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Pre-atmospheric depths and thermal histories of Canyon Diablo spheroids

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Abstract–Despite having melted during formation, seven of eight Canyon Diablo spheroids weighing from 0.6 to 13 mg retain cosmic-ray-produced ^{38}Ar ($^{38}Ar_{cos}$) in concentrations (10^{-10} cm^3 STP/g) ranging from 0.35 to 68. The presence of $^{38}Ar_{cos}$ is consistent with pre-atmospheric depths of <2.3 m and most likely rules out an origin for the spheroids deep within the projectile, which had a radius of ~15 m. Low levels of $^{21}Ne_{cos}$ indicate gas loss from these spheroids. Relative to most Canyon Diablo meteorites, the spheroids contain lower concentrations of cosmogenic noble gases. The difference partly reflects diffusion losses from the spheroids, especially for ^{3}He and ^{21}Ne, but also suggests deeper locations on average for the precursor material, consistent with independent results from ^{59}Ni.

INTRODUCTION

The impact of the Canyon Diablo (IAB) projectile peppered the soil around Meteor Crater with millimeter-sized spheroids consisting mainly of metallic Fe and Ni (Nininger, 1956). Nininger speculated that the spheroids condensed from a vapor cloud as fiery rain. Several authors have argued against this speculation (Kelly *et al.*, 1974; Blau *et al.*, 1973; Mittlefehldt *et al.*, 1994), suggesting instead that the spheroids formed from a liquid generated either by atmospheric friction and/or by shock melting on impact.

We wanted to find out more about the quantity and location of projectile material that melted to form spheroids. From sampling data, Nininger (1956) estimated a total spheroid mass of 4000 to 7500 metric tonnes, roughly 5% of the impactor. More recently, E. Pierazzo determined through theoretical modeling calculations that a 1 to 2 m cap on the trailing surface of the projectile would have remained solid (Schnabel *et al.*, 1999). This result is consistent qualitatively with several other lines of evidence, namely, an earlier theoretical treatment (Bjork, 1961), which showed that a reflected shock wave would shear (solid) meteorites off the rear surface of the projectile; track measurements, which show that despite heavy ablation, numerous meteorites consist of fragments that originated near the pre-atmospheric surface (Bhandari *et al.*, 1980); and experimental results for noble gases in Canyon Diablo meteorites (Heymann *et al.*, 1966), which indicate pre-atmospheric depths of <2 m.

The theoretical modeling calculations of Pierazzo predict that the rest of the projectile, some 80% of the total, melted, thereby yielding more than enough material to account for the spheroids. By the same token, with so much of the projectile liquefied, the calculations were unavoidably mute as to where, exactly, the incipient spheroids were located within the parent projectile.

In large iron meteoroids such as the one that was to become Canyon Diablo, the concentrations of certain nuclides produced by cosmic rays—^{21}Ne and ^{38}Ar, for example—change unambiguously and in known ways with depth. In principle, then, the measurement of cosmogenic nuclides in Canyon Diablo spheroids should help to pin down the depth of the spheroids' precursor material in the projectile. The realization of this idea poses some practical problems. The spheroids typically have masses of 10 mg or less, and may therefore contain relatively few atoms of interest. To a degree, improvements in analytical sensitivity address this issue. More important, the spheroid formation process, which included not only melting, but also reaction with oxygen, mass loss, and incorporation of terrestrial target rock, presented many opportunities for the corruption or even obliteration of the cosmogenic nuclide record. The spheroids probably lost ^{10}Be and ^{26}Al, for example, as a consequence of oxidation (Xue *et al.*, 1995). Schnabel *et al.* (1999) circumvented many of these problems by taking advantage of the fact that spheroids should preserve their original $^{59}Ni/Ni$ isotope ratios through any chemical fractionation. Their measurements of $^{59}Ni/Ni$ ratios placed the embryonic spheroids at pre-atmospheric depths of 1–2 m. Only with pooled samples consisting of several spheroids, however, did Schnabel and co-workers obtain enough mass to analyze. Thus, each of their measurements could have

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averaged, at least theoretically, the ^{59}Ni activities produced over a considerable range of depths.

Looking for ways to press further and to determine the pre-atmospheric depths of individual spheroids, we considered the cosmogenic noble gases. At first glance, a search for cosmogenic noble gases in Canyon Diablo spheroids seemed an unpromising enterprise. Why would objects that melted retain any gas at all? On reflection, the details left room for hope. In the temperature range over which solidification occurs, 1773 to 1273 K, metallographic estimates of the maximum cooling rates lie between 500 and 30 000 K/s with a geometric mean of 2700 K/s (Blau *et al.*, 1973). The cooling rates tell us that the spheroids probably spent at most a second or two as a melt, and that many froze faster. We wondered whether such short heating times might permit the retention of some gas. Among the candidate isotopes for analysis, those of argon stood out by virtue of their higher production rates by cosmic rays and their higher activation energy for diffusion in iron meteorites (Fechtig *et al.*, 1963). At the time we began to consider these measurements, we had just improved the mass spectrometer system in ways that lowered significantly the blanks for noble gases. With lowered blanks, the measurements seemed, at least, worth a try. We present here noble gas analyses of several samples of Canyon Diablo spheroids, including individual spheroids, and then explore the implications for the spheroid formation process. Leya *et al.* (2000a, 2001a) have presented these results in preliminary form.

EXPERIMENTAL METHODS

Samples

Dr. Carleton Moore kindly supplied three batches of spheroids, III, IV, and V, with average masses (mg) of 6.6, 1.0, and 10, respectively. The samples described by Xue *et al.* (1995) and Schnabel *et al.* (1999) came from these same batches. We took three different types of spheroid samples for noble gas analysis: individual whole objects (sp), individual metallic cores (mc), and non-magnetic material collected from the exterior of several spheroids (nm). To isolate metal cores from spheroids, we ground the whole spheroids gently to remove exterior material and then etched twice with HF in an ultrasonic bath for 5 min. We separated non-magnetic material from separate groups of spheroids by etching with HF in an ultrasonic bath for 5 min, collecting particles that flaked off, and removing from them remaining magnetic particles with a hand magnet.

Noble Gas Measurements

The noble gas measurements were then performed at the ETH Zürich using a newly developed laser-extraction system. The spheroid samples were loaded into aluminum holders with 2 mm-sized holes set ~5 mm apart. We will refer to the set of measurements made for each sample mount as a "run". We measured the He and the Ne but not the Ar released from the spheroids of sample set G; we analyzed the H-series samples for all three gases. In particular, noble gases were extracted by melting individual spheroids with a Nd-YAG laser (1064 nm) operated in continuous wave mode. To avoid gas losses from neighboring grains on the sample mount, the sample holder is water-cooled. Aluminum has a good thermal conductivity and promotes a homogeneous temperature distribution.

Tests with indium emplaced near the laser-irradiated sample have shown that material adjacent to the irradiated grain never reaches temperatures of 150 °C. Tests with individual lunar grains have demonstrated that the laser heating degasses the samples completely.

During the measurements reported here, the $^{20}Ne/^{21}Ne$, $^{22}Ne/^{21}Ne$, and $^{36}Ar/^{38}Ar$ ratios for the background changed little. Their constancy allowed us to correct the measured data with an internal blank as described below. Ratios involving ^{40}Ar, on the other hand, varied due to memory effects.

Blanks

Blanks were determined by aiming the laser at degassed spheroids. The signal at mass 3 came primarily from spectrometer background, is attributed to HD, and corresponds to $(2–4.5) \times 10^{-12}$ cm^3 STP. The amounts of ^4He, ^{20}Ne, and ^{40}Ar in the blanks (10^{-12} cm^3 STP) were typically 50, 5, and 2000, respectively. Though small by the standards of normal static noble gas mass spectrometry, these blanks were significant relative to the amounts of gas released from the spheroid samples. They also varied appreciably within each run (*i.e.*, by factors of 2, 2.5, and 1.4 for ^4He, ^{20}Ne, and ^{40}Ar, respectively). For ^4He in different runs the variations were larger—a factor of 10. To obtain the ^4He concentrations reported in Table 1, we subtracted blanks of 30×10^{-12} cm^3 STP and 300×10^{-12} cm^3 STP for the samples of the G and of the H series, respectively. Fortunately for our purposes, the neon and the argon isotopic ratios of the blanks were atmospheric within the uncertainties. For this reason, we chose to make no blank corrections in reporting the neon and the argon data of Table 1. Instead, for the calculation of cosmogenic neon and argon below, we carried out a two-component deconvolution of the measured concentrations, assuming that the gas comprised only atmospheric and cosmogenic components. This procedure also assumes that no isotopic fractionation occurred when the spheroids gained or lost neon or argon.

RESULTS

In Table 1, we present the results of the noble gas measurements; only ^4He has been corrected for blanks. For comparative purposes we have included in Table 1 certain data for Canyon Diablo meteorites, namely, (a) average values

TABLE 1. Light noble gases in Canyon Diablo spheroids*.

Sample	Mass	^{3}He	^{4}He	^{22}Ne	^{20}Ne/^{22}Ne	^{21}Ne/^{22}Ne	^{38}Ar	^{36}Ar/^{38}Ar
Canyon Diablo spheroids								
III-G2-sp	=6.6†	15.6	450 ± 45	36.1	11.8 ± 2.2	0.063 ± 0.002	–	–
III-G3-sp	=6.6†	–	75 ± 8	<2.1	–	–	–	–
IV-G1-sp	=1†	–	23 ± 8	–	–	–	–	–
V-G1-sp	=10†	0.18	5.3 ± 0.5	–	–	–	–	–
III-H1-mc	9.1	–	210 ± 4.5	2.5 ± 1.0	6.4 ± 2.4	0.001 ± 0.016	109 ± 21	4.4 ± 0.2
III-H2-mc	11.2	–	3.3 ± 0.9	2.8 ± 0.6	9.0 ± 1.9	0.038 ± 0.018	53 ± 10	4.6 ± 0.1
IV-H3-mc	1.06	–	128 ± 31	18.3 ± 7.4	8.9 ± 3.6	0.013 ± 0.034	997 ± 196	5.0 ± 0.2
IV-H4-mc	1.88	–	0.9 ± 0.5	2.3 ± 3.8	6.4 ± 10.6	0.138 ± 0.238	3 ± 1	4.7 ± 0.2
IV-H5-nm	0.61	–	49 ± 14	5.5 ± 11.3	4.6 ± 9.4	0.020 ± 0.151	48 ± 9	4.6 ± 0.2
IV-H6-nm	0.87	–	18 ± 12	8.8 ± 11.4	1.9 ± 2.4	0.121 ± 0.164	25 ± 8	3.3 ± 0.9
V-H7-nm	13.23	–	57 ± 18	2.0 ± 0.8	7.4 ± 2.8	0.011 ± 0.010	–	
V-H8-nm	9.80	–	94 ± 40	0.7 ± 0.8	10.2 ± 11.8	–	28 ± 5	4.7 ± 0.1
Atmospheric	–	–	–	–	9.8	0.0292	–	5.32
Canyon Diablo meteorites								
Average‡	–	3500	282	90$	–	–	430	0.97
Average§	–	2400	283	–	–	–	434	1.14
Minimum#	–	20	7.0	2$	–	–	13	0.57

*^{4}He in 10^{-8} cm^{3} STP/g; ^{3}He, ^{21}Ne, ^{22}Ne and ^{38}Ar in 10^{-10} cm^{3} STP/g. Masses in milligrams. Uncertainties are 1σ. Sample naming is explained in the text.
†Set equal to the average mass for the spheroid batch.
‡Schultz and Franke (2000).
§Heymann *et al.* (1966).
#Minimum values reported for various meteorite specimens (Schultz and Franke, 2000).
$As relatively few ^{22}Ne contents have been reported for Canyon Diablo, we have estimated the values shown from published ^{21}Ne contents and the relation $^{22}\text{Ne} \approx 1.07 \times {}^{21}\text{Ne}$ established for other iron meteorites (Signer and Nier, 1960).

calculated from Schultz and Franke (2000); (b) average values calculated from the study of Heymann *et al.* (1966) only; and (c) the minimum value measured in any Canyon Diablo meteorite for each isotope; these minimum values are generally from different samples (Schultz and Franke, 2000).

Helium

Only for one sample of 12 analyzed, the spheroid III-G2-sp, does the observed ^{3}He signal rise convincingly above the level of the HD background. For this sample, a two-component deconvolution of the cosmogenic (cos) component based on ^{4}He/^{3}He ratios of 4.2 for cosmogenic (Heymann *et al.*, 1966) and 7.30×10^{5} for atmospheric helium (IUPAC, 1991) gives ^{3}He$_{cos}$ = 15.5×10^{-10} cm^{3} STP/g (Table 2).

In general, the ^{4}He concentrations of the spheroids must be the result of terrestrial contamination. We reach this conclusion as follows. In Canyon Diablo meteorites the median ^{4}He/^{3}He ratio is 4.2 (Heymann *et al.*, 1966) and we would expect a similar value in the spheroids' precursors. Thus, if an appreciable fraction of the ^{4}He were cosmogenic, then cosmogenic ^{3}He would have been easy to detect, contrary to what we find. Consistent with this conclusion, the two spheroid samples with the lowest ^{4}He contents, III-H2-mc and IV-H4-mc, are both metallic cores, just as one might expect if altered meteoritic material or a terrestrial contaminant were somehow responsible for the terrestrial ^{4}He.

Neon

The spheroid samples also contain mostly terrestrial neon (Fig. 1). In three or perhaps four samples, III-G2-sp, IV-H4-mc, IV-H6-nm, and III-H2-mc, we see hints of displacement from the atmospheric ratios of neon. A two-component deconvolution results in the nominal cosmogenic ^{21}Ne concentrations given in Table 2. We will treat them as upper limits. The largest upper limit, 1.06×10^{-10} cm^{3} STP/g for IV-H6-nm, is about half the minimum ^{21}Ne content reported for any Canyon Diablo meteorite.

For purposes discussed below, we have also estimated upper bounds on the ^{21}Ne$_{cos}$ contents of the other samples. We calculated the upper bounds by assuming that the upper limit for ^{21}Ne in the sample is given by 3× the excess ^{21}Ne over atmospheric that we would be able to detect. The upper limits calculated in this way are between 5.4×10^{-12} cm^{3} STP/g and 2.4×10^{-10} cm^{3} STP/g, with an average of 8.9×10^{-11} cm^{3} STP/g.

TABLE 2. Cosmogenic gases in Canyon Diablo spheroid samples and inferred sample depths.

Sample	^{3}He	^{21}Ne	^{38}Ar	Depth (cm)		
	(10^{-10} cm^3 STP/g)			*	†	‡
III-G2-sp	16 ± 8	<1.0	–	220	–	–
III-H1-mc	–	–	21 ± 6	130	–	121
III-H2-mc	–	<0.02	8.3 ± 1.7	150	<245	140
IV-H3-mc	–	–	68 ± 20	100	–	90
IV-H4-mc	–	<0.28	0.35 ± 0.08	240	<172	229
IV-H5-nm	–	–	7.6 ± 1.6	160	–	146
IV-H6-nm	–	<1.06	10.9 ± 2.2	145	<146	134
V-H8-nm	–	–	3.5 ± 0.07	180	–	168
Minimum§	20	11	22	97	–	–

*Calculated from ^{38}Ar or ^{3}He assuming a cosmic-ray exposure age of 540 Ma.
†Upper limit calculated from ^{21}Ne.
‡Calculated from ^{38}Ar assuming ^{38}Ar diffusion losses of 33% and a cosmic-ray exposure age of 540 Ma.
§For meteorites; see Table 1.

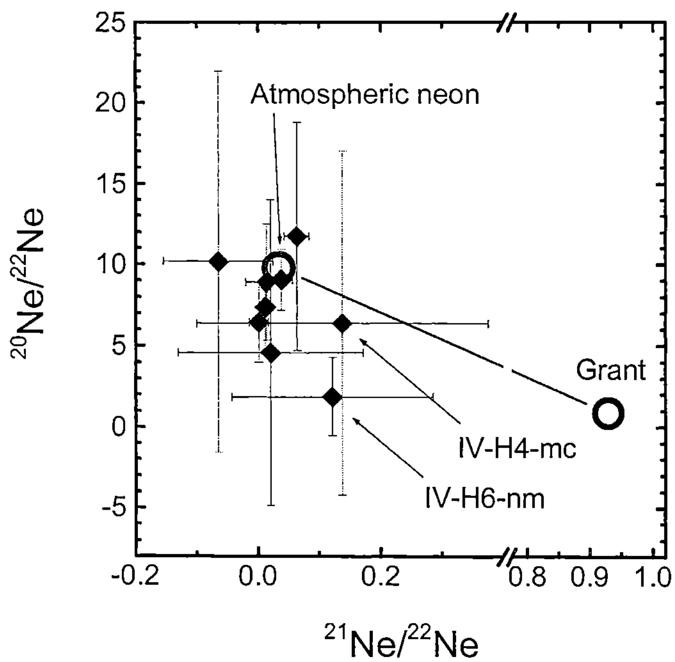

FIG. 1. Isotopic composition of neon in Canyon Diablo spheroids, in the Grant iron meteorite (cosmogenic neon; Schultz and Franke, 2000), and in the Earth's atmosphere. Most of the neon in the spheroids is atmospheric although the data hint at the presence of small concentrations of cosmogenic neon in some samples (see text).

Argon

We were able to analyze for argon in all but one (V-H7-nm) of the eight samples of set H. Of seven spheroid samples in which argon was detected, six have $^{36}Ar/^{38}Ar$ ratios that are more than 2σ lower than the atmospheric value of 5.32. The weighted average ratio for these six samples is 4.62 ± 0.07; the grand average for all seven spheroids analyzed is 4.65 ± 0.07. In Canyon Diablo meteorites, $^{36}Ar/^{38}Ar$ ratios average to ~1.0. We conclude that many spheroids retain appreciable concentrations of cosmogenic argon. To extract the cosmogenic component of ^{38}Ar, we assumed the argon to have been a mixture of an atmospheric component with a $^{36}Ar/^{38}Ar$ ratio of 5.32 and a cosmogenic component with a $^{36}Ar/^{38}Ar$ ratio of 0.65. The cosmogenic ^{38}Ar concentrations (10^{-10} cm^3 STP/g) calculated in this way range from 0.35 to 68, and average to 18 (Table 2). In Canyon Diablo meteorites, cosmogenic ^{38}Ar concentrations (again in 10^{-10} cm^3 STP/g) tend to be higher by about a factor of 20, ranging from 7 to 1760, and averaging ~400. Though appreciable, the relative difference between spheroids and meteorites is smaller than the corresponding difference in $^{21}Ne_{cos}$. Specifically, we may compare the average concentration of $^{21}Ne_{cos}$ (10^{-10} cm^3 STP/g) in Canyon Diablo meteorites, 90 (Schultz and Franke, 2000), with the upper bound of 1 for spheroids (Table 2). In Canyon Diablo meteorites, the average reported cosmogenic $^{21}Ne/^{38}Ar$ ratio is ~0.33. For the spheroids, we were unable to detect both $^{21}Ne_{cos}$ and $^{38}Ar_{cos}$ in the same samples and hence cannot calculate their $^{21}Ne/^{38}Ar$ ratios. It seems likely that heating drove out most of the cosmogenic neon. It is puzzling that the two samples with the highest cosmogenic ^{38}Ar, III-H1 and IV-H3, show no cosmogenic ^{21}Ne.

Non-Cosmogenic Component

The ratio (atom/atom) of $^{4}He/^{20}Ne$ in the Earth's atmosphere is ~0.32, much smaller than the ratios of 6 to 1300 (average, ~400; geometric mean, 100) observed for the spheroid samples. As suggested above, the high $^{4}He/^{3}He$ ratios rule out a cosmogenic origin for most of the ^{4}He in the spheroids. Unless the ^{4}He is released by some unknown process from the extraction line when spheroids—and only undegassed spheroids—are heated, they appear to contain unsupported radiogenic ^{4}He, accumulated, somehow, during the spheroid formation process. Mead *et al.* (1965) observe that directly below a thin brown layer of oxide, most spheroids have a "fragile thin white coating of silica or siliceous glass generally a fraction of a millimeter thick. This white isotropic glass coating...contains numerous powdery angular fragments of quartz. Inside the siliceous glass coating, commonly a layer of gray iron oxide of variable composition and thickness wraps around a core of metallic nickel iron." Perhaps one or more of the oxide phases hosts a portion of the non-cosmogenic helium. If so, the concentration of ^{4}He would have to be very high. The assumption that the silicate glass makes up 10% of the total mass results in ^{4}He concentrations between 3×10^{-5} cm^3 STP/g and 1×10^{-2} cm^3 STP/g with an average of 3×10^{-3} cm^3 STP/g.

DISCUSSION

Negligible Terrestrial Production of Noble Gases in Spheroids

The terrestrial age of Canyon Diablo material is too short, <100 ka (Sutton, 1985; Nishiizumi *et al.*, 1991; Phillips *et al.*, 1991; Schnabel *et al.*, 2001) to have allowed the production of detectable concentrations of ^{3}He, ^{21}Ne, or ^{38}Ar on the Earth's surface. On scaling sea-level production rates (in atom (g Fe)$^{-1}$ year^{-1}) of 40 for ^{3}He and 0.2 for ^{21}Ne (Masarik and Reedy, 1996) by a factor of 2.57 (Lal, 1991) to account for the altitude of Meteor Crater, 1561 m, and assuming a terrestrial age no greater than 100 ka, we estimate total concentrations (cm^3 STP/g) from *in situ* production of $\sim 2 \times 10^{-13}$ and $\sim 1 \times 10^{-15}$, respectively. For ^{38}Ar, we calculated a sea-level production rate of 1.2 atom (g Fe)$^{-1}$ year^{-1} using the differential particle spectra given by Masarik and Beer (1999) and the cross sections discussed below. The total ^{38}Ar *in situ* production (cm^3 STP/g) then is $\sim 5 \times 10^{-15}$.

Maximum Spheroid Depths Inferred from Cosmogenic Gases

While Canyon Diablo spheroids might well have lost cosmogenic ^{3}He, ^{21}Ne, or ^{38}Ar by diffusion, it seems unlikely that they gained any from the terrestrial environment. Very likely then, the observed concentrations of the cosmogenic gases set upper bounds on the original concentrations in the incoming meteoroid and hence lower limits on sample depths. In considering these depths, we begin with ^{38}Ar$_{cos}$ because we have the most results for that isotope.

To translate a cosmogenic ^{38}Ar content for a spheroid sample into a pre-atmospheric depth, we compare the measured values with the results obtained from theoretical modeling of ^{38}Ar production. By using our computer codes (Leya *et al.*, 2000b), the particle fluxes for Canyon Diablo developed by J. Masarik (see Schnabel *et al.*, 1999), updated ^{38}Ar cross sections (Leya *et al.*, 2001b), and a cosmic-ray-exposure age for Canyon Diablo of 540 Ma (Heymann *et al.*, 1966; Michlovich *et al.*, 1994), we modeled the ^{38}Ar depth profile for Canyon Diablo. Figure 2a shows the ^{38}Ar$_{cos}$ contents plotted to fall on the modeled curve. Given the likelihood of some diffusion losses for ^{38}Ar$_{cos}$ (see below), the depths read from Fig. 2a and presented in Table 2 are upper limits. They range from 1.0 to 2.4 m with an average of 1.6 ± 0.4 m where $n = 6$ and the uncertainty is the standard deviation of the mean. Schnabel *et al.* (1999) estimated from ^{59}Ni activities of spheroid samples depths between 1.3 and 1.6 m (average 1.47 ± 0.14 m; where the comparable, relevant uncertainty for these pooled samples is the standard deviation with $n = 7$). A somewhat larger range for the ^{38}Ar-based depths, which apply to individual spheroids rather than to a group of samples, is not surprising. We return below to a comparison of the depths derived from ^{38}Ar and ^{59}Ni.

Proceeding in a similar way with ^{3}He$_{cos}$ and ^{21}Ne$_{cos}$, we obtain the estimates of depth shown in Table 2 and plotted in Fig. 2b. For sample IV-H4-mc, the lower limit on depth derived from the upper limit on ^{21}Ne, 172 cm, is shallower than the depth derived from ^{38}Ar, 240 cm. The expected ^{3}He content for this sample is 0.10×10^{-8} cm^3 STP/g, which must have been largely lost by diffusion. The results for sample III-H2-mc indicate significant loss of both ^{3}He and ^{21}Ne. In the absence of diffusion losses, the measured ^{38}Ar concentration would correspond to ^{3}He and ^{21}Ne concentrations of 1.9×10^{-8} cm^3 STP/g and 7.8×10^{-11} cm^3 STP/g, respectively. Therefore, most of the ^{3}He and the ^{21}Ne are lost by diffusion.

Diffusion Losses

Equation (1) gives an expression for the fraction of gas retained, f_{ret}, by a spherical body undergoing diffusion losses at constant temperature for a time t:

$$f_{ret} = \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} \exp(-n^2 \pi^2 D t / a^2) \qquad (1)$$

Here D is the diffusion coefficient and a is the characteristic diffusion length for the object (see Carslaw and Jaeger, 1959). Equation (2) shows the relation between the values of D/a^2 at temperatures T_2 and T_1 (Levine, 1978).

$$\frac{D}{a^2}(T_2) = \frac{D}{a^2}(T_1) \times \exp\left(\frac{-E_a}{R}\left\{\frac{1}{T_2} - \frac{1}{T_1}\right\}\right) \qquad (2)$$

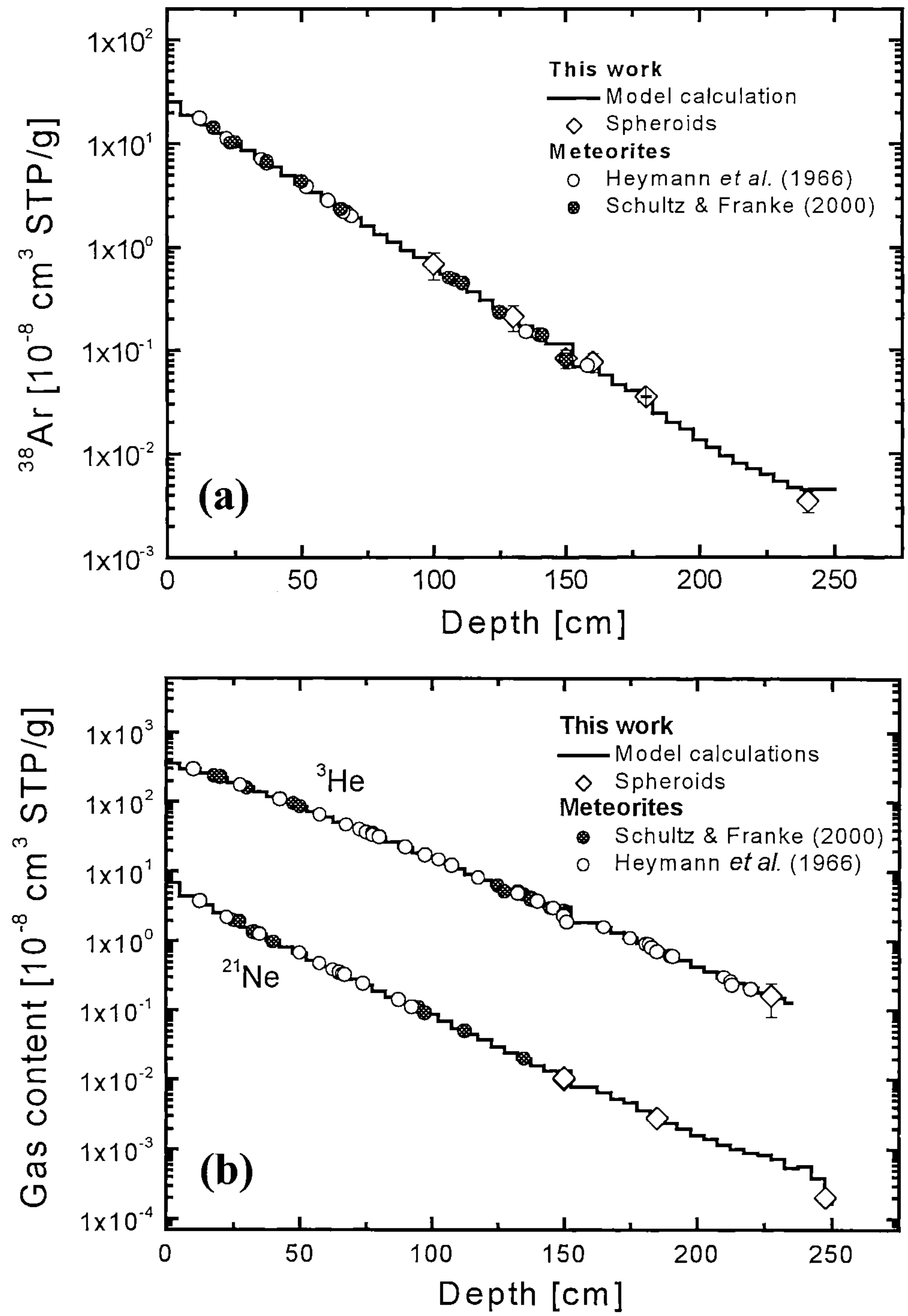

FIG. 2. (a) The expected concentrations of cosmogenic ^{38}Ar in Canyon Diablo material after 540 Ma of exposure in space calculated from the model of Leya *et al.* (2000b) with a particle flux provided by J. Masarik (Schnabel *et al.*, 1999). The data points represent analyses of noble gases in various Canyon Diablo meteorites and spheroids, with each point placed on the appropriate line. If a sample lost any gas, as many spheroids did, the depth read for that point is an upper limit. (b) Same as (a) but for ^{3}He and ^{21}Ne.

Here R is the gas constant, 8.314 J mol^{-1} K^{-1}, and E_a is the activation energy. Fechtig *et al.* (1963) studied diffusion of the light noble gases from the iron meteorite Sikhote Alin. They present the following values of D/a^2 (s^{-1}) and activation energies, E_a (kJ/mol) at 303 K: ^{3}He, 10^{-30}, 230; ^{21}Ne, 10^{-34}, 255; and ^{38}Ar, 10^{-36}, 259. To estimate the fractions of ^{3}He, ^{21}Ne, and ^{38}Ar that the spheroids retain, we also need an effective temperature and time for diffusion. In calculating the cooling histories of spheroids, Blau *et al.* (1973) adopt 1523 K as the midpoint of the temperature range over which the spheroid

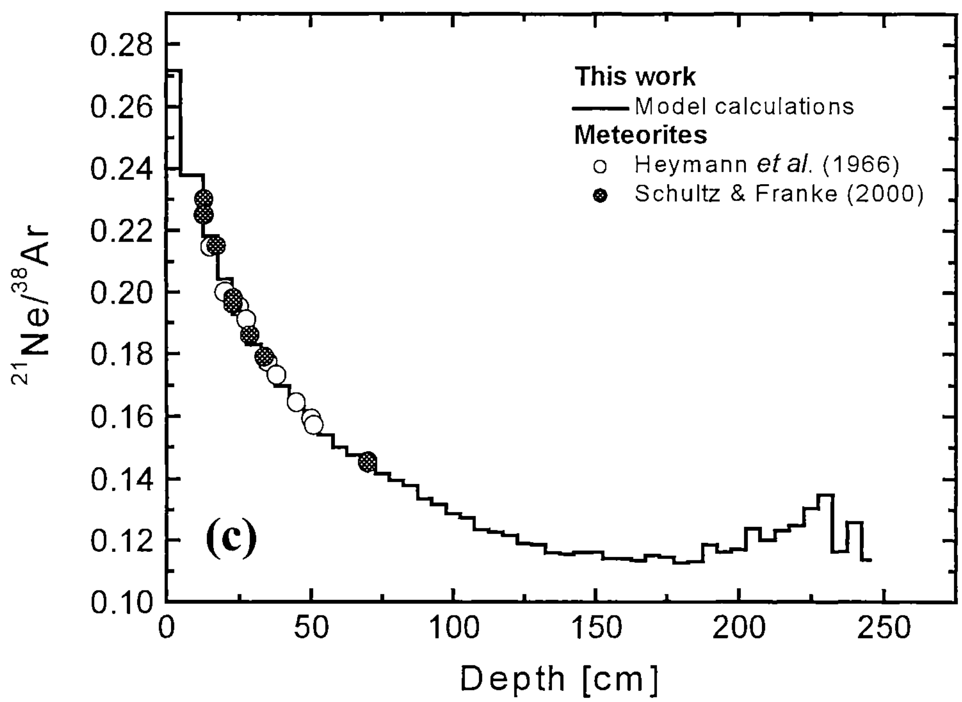

FIG. 2. *Continued.* (c) Model calculations of $^{21}Ne/^{38}Ar$ ratios for Canyon Diablo material as a function of depth.

droplets solidify. Figure 3 shows for effective temperatures of 1200 and 1523 K the fractions of the gas retained for various heating periods. We do not attach much quantitative importance to the results because it seems doubtful that a formula for isothermal diffusion can capture the complex cooling histories of the spheroids. Nonetheless, qualitatively, the calculations suggest that ^{38}Ar can be largely retained over a range of heating times during which much of the ^{3}He and ^{21}Ne are lost. Our results for the spheroids bear out this feature of the calculations.

Depths of Spheroids from Gas Contents Adjusted for Estimated Diffusion Losses

The most extreme scenario for diffusion loss places all the spheroids at the surface of the meteoroid, where production rates reached maximum values and irradiated material would have acquired ~25 × 10^{-8} cm^3 STP/g of ^{38}Ar. Unfortunately, we cannot rule out this possibility on the basis of the noble gases alone. If true, it would imply that the spheroids retain only 0.014 to 2% of their initial argon and virtually none of their ^{3}He or ^{21}Ne (Fig. 3). If such a large fraction of the Ar were lost in Rayleigh evaporation, we would also expect reductions of 13% or more in the $^{36}Ar/^{38}Ar$ ratios of the spheroids. Our current blanks make it impossible for us to see any such effect. It is worth reiterating, however, that the results for ^{59}Ni (Schnabel *et al.*, 1999) do not support the hypothesis that spheroids came from the surface.

A less radical way to arrive at ^{38}Ar diffusion losses is to assume that the ^{21}Ne contents of the spheroids are about half the minimum detection limit (HMDL) for that isotope. Although largely a guess, this assignment of ^{21}Ne is based on the observation, noted above, of hints of cosmogenic ^{21}Ne in three out of the eight spheroid samples.

We calculated the ^{21}Ne detection limits from the ^{22}Ne concentrations and $^{21}Ne/^{22}Ne$ ratios given in Table 1. Assuming all ^{20}Ne and ^{22}Ne to be atmospheric contamination gives the ^{21}Ne blank value for each spheroid. If we set the ^{21}Ne detection limit at 3× the detectable excess of ^{21}Ne over atmospheric, as explained above, then we obtain the following HMDL-values (10^{-11} cm^3 STP/g): III-H1-mc, 1.2; III-H2-mc, 1.3; IV-H3-mc, 18; IV-H4-mc, 4.6; IV-H5-nm, 24; IV-H6-nm, 1.3; and V-H7-nm, 0.5. With these HMDL-values and the $^{38}Ar_{cos}$ concentrations from Table 2, we calculate cosmogenic $^{21}Ne/^{38}Ar$ ratios between 0.005 and 0.027. We reject the results for samples IV-H4-mc and IV-H5-nm because the $^{21}Ne/^{38}Ar$ ratios of 1.3 and 0.3, respectively, are higher than the predictions (based on nuclear modeling calculations; see above) for any depth within the meteoroid. They are also higher than the $^{21}Ne/^{38}Ar$ ratios observed in most iron meteorites (see Voshage and Feldmann, 1978).

In Fig. 2c, we show the $^{21}Ne/^{38}Ar$ ratio obtained from our modeling calculations (no diffusion loss) as a function of shielding depth for large iron meteoroids together with some Canyon Diablo data. The model predicts $^{21}Ne/^{38}Ar$ ratios between 0.11 and 0.27. The estimates for the spheroids are lower by factors 4.0–54. If we attribute lowering of the ratio to diffusion losses of ^{21}Ne and ^{38}Ar, then we can deduce temperatures and heating times by using the data from Fig. 3. Heating times of ~0.1 s at 1523 K or ~1.4 s at 1200 K reproduce the estimates of the $^{21}Ne/^{38}Ar$ ratio (*i.e.*, reduce the undisturbed

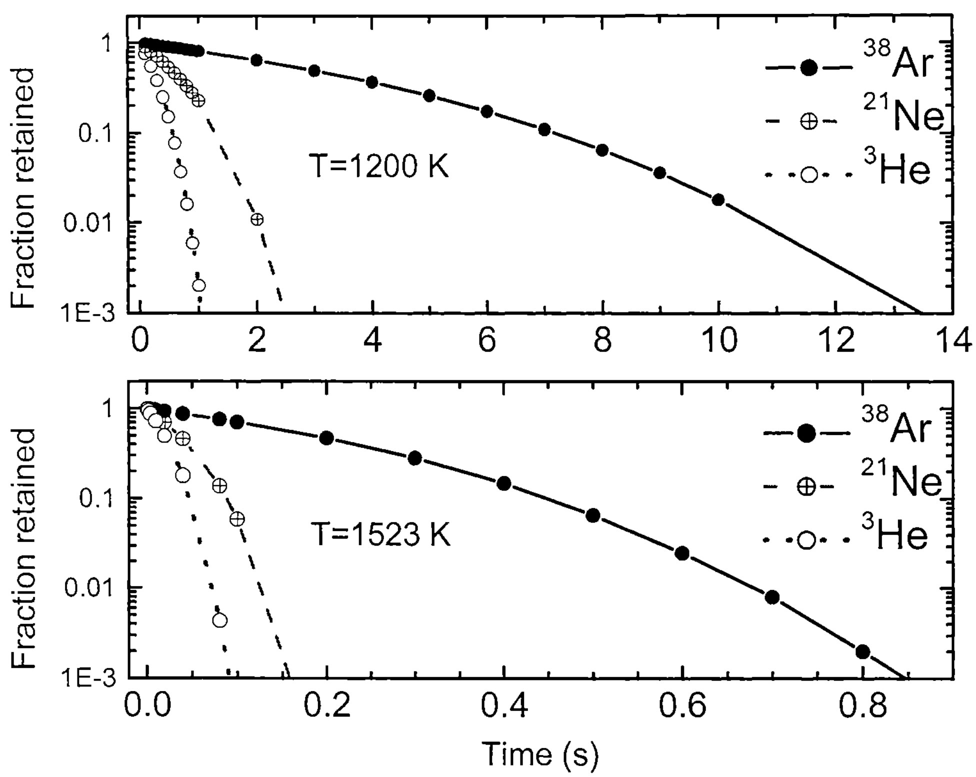

FIG. 3. Diffusion losses of cosmogenic noble gases from spheroids estimated assuming isothermal heating of spheres at two different temperatures. Although the mathematical model is no doubt too simple, the results suggest that spheroids can retain substantial fractions of cosmogenic ^{38}Ar under conditions where most of the cosmogenic ^{21}Ne and ^{3}He are lost.

$^{21}Ne/^{38}Ar$ ratio by a factor of 10). The former heating scenario (1523 K) corresponds to ^{21}Ne and ^{38}Ar diffusive losses of 94 and 30% and the latter (1200 K) to losses of 88 and 36%. As noted above, Blau *et al.* (1973) estimate maximum cooling rates ranging from 550 to 33000 K/s for the temperature range from ~1250 to 1750 K (see their Table 3, page 369), a range over which loss of noble gases might be expected. Our estimates of the cooling times are thus in the same range as those of Blau *et al.* (1973).

We checked our estimates of sample depths for robustness by assuming the $^{21}Ne_{cos}$ detection limit to be ~10×, rather than 3×, the excess ^{21}Ne over atmosphere we would be able to detect. Again excluding samples IV-H4-mc and IV-H5-nm, we find $^{21}Ne/^{38}Ar$ ratios between 0.015 and 0.089. These ratios are closer to but are still lower than the modeled ratios by factors of 1.2–18. The required heating times are ~0.12 s at 1523 K or ~1.8 s at 1200 K. The corresponding diffusion losses for ^{21}Ne and ^{38}Ar, respectively, are >99 and 50% at 1523 K and ~99 and ~35% at 1200 K. The relatively small change in the fractional losses of ^{38}Ar requires minimal adjustments to the estimates of pre-atmospheric sample depth given above. We conclude that the spheroids came from pre-atmospheric depths between 90 and 230 cm. In the next section we compare Canyon Diablo spheroids and meteorites with respect to their pre-atmospheric depths.

Depths of Spheroids and Depths of Canyon Diablo Meteorites Compared

Heymann *et al.* (1966) and Michlovich *et al.* (1994) estimated pre-atmospheric depths for various Canyon Diablo meteorites. Here we present new depth estimates based on published cosmogenic ^{3}He, ^{21}Ne, and ^{38}Ar contents (Schultz and Franke, 2000), our production rates from model calculations (see above), and an exposure age of 540 Ma (Heymann *et al.*, 1966; Michlovich *et al.*, 1994). The approach is similar to the one adopted above for spheroids, except that we assume no diffusion losses for the meteorites. Specifically, we took each published determination of cosmogenic ^{3}He, ^{21}Ne, or ^{38}Ar, divided by 540 Ma to obtain a production rate, and then, by inspection of Fig. 2a,b, determined the depth at which our model calculations gave the required production rate. Overall, the average depths obtained from ^{38}Ar, 75 ± 45 cm ($n = 26$), and from ^{21}Ne, 60 ± 31 cm ($n = 24$) are comparable; the uncertainty quoted is σ, the standard deviation. These average depths are smaller than the one obtained from ^{3}He, 130 cm ($\sigma = 60$ cm; $n = 62$), probably for two reasons. First, the number of samples analyzed for ^{3}He is larger. Second and likely more important, the concentrations and the instrumental sensitivity are larger for ^{3}He; both factors make it easier to analyze heavily shielded samples for ^{3}He than for ^{21}Ne and

^{38}Ar. For meteorites in which *both* ^{38}Ar and either ^{3}He and/or ^{21}Ne are reported, the depths inferred from ^{3}He and ^{21}Ne tend to be lower by ~25% than those inferred from ^{38}Ar. These differences may reflect experimental uncertainties, diffusion losses of ^{3}He from some samples, and/or uncertainties in the model calculations (Heymann *et al.*, 1966).

The depths calculated from the ^{38}Ar contents of the spheroids are generally larger than those estimated for Canyon Diablo meteorites (Fig. 2a) although the ranges for the two types of sample overlap for depths of about 1–1.5 m. The ^{3}He and ^{21}Ne contents of the spheroids are clearly lower than most of the values measured for the Canyon Diablo meteorites. This observation and the numbers of samples for which we were able to estimate cosmogenic gases—seven for ^{38}Ar, four upper limits for ^{21}Ne, and one for ^{3}He—are consistent with expectations concerning relative diffusion losses for the three nuclides.

Vertical Mixing of the Projectile Melt

It is striking that seven of eight samples of spheroids analyzed individually for argon came from a relatively narrow range of pre-atmospheric depths below but relatively close to the surface of the meteoroid—from ~1 to 2 m. The good overlap between the depths inferred from ^{38}Ar for single spheroids and from ^{59}Ni for groups of spheroids suggests that spheroids from the center (if they exist) and the exterior of the meteoroid did not mix extensively after the spheroids froze. If we take our calculated depths at face value, and assume that the Canyon Diablo projectile had a pre-atmospheric radius of ~15 m (Roddy *et al.*, 1980), then at most one-fourth of the mass, and probably less, contributed to spheroid formation. Heymann *et al.* (1966) point out that among Canyon Diablo meteorites, the specimens collected closest to the crater rim tend to be more heavily shocked and to have come from greater depths than do meteorites collected further afield. Moreover, both the heavily shocked rim specimens and the spheroids are concentrated to the northeast and southeast of the crater. The obvious inference is that the two types of samples came from adjacent or nearby regions in the projectile and sampled different portions of a continuum of materials heated to differing degrees. In the calculations of E. Pierazzo, those regions would have been in the trailing half of the projectile (Schnabel *et al.*, 1999).

For completeness, we note another possible explanation of our results. It is conceivable, although it seems farfetched, that prior to forming spheroids, large volumes or sheets of liquid from different portions of the meteoroid mixed incompletely, but enough to insure that most spheroids-to-be incorporated some near-surface material.

CONCLUSIONS

Seven of eight Canyon Diablo spheroid samples analyzed for cosmogenic helium, neon, and argon contained at least traces of cosmogenic ^{38}Ar. We conclude that the spheroids did not condense from a gas that formed when the projectile vaporized because it is hard to imagine how the spheroids could have recaptured the cosmogenic gases. Blau *et al.* (1973) and Kelly *et al.* (1974) reached the same conclusion based on different kinds of compositional evidence. The widespread presence of cosmogenic ^{38}Ar in Canyon Diablo spheroids strongly suggests but does not prove that they contain very little material from the interior portions of the projectile, where virtually no production of ^{38}Ar occurs. Comparisons of the experimental data with theoretical calculations of ^{38}Ar production in the projectile imply that the spheroids originated at depths of 0.9 to 2.3 m; we assume here a single-stage exposure of 540 Ma. This range of depths is consistent with the findings of Schnabel *et al.* (1999) for groups of spheroids and extends them to individual particles. Evidently, conditions during the impact did not lead to extensive mixing of solid spheroids formed from material at different depths. Although possible, it also seems unlikely to us that melt from different depths in the projectile mixed extensively before the spheroids quenched. We conclude that the spheroids formed from material just below or adjacent to the region that gave rise to the Canyon Diablo meteorites, probably in the trailing hemisphere of the projectile. Heating of the spheroids was sufficient to drive out most of the ^{3}He and ^{21}Ne; with large uncertainty, we estimate that ^{38}Ar losses were between 30 and 50%. Strong temperature gradients, increasing toward the interior of the projectile (see Schnabel *et al.*, 1999), should have affected meteorites as well as spheroids. We might then predict that Canyon Diablo meteorites with the smaller ^{38}Ar contents typical of deeper locations should have lower ^{3}He/^{38}Ar ratios as a result of ^{3}He diffusion (*i.e.*, that they should increasingly take on the characteristics of spheroids). The ^{3}He/^{38}Ar ratios for samples with the lowest ^{38}Ar contents scatter appreciably (Fig. 4). Modern noble gas analyses of Canyon Diablo meteorites with low gas contents might be rewarding.

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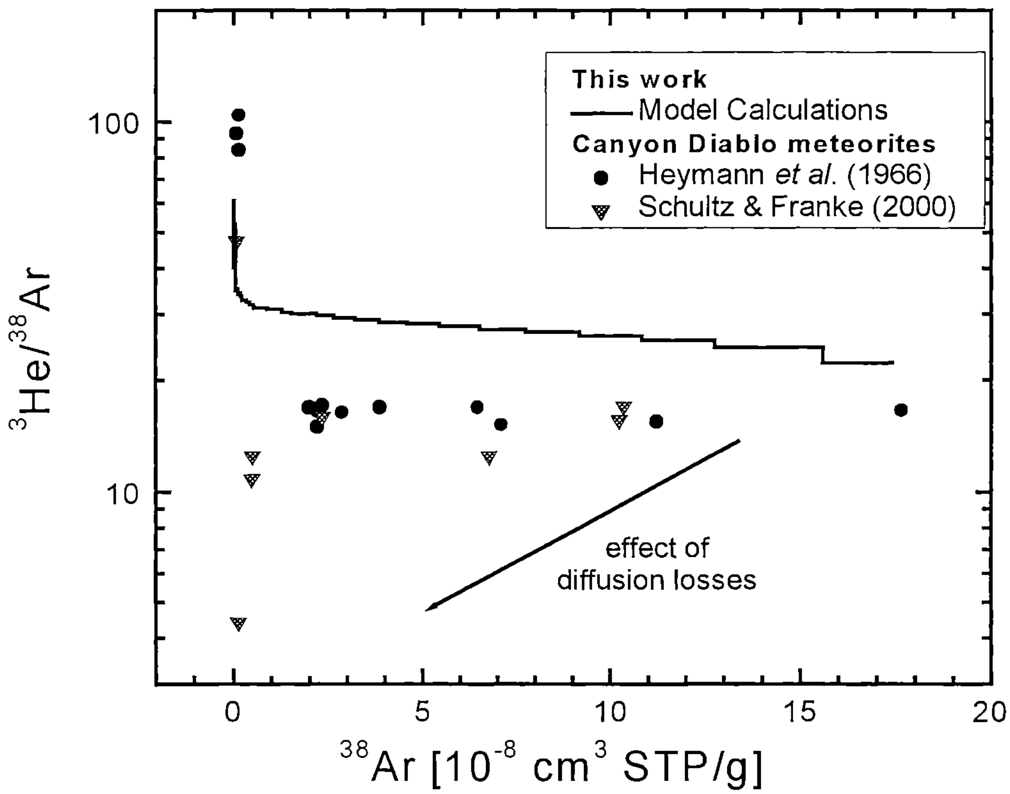

FIG. 4. Measured and modeled $^3He/^{38}Ar$ ratios in Canyon Diablo meteorites as a function of cosmogenic ^{38}Ar concentrations. The solid line is the result of our model calculations (no diffusion). Published calculations that model the impact of the Canyon Diablo meteoroid predict a strong positive temperature gradient toward the interior of the projectile. Higher temperatures at depth should have affected both meteorites and spheroids. We therefore would predict that Canyon Diablo meteorites with lower ^{38}Ar concentrations, which originate from deeper inside the meteoroid, should have lost more ^3He by diffusion compared to samples from shallower depths. Consequently, the $^3He/^{38}Ar$ ratios should decrease relative to the model calculations with decreasing ^{38}Ar concentration. This trend is not seen in samples with ^{38}Ar contents $>2 \times 10^{-8}$ cm^3 STP/g, suggesting that material at pre-atmospheric depths of <50 cm did not attain temperatures necessary to cause appreciable diffusive losses. Results for samples with lower ^{38}Ar contents show no clear trend.

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