priate OH energy levels have been proposed (*10, 11*); the only one that leads directly to circular and elliptical polarization is that of Litvak *et al.* (*11*).

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Implantation in Interplanetary Dust of Rare-Gas Ions from Solar Flares

Abstract. *Measurements of excess Ar^{36} + Ar^{38} (released mainly at 1200°C) in magnetic concentrates of Pacific sediments and in a dense concentrate of Greenland dust agree within an order of magnitude with expected concentrations implanted by solar-flare ion streams of energy less than 10 Mev per atomic-mass unit. The agreement implies that more than 10 percent of each concentrate may be extraterrestrial, depending on size distribution and flare spectra. Rare-gas measurements on fine-grained dust can provide data on: solar-flare "paleo-ion" fluxes, energy spectra, and isotopic abundances; identification, mineralogy, and chemistry of interplanetary dust; influx rates to Earth and sedimentation rates of oceanic cores; and lunar-surface residence and mixing times.*

An approximation of the flux of solar-flare protons in interplanetary space was derived from measurements of Al^{26} in oceanic sediments (*1*). Measurements of solar-flare ions stopped in extraterrestrial material are an alternative source of information about average flare ion fluxes in space, and the rare gases are ideally suited for this purpose. I shall summarize some recent mass-spectrometric measurements bearing on this problem, present calculations of expected concentrations of the rare gases implanted from a solar-flare source, and compare observed concentrations with expected values.

Table 1. Minimum excess argon, assuming that all Ar^{40} is atmospheric whenever Ar^{40}: Ar^{36} is less than the ratio in air, that there is no excess Ar^{36} whenever Ar^{40}: Ar^{36} exceeds the ratio in air, and that Ar^{36}: Ar^{38} equals the ratio in air.

Minimum excess argon (10^{-10} cm^3g^{-1} at STP)	
Ar^{36}	$Ar^{36} + Ar^{38}$
Three marine sediments (magnetic fraction)	
7 (2)	8 (2)
8	9.5
6	7
Greenland dust (dense fraction: $\rho > 3.2$)	
8	11

Figure 1 presents measured Ar^{40}: Ar^{36} ratios found in argon released during successive 1-hour heatings from four concentrates—three magnetic concentrates of a Pacific red clay and a high-density concentrate ($\rho > 3.2$) of particulate matter from Greenland ice. The solid line represents Merrihue's initial discovery of a red-clay concentrate with Ar^{40} : Ar^{36} lower than the value of 296 found in air (*2*). All the concentrates have argon, released at one or more temperatures, with an Ar^{40} : Ar^{36} ratio of 235 or less; the argon from each appears to be a mixture of radiogenic Ar^{40} from potassium, excess Ar^{36} + Ar^{38}, and atmospheric argon (*2, 3*).

At all temperatures with observable Ar^{40} : Ar^{36} anomalies, the Ar^{36} : Ar^{38} ratio was indistinguishable from that in air. There is no strong positive evidence of argon or other rare-gas isotopic anomalies produced by cosmic ray–spallation nuclear reactions in any of the concentrates. The apparent minimum excesses of Ar^{36} and Ar^{36} + Ar^{38} have been calculated (Table 1) and are strikingly similar.

Table 2 compares data on He^4 and Ne^{20} released from the dense Greenland sample with similar findings by Merrihue in a magnetic sample of Pacific sediment (*2*). The range of 20 to 40 mg/cm² for α-particles emitted by nuclides in the U and Th decay chains will cause loss of radiogenic He^4 from small grains. The K-A age of the Greenland concentrate is 25 times greater than that of the sea-sediment concentrates, yet the latter are the richer in He^4. Although there is no positive evidence of correlation of He^4 concentration with apparent age, U and Th have not been measured. Here we shall neglect radiogenic He^4.

The He^4:Ne^{20} ratios at 500° to 600°C are approximately the same as the relative "cosmic" abundances. The evident similarities of amounts of excess argon, of high-temperature argon isotopic ratios, and of amounts of 500°C helium and neon all emphasize the worldwide occurrence of the rare-gas abundance patterns.

No terrestrial samples having this pattern of rare-gas abundances or these subatmospheric Ar^{40} : Ar^{36} ratios have yet been found; nor is there a plausible terrestrial mechanism for explaining these observations. Three extraterrestrial mechanisms have been suggested (*2, 3*) to explain these observations in fine-grained material from low-accumulation locations. A solar flare source was one such suggestion.

The only mineral detectable in common by x-ray diffraction in concentrates from both geographic locations is magnetite. Fine-grained magnetite is a plausible extraterrestrial material (*4*), and sufficiently fine-grained material of low velocity (*5*) penetrates the atmosphere without melting. In view of the lack of major isotopic fractionation of excess Ar^{36} and Ar^{38}, and the lack of major elemental fractionation be-

Table 2. Releases of He^4 and Ne^{20} at various temperatures.

T (100°C)	Release (cm^3g^{-1} at STP)		He^4: Ne^{20}
	He^4 ($\times 10^{-6}$)	Ne^{20} ($\times 10^{-8}$)	
Greenland dense, $\rho > 3.2$			
5	5.2	1.2	420
8	0.94	7.0	13
10	.07	7.0	1
12	< .01	5.0	< 0.2
Pacific magnetic (2)			
6	6.1	1.3	470
10	9.1	4.0	230
14	0.29	1.0	29

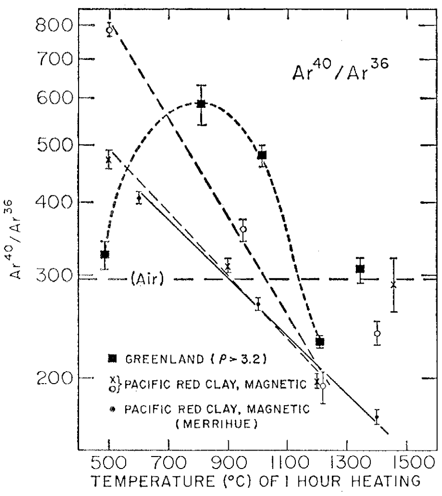

Fig. 1. Ar^{40}:Ar^{36} ratios in concentrates of fine-grained samples.

tween helium and neon (released more easily at low temperature) and excess argon (released at high temperature), these anomaly-bearing materials do not appear to have lost a large fraction of any volatile rare gases, originally of cosmic relative abundance, during heating accompanying entry into the atmosphere.

This lack of evidence of major loss of gas, combined with the observed similarity of rare-gas concentrations, suggests that a significant fraction of each concentrate is in fact extraterrestrial. Terrestrial contamination rates must surely differ between the vastly different sources of these samples; yet, as the fraction of terrestrial material from either source approaches one, the likelihood of finding net-anomaly concentrations that are the same within 50 percent (Tables 1 and 2), in mixtures of minute amounts of extraterrestrial material with large amounts of terrestrial material, becomes increasingly improbable.

Table 3. Solar-flare protons averaged over the solar cycle.

Protons > 10 Mev (No./cm^2 sec)	Comment
100	At 2 A.U. if Al^{26} is undersaturated by factor of 5 (*1*)
200	At 2 A.U. if Al^{26} is undersaturated by factor of 10 (*1*)
800	Assuming $1/r^2$ radial dependence, expected at 1 A.U. if undersaturation is by factor of 10 (*1*)
1300	1 A.U., over 1954–63 solar cycle (*8*)
30	1 A.U., typical solar cycle (*9*)
1000	(> 5 Mev) 1 A.U. (*10*)
600	1 A.U., estimated from 30 Mev + 100 Mev data from last solar cycle (*11*)

The high temperature of release (500 to 1000°C for He^4 and Ne^{20}; > 1000°C for anomalous argon) of the rare gases suggests that a very shallowly implanted, low energy solar-wind component is probably not the principal explanation of our observations. The disagreement (about 10^7) between calculated solar-wind (*6*) and observed concentrations in dust, combined with the lack of large elemental or isotopic-abundance fractionation of the rare gases, strengthens this suggestion. Observations of gas released from dust at close to room temperature may aid future searches for a solar-wind gas component. Possible reasons for nondetection of a solar-wind component are presented elsewhere (*3*).

I have calculated expected noble-gas concentrations from solar-flare bombardments. Data are required on the intensity and energy spectra of flare-particle streams averaged over long times; ranges of heavy ions; density, radius, composition, and lifetime of dust in space; and elemental abundance in average solar-particle streams.

The approximate ranges for helium and argon (Fig. 2) are based on a survey of published experimental values. They depend on Z, the atomic number of the target, but, for reasonable combinations of target materials between carbon and iron, they are probably reliable within a factor of 2. Mean ranges depend on perfection of single crystals, but for polycrystalline or amorphous materials such channeling effects can be neglected.

For lifetimes in space I shall assume Poynting-Robinson values, the evidence for which is not overwhelming, but which is consistent with available data (*1, 6*). The number of stopped ions per gram of dust arriving at Earth is given by (*6*)

$$N = 1.05 \times 10^7 W_0 \ln A_0 \qquad (1)$$

where W_0 is the flux [atoms per square centimeter per year at 1 astronomical unit (A.U.)], outside the magnetosphere, of ions of a given isotope with energy in a suitable interval to stop in a grain of given size and density. A_0 is the distance (in A.U.) at which the dust grains were released from an object large compared to their final size. For this formula we assume an average $1/r^2$ radial dependence of flare-ion fluxes, and in subsequent calculations we assume a 3-A.U. starting point (*6*) and idealized circular orbits for the dust.

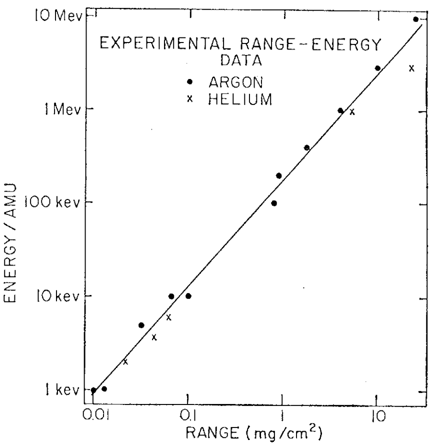

Fig. 2. Experimental range-energy data for argon and helium.

In this problem one must consider energy spectra and ranges of the flare ions, and size-density distribution of the dust particles in space. Unlike the very low energy solar-wind ions, many flare particles have sufficient energy to pass right through a dust grain, requiring correction.

From estimates of the number of solar-flare protons exceeding 10 Mev (Table 3), I take 180 proton cm^{-2} sec^{-1} > 10 Mev at 1 A.U., recognizing that the extremes are within a factor of 7 of this value. I further assume that it is correct to extrapolate the rigidity spectra, observed at higher energies (*7*), down to 1-kev energy and corresponding rigidity. These spectra, of the form

$$dN = ke^{-R/R_0}\, dR \qquad (2)$$

have often been observed with characteristic R_0 from about 75 to 175 Mv; although R_0 has been reported as low as 50 Mv [inference during 1957–59 (*8*)] and higher than 225 Mv (*7*), I shall calculate for R_0 of 100 Mv and 150 Mv, which probably span the long-term average value.

The relative abundances of ions heavier than protons in the solar-flare streams are reproducible and consistent with solar or "cosmic" abundances if one compares ions of the same energy per nucleon (*7*). The proton : helium ratio is more variable, both from event to event and as a function of energy, but extrapolated values below 10 Mev appear to lie between 5 and 20 (*7*)—

again in reasonable agreement with estimated solar abundances. I assume a value of 10 for H:He of the same energy per nucleon and 2.5×10^4 for He:Ar of the same energy per nucleon, the values observed in hot stars and nebulae (*12*) for all energies below 10 Mev per nucleon.

The first two lines of Table 4 give separately, for the chosen characteristic rigidities, the calculated ratio of ions in a given energy interval per nucleon to the number greater than 10 Mev. The third line gives approximate ranges for heavy ions of the maximum energy per a.m.u. (atomic mass unit) of each tabulated energy interval; the next two give corresponding radii of particles whose diameter is equal to the tabulated range for each of two reasonable densities—the first, that of magnetite (*4*); the second, that of fairly low density cometary debris (*13*).

The sixth and seventh lines give, separately for R_0 of 100 and 150 Mv, calculated values for concentrations of $Ar^{36} + Ar^{38}$ and of He^4 from this source. I have assumed that solar-flare argon is low in Ar^{40}, as predicted (*14*). For simplicity and ready comparability, the calculations are for slabs of thickness $2r$ bombarded normally. A realistic calculation, taking account of irregular and nonoriented shapes, would reduce these values by a factor of about 2.

I next compare the (halved) tabulated values with the highest observed value for minimum excess argon, 1.1×10^{-9} cm^3/g at STP (standard temperature and pressure), and the average 500°C value (consistent with expected cosmic $He^4 : Ne^{20}$) of He^4, 5.5×10^{-6} cm^3/g at STP (Tables 1 and 2). The ratios of observed to calculated values (last lines of Table 4) are a direct measure of the agreement of calculated and observed values.

The fact that the ratios are lower for helium than for argon by a factor of 5 reflects my use in the calculations of the estimated cosmic $He^4 : (Ar^{36} + Ar^{38})$ ratio of 2.5×10^4, whereas the observed $(He^4)_{500°C} : (Ar^{36} + Ar^{38})_{excess}$ is 5×10^3—also lower by a factor of 5. There is indication [Tables 1 and 2; (*2*)] that at least in some samples the observed $(He^4)_{total} : (Ar^{36} + Ar^{38})_{excess}$ may indeed be higher than the values used in the previous paragraph by a factor of roughly 5. However, because of the possible presence of radiogenic He^4, the possible diffusive loss of He^4 in space or during the prebake to which all samples were subjected, the minimal nature of the excess $(Ar^{36} + Ar^{38})$ numbers, and the uncertainties of the cosmic He:Ar ratio, only further experiments can elucidate this discrepancy.

Because of the greater observed variability in intermediate temperature release of helium and the greater possibilities for its loss, as well as the greater number of useful argon measurements, the argon results are tentatively more reliable; on the basis of the mineralogical results, the most appropriate density for these concentrates is near 5.

Then, for any size distribution between 0.6 and 40 μ, the numbers in the second-last pair of lines (Table 4), if taken literally, imply that the measured concentrates comprise from 10 to 100 percent extraterrestrial material, with the rest terrestrial; apparent variability for the several concentrates is less than a factor of 2. Of course, if the true fluxes of solar-flare ions exceed the assumed average of 180 proton cm^{-2} sec^{-1}, the calculated extraterrestrial fractions will be reduced. However, arguments for the probability of dilution also suggest that the extraterrestrial component is not very low in the concentrates; they support the rough reality of the calculated dilutions. Alternatively, for a given grain size, dilution by terrestrial material may be less than that calculated if lower estimates for long-term average flare fluxes (*9*) are correct, or if the higher proton:helium ratios, often observed at higher energies, extend down to the low energies considered here. A further complication exists: the possibility that the present particles were incorporated in aggregates while in space.

The smallest particles in the last column of Table 4, if unaggregated in space, will be quickly removed from the solar system by radiation pressure, and very few will reach Earth; they are unlikely to contribute to the rare-gas observations. Similarly the less-than-10-kev flare ions can probably be neglected. Studies of submicron-particle rare-gas concentrations may provide data on degrees of aggregation in space.

Large area-time direct collections of extraterrestrial material that is uncontaminated by terrestrial debris, combined with precision range-energy data, may enable fairly precise estimates of long-term average solar fluxes and rare-gas isotopic and elemental abundances. In view of the deep embedment and high temperatures of release of the observed gas, diffusive losses during the short lifetime of free grains in space may be small and can be checked experimentally.

Our information is for an energy region below threshold for production of radioactivities; it is in an energy interval that is difficult for direct study. Study of concentration as a func-

Table 4. Calculated relative fluxes, estimated ranges, calculated concentrations, and ratios of observed to calculated concentrations as functions of grain size and density (based on Eqs. 1 and 2 and Fig. 2; see text for details).

Parameter	ΔE per atomic mass unit: energy interval 1 kev to			
	10 Mev	1 Mev	100 kev	10 kev
Characteristic rigidity	$F = N(\Delta E)/N(>10\ Mev)$			
$R_0 = 100$ Mv	3.0	1.4	0.5	0.1
$R_0 = 150$ Mv	1.5	0.6	0.2	0.05
	Maximum range (*mg/cm*^{2})			
	40	5	0.6	0.09
	Radius (μ)			
$\rho = 5$ g/cm^3	40	5	0.6	0.09
$\rho = 0.1$ g/cm^3	2000	250	30	4.5
	Slab concentrations (*cm*^{3}*g*$^{-1}$ *STP*)			
$Ar^{36} + Ar^{38}$, $R_0 = 100$	27×10^{-9}	13×10^{-9}	4.5×10^{-9}	0.9×10^{-9}
$Ar^{36} + Ar^{38}$, $R_0 = 150$	14×10^{-9}	5.6×10^{-9}	1.8×10^{-9}	$.5 \times 10^{-9}$
He^4, $R_0 = 100$	6.7×10^{-4}	3.2×10^{-4}	1.1×10^{-4}	2.2×10^{-5}
He^4, $R_0 = 150$	3.4×10^{-4}	1.4×10^{-4}	0.4×10^{-4}	1.1×10^{-5}
	Ratios, observed: calculated (see text)			
$Ar^{36} + Ar^{38}$, $R_0 = 100$	0.08	0.17	0.49	2.4
$Ar^{36} + Ar^{38}$, $R_0 = 150$	.16	.38	1.2	4.8
He^4, $R_0 = 100$	.016	.035	0.10	0.5
He^4, $R_0 = 150$	.032	.082	.25	1.0

tion of grain size and density should enable direct derivation of data on average energy spectra, and may be the only method of getting long-term average energy spectra for solar flare particles in this energy region.

Conversely, detailed knowledge of these fluxes will enable (i) determination of the extent of terrestrial contamination of samples, whether collected directly or on Earth's surface, that have been outside the magnetosphere, and (ii) definitive mineralogical and chemical studies of material that can, with noble-gas anomalies, be incontrovertably shown to have been in space. Application of similar measurements to lunar surface material may enable determination of average residence times for fine-grained material on the extreme surface, and of long-term mixing or stirring parameters as a function of depth.

As we acquire detailed knowledge of the concentration and origin of rare gases in "pure" interplanetary dust, we can study long oceanic cores to determine variations in extraterrestrial influx rate and in oceanic sedimentation rates over the entire sediment column. This work provides another application of "the poor man's space probes" currently arriving at Earth.

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Evidence of Early Pyrometallurgy in the Kerman Range in Iran

Abstract. *Physical and chemical analysis of pottery fragments, including a crucible shard and ore samples from Tal-i-Iblis, Iran, suggests that copper smelting may have been well advanced late in the fifth millennium B.C.*

Despite the recent interest in the origins of metallurgy, definitive evidence relating to the locus and sequence of events that led to the production of useful metal objects from ores remains sketchy (*1*, *2*). There is evidence to indicate that the first useful copper artifacts were produced by cold-working or by hammering and annealing native copper (*1*). This first use of hard metals may have occurred in the Near East as early as the 9th or 10th millennium B.C. (*2*). The transition from the use of native metals to the smelting of carbonate and oxide or sulfide ores was revolutionary.

Thompson has indicated that it would be feasible for a primitive smith to reduce copper ore and to fashion artifacts without developing the technology required for the production of the molten metal (*3*). However, there is at present no compelling evidence in support of this view when compared with the hypothesis that the smelting and casting of native copper antedated the discovery of smelting (*1*).

In the course of an archeological survey in Kerman Province, southeast Iran, certain artifacts were recovered (*4*, *5*). In 1964, Stein's site of Tal-i-Iblis in the Lalihzar Valley (*6*) was revisited. The center of the mound (originally 118 meters across and 11 meters high) was being removed for fertilizer. This operation exposed successive occupation layers in profile. Radiocarbon samples and a wide variety of pottery fragments and artifacts were quickly recovered from these levels. Several crucible shards were among the artifacts recovered from Tal-i-Iblis levels 1 and 2, the earliest mound levels [4091 ± 74 B.C. (P-925) and 4083 ± 75 B.C. (P-926A), respectively]. We have examined one of the shards from level 1.

The ceramic of the crucible shard was derived from a predominately kaolinite clay (*7*). It was poorly fired, as evidenced by its high porosity and spalling at the outer edges (see Fig. 1). The inner surface of the ceramic was covered with partially vitrified material that had the appearance of dross or slag which contained small pieces of slaked lime. Also noted were two prominent copper stains. Under microscopic examination of the inner surface a general pattern of copper stain was observed. The ceramic had a definite black core that extended to within 2 mm of the outer edge; the outer surface had a tan-salmon color. These data suggest that the crucible was intentionally fired in a reducing atmosphere, because even earlier pottery at this site was fired well enough to oxidize the organic materials that are normally present in all clays (*8*). The tan-salmon color of the outer surface, together with flaky composition of the ceramic, indicates that the maximum temperature obtained during the firing process was probably below 1000°C—possibly from 700° to 800°C. These temperatures are sufficient for the reduction of copper ore (*3*), but they are well below the melting point of the metal (1083°C).

Spectrochemical analysis of the obvious copper stains on the shard's inner surface was consistent with the hypothesis that the copper metal that produced the stain originally came from a copper ore. In addition to copper, the stain contained significantly higher concentrations of cobalt, nickel, phosphorus, and tin, than the surrounding ceramic or the surface dross. If the source of the copper was an ore, these elements would be expected. They could not have been present in such amounts (0.1 to 1 percent) in a native copper sample.

Melting points for the ceramic were determined with an optical pyrometer (*6*, *9*). The samples were melted on a tungten filament in flowing nitrogen. The outer surface of the crucible melted at 990° ± 50°C, and the inner surface melted at 1150° ± 50°C. The melting point of the inner layers of ceramic was the same as that of the outer surface. All samples gave clear glasses. If the crucible had been used for melting native copper there should have been no difference in the three melting points because the metal-working process would not have appreciably altered the composition of the ceramic. The fact that the unaltered ceramic melted at about 1000°C makes it seem unlikely that the crucible was used for melting copper in any form. The temperature required to melt cop-