantitative gas loss is not required if the parent regolith itself was very coarse-grained, i.e. had a mean particle size of several centimeters. The gas concentrations ($cm^3\ g^{-1}$) of such a regolith should be comparable to those now seen in 15426 spherules. Even then, the puzzle of the large $(Ne^{20}/Ar^{36})_T$ ratios in the parent regolith remains.

The best documented case of a material in which solar-wind Ne^{20} and Ar^{36} are *directly* trapped with $(Ne^{20}/Ar^{36})_T$ ratios greater than 20 is ilmenite (Eberhardt *et al.*, 1970), but ilmenite is obviously not the parent material from which the spherules formed. Could it be that the green glass, or its parent material is similar to ilmenite in this respect, i.e. that it, too, has the property of direct entrapment of solar-wind Ne^{20} and Ar^{36} with relatively large ratios? There is evidence in Table I which suggests that this might be the case. Spherules from 15301 contain about ten times more trapped gas than those from the 'clod'. Also, the former show an anticorrelation of gas content and particle size, hence these spherules have probably been directly exposed to solar-wind. And they show consistently large $(Ne^{20}/Ar^{36})_T$ ratios, with values ranging from 15.2 to 20.3.

Judging from the data, one may conclude that the 'clod' spherules could have formed from a solar-wind impregnated regolith, possibly a rather coarse-grained one. In the formation process part of the original gas was retained by the liquids and solids as they cooled; He^4_T, the most mobile of the inert gases was substantially fractionated.

A variant of this hypothesis is that the liquid droplets from which the spherules congealed were first quantitatively outgassed, but that the subsequent cooling of the solid spherules took place in the presence of an ambient gasphase, which itself was of solar-wind origin, i.e. had been produced by the outgassing of vast quantities of regolith. This variant is more consistent with the observation that many of the spherules in the 'clods' are recrystallized, and that the orthopyroxene crystals in them are rather coarse-grained: 0.1 mm, sometimes larger (we thank Dr A. El Goresy for having brought this point to our attention). In this case the gases diffused through the surface of the spherules into their interiors, and when equilibrium conditions were established, the gases had become volume, not surface correlated. The evidence seems to suggest that different 'clod' spherules were exposed to slightly different partial pressures of the inert gases.

A similar process has been postulated for the formation of breccia 10065 (Heymann and Yaniv, 1971), namely a base-surge type event in which regolith particles were transported, heated, melted, and welded together in the presence of a gasphase. It is interesting to note that the gas which appears to be trapped in pores of 10065 also shows large $(Ne^{20}/Ar^{36})_T$ ratios; these range from 10.2 to 26.4. We do not wish to imply, however, that the green spherules must have been transported on the lunar surface by a gasphase, they might have been. Moreover, the formation of the 'cloddy rocks' themselves might have occurred in a 'nuée-ardente' like event.

B. PRIMORDIAL LUNAR GAS

Prior to the Apollo 11 landing there was considerable speculation concerning the possibility of finding genuine primordial gas, i.e. inert gases acquired by the Moon during its formation. The studies of Apollo 11 rocks and fines immediately showed why the detection of primordial gas in surface samples would always be difficult. Basaltic rocks for example were derived from a parent material that may have contained primordial gas, but the liquids from which the basalts crystallized were apparently near-quantitatively outgassed, such that the gas, if any was present, escaped into the lunar atmosphere, from which it was relatively quickly removed into interplanetary space. The partial melting of vast near-surface regions of the Moon may have been an even more efficient process for the removal of primordial inert gases to considerable depths; tens if not hundreds of kilometers downward from the surface. In addition, the regolith is now impregnated with solar-wind gases, which always tend to 'mask' if not overwhelm a genuine primordial component. The scenario for detecting primordial gas in lunar surface samples is akin to the proverbial search for the needle in the haystack. It calls for a parent material that contained primordial gas, but that was never quantitatively outgassed. Rocks, minerals, or glasses that formed from parent materials may never have been quantitatively outgassed themselves, and these objects may not have been exposed to solar wind for very long. Obviously there are no compelling arguments in favor of a primordial origin for the trapped gas in 15426 spherules. But among all the lunar materials investigated to date, these spherules are the prime candidates for which this origin may be claimed with some justification. Ridley *et al.* (1972) have proposed that the parent material of the green glass is an ultramatic rock that has formed at a depth of several kilometers and possibly much deeper. The small negative europium anomaly in the rare earth pattern indicates that feldspar fractionation has apparently not played a major role in the formation of the green glass composition, i.e. that the parent rocks of the green glass are unlikely to be residues from or complimentary differentiates to the anorthositic gabbros of the lunar highlands. Hence, these deep-seated parent rocks may have escaped quantitative outgassing. Ridley *et al.* (1972) have further proposed that the parent rock was brought close to the surface in upthrust Apennine fault blocks of Imbrium ejecta, and that subsequent impacts in the front produced the spherules. Hence the greatest danger for quantitative outgassing occurred when the liquid droplets formed, some 3.4×10^9 yr ago (Drs J. Huneke and F. Podosek, private communication). However, there is trapped gas now present in the 15426 spherules; it is apparently not directly implanted solar wind. Hence, whatever its origin – solar wind or primordial lunar – the gas must have survived the formation stage of spherules.

Once formed, the spherules were liable to become exposed to the solar wind. We believe that there is ample justification for the conclusion that the cloddy material was formed either at the same time with the spherules or only shortly thereafter. Again the evidence is the apparent absence of directly implanted solar wind in the spherules from the 'clod'. In conclusion we would like to suggest that the spherules from 15426 may contain a sample of genuine primordial lunar gas, albeit strongly fractionated.

With this conclusion before us, let us comment on the composition of the unfractionated primordial gas. Its He^4/Ne^{20} ratio is greater, perhaps much greater than 10. Primordial gases in carbonaceous chondrites show $He^4/Ne^{20} \approx 300$ (Mazor *et al.*, 1970); the ratio in present day solar wind is even greater at 430–620 (Geiss *et al.*, 1972). Obviously He was strongly fractionated. The Ne^{20}/Ar^{36} ratio is greater than 15 (see Table I); its Ne^{20}/Ne^{22} ratio in the range 12–13 (see Figure 2; we have assumed Ne^{21}/Ne^{22} primordial about 0.03).

These ratios indicate a great similarity in composition to the so-called 'solar' or 'unfractionated' trapped component in gas-rich meteorites (Anders, 1964) but also to the trapped gas in the howardite Kapoeta (Zähringer, 1962). However, lunar primordial gas is dissimilar to the trapped gases in the great majority of carbonaceous chondrites which show $(Ne^{20}/Ne^{22})_P < 12$ and $(Ne^{20}/Ar^{36})_P < 10$ (Mazor *et al.*, 1970).

C. GAS FROM AN EXTRALUNAR OBJECT

If the spherules had been formed by the impact of an extralunar object, it is conceivable that the trapped gases are derived, at least in part, from the projectile which could have been a comet or a gas-rich meteorite. In fact, one cannot exclude the possibility that the spherules themselves are largely derived from an impacting projectile. As before, the gases now seen in 15426 spherules may represent in the main gas that was retained in the liquid and solid droplets after the impact, but they could also have been absorbed from an ambient gasphase present immediately after the collision. If the gas came principally from the extralunar object, then the latter was almost certainly not a carbonaceous chondrite.

5. Ar^{36}–Ar^{40} Systematics

Figure 3 shows a plot of Ar^{40} vs Ar^{36}. The data points do not scatter randomly but fall, grossly, in one of two groups. The first group comprises the 'clod' spherules from 15426 and 15421, and possibly spherules from 15401. These points fall near the curves with slopes between about 4 and 5. The second group consists of spherules from fines; these points fall near the curves with slopes between about 1.4 and 1.9.

The curves in Figure 3 were obtained by linear regression fits to different combinations of data points as listed in Table III. The standard errors of intercepts and slope-values are always considerable; for example, the curve fitted to the 15426 points only is

$$Ar^{40} = (8.71 \pm 2.11) \times 10^{-6} + (3.81 \pm 2.00)\, Ar^{36}.$$

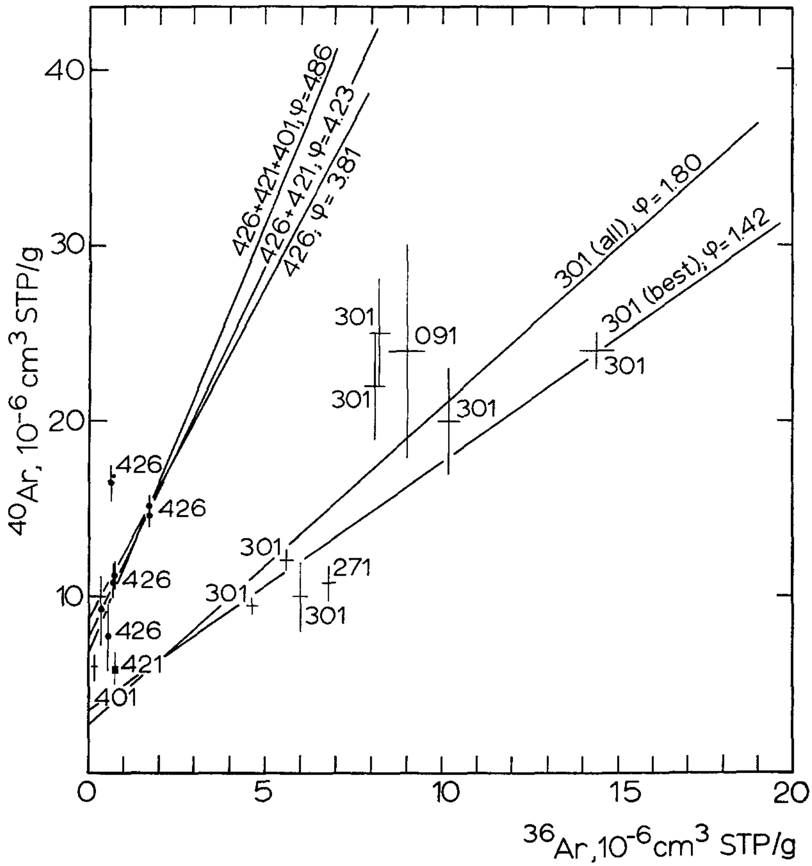

Fig. 3. Ar^{40} vs Ar^{36}. The data fall, grossly, into two groups: (a) spherules from 15426, and possibly 15401, which fall near straight lines with slopes between 4 and 5; (b) spherules from fines which fall near lines with slopes between 1.4 and 1.9. Ar^{40} intercepts range from 2.64 to 8.71×10^{-6} cm^3 STP g^{-1}. The corresponding K–Ar^{40} age of the spherules could be as old as 4400 or as young as 2500×10^6 yr.

TABLE III

Least-squares fits of data points in Figure 3 ($Ar^{40} = a + b \times Ar^{36}$; a in 10^{-6} cm^3 STP g^{-1})

Points[a]	*a*	*b*
426	8.710	3.806
426 + 421	7.615	4.231
426 + 421 + 401	6.839	4.864
301[b]	3.504	1.424
301 (all)	2.823	1.800
301 + 091 + 401 + 271	2.635	1.875

[a] 426 stands for 15426, etc.

[b] Three points with smallest errors.

The most precise fit was obtained for the three 15301 data points with the smallest experimental error: namely,

$$Ar^{40} = (3.50 \pm 1.07) + (1.42 \pm 0.11)\, Ar^{36}.$$

The linear Ar^{40}–Ar^{36} correlation of the 'clod' spherules probably means that these spherules trapped argon with $Ar^{40}/Ar^{36} \sim 4$–5 at the time of their formation, but in variable amounts, uncorrelated with spherule size. It is only with this assumption that one may interpret the intercept value as *in situ* produced radiogenic Ar^{40} since the formation of the spherules.

In the case of spherules from the fines, which have been exposed to solar-wind, one may assume that most, if not all of the correlated Ar^{40} was implanted by the solar-wind mechanism as proposed by Heymann and Yaniv (1970). The Ar^{40} intercept value has always been accepted to represent *in situ* produced radiogenic Ar^{40}.

One may speculate about the significance of the Ar^{40}/Ar^{36} ratio of about 4–5 seen in the trapped argon of the 'clod' spherules. If the trapped argon is of solar wind origin (see Section 4) the trapped gas is derived from a gas-impregnated material, presumably regolith fines with a large Ar^{40}/Ar^{36} ratio. Yaniv and Heymann (1972) have suggested that large ratios occur in relatively 'old' regolith. Judging from their work, this regolith may have existed more than 4000×10^6 yr ago.

Let us assume, however, that all the trapped argon in the 'clod' spherules is of primordial origin. Whence did the Ar^{40} come, now seen to correlate with Ar_P^{36}? Obviously from K^{40} decay in the parent rocks of the green glass. The maximum concentration of Ar_P^{36} in the parent rock can then be estimated by assuming:

(a) that the parent rock formed 4600×10^6 yr ago;

(b) that the spherules formed 3400×10^6 yr ago (see below);

(c) that the K content of the parent rock was the same as that of these spherules, 113 ppm (Drs J. Huneke and F. Podosek, private communication);

(d) that Ar^{40} was zero 4600×10^6 yr ago;

(e) that the parent rock was a closed system until the glass formed.

With these assumptions one calculates that the parent rock contained about 2×10^{-6} cm^3 STP g^{-1} of Ar_P^{36}, an amount only slightly greater than the amounts of Ar^{36} now seen in the spherules from the 'clods'. This would seem to imply that only little Ar_P^{40} was lost during the formation of the spherules.

We have already suggested that the Ar^{40} intercept values probably represent *in situ* formed radiogenic Ar^{40}. For *bulk* fines, which consist of many components, a calculated K–Ar^{40} age is meaningless, because the apparent age is almost certainly a 'mix' of component ages which may be widely different. In the case of the green spherules, however, the 'Ar^{40}-intercept age' may be meaningful, and may be identical with the age of formation of the spherules. Using the K content determined in 15426 spherules by Drs J. Huneke and F. Podosek (private communication), 113 ppm, we have calculated K–Ar^{40} ages for all the intercept – values listed in Table III. The results indicate that the spherules may be as old as 4400 and as young as 2500×10^6 yr. The preliminary results of an Ar^{39}–Ar^{40} age-determination of 15426 spherules (Drs J. Huneke and F. Podosek, private communication) at Caltech gives about 3400×10^6 yr.

6. Origin of the Spherules

The greatest concentration of spherules, green glass, and 'cloddy' materials were found near the rim of Spur Crater. Could it be that the spherules and the 'clods' were formed by the Spur Crater event, perhaps from the impacting projectile? This can be ruled out on the basis that the formation age of the spherules is greater than 3000×10^6 yr, whereas the Spur Crater event must be younger than about 350×10^6 yr, the radiation age of the 'clod' spherules.

Spur Crater must therefore be underlain by a body, or even a layer of green glass, presumably a 'cloddy' layer, which was deposited between 2500 and 4400×10^6 yr ago, most likely about 3400×10^6 yr ago.

LSPET (1972) and Ridley *et al.* (1972) have argued that the green glass must have come from upslope, i.e. from the Apennine Front, because of the paucity of the green glass at the Mare and Rille stations. However, this is not necessarily so, if the deposition of the green glass *predates* the most recent igneous flow in the Mare terrain. If the age of crystalline rocks from Apollo 15, about 3300×10^6 yr (Wasserburg *et al.*, 1972) represents the date of a local extrusion, any such layer may have been destroyed in the lower lying areas.

The presence of trapped gas in the 'clod' spherules, which is not directly implanted solar wind can be reconciled with the formation of the spherules in the presence of an ambient gasphase, but does not require a gasphase. However, the occurrence of many recrystallized spherules suggests relatively slow cooling of the 'clods', which favors cooling in the presence of a gasphase. This, in turn, could mean that the green material was carried to its present location by a gasphase, possibly in a base-surge type event, and that the weakly coherent breccias, the 'clods' were formed by this event also.

The variation in the radiation ages seems to suggest that the green glass is not restricted to a relatively narrow body at Spur Crater, but may underly much of the front. The radiation age of spherules from 15401 could mean that the layer of green material itself is very thick, several meters at least, with 15401 spherules coming from deeper than 15426 spherules, or that this layer became covered by several meters of normal regolith fines within a few tens of millions of years after its formation at the original location of the 15401 spherules, and within a few hundred million years at Spur Crater.

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