Upper limit concentrations of trapped xenon in individual interplanetary dust particles from the stratosphere

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Abstract–The Xe contents in 25 individual stratospheric interplanetary dust particles were measured in two different laboratories using focused laser micro-gas extraction and (1) a conventional low-blank magnetic sector mass spectrometer (Washington University), and (2) a resonance ionization time of flight mass spectrometer (RELAX-University of Manchester). Data from both laboratories yielded a remarkably similar upper-limit ^{132}Xe concentration in the IDPs (< 2.7, 6.8 and 2.2×10^{-8} ccSTP/g for Washington University Run 1, Washington University Run 2 and University of Manchester analyses, respectively), which is up to a factor of five smaller than previous estimates. The upper-limit $^{132}Xe/^{36}Ar$ ratio in the IDPs ($^{132}Xe/^{36}Ar < \sim 8 \times 10^{-4}$ for Run 1 and $^{132}Xe/^{36}Ar < \sim 19 \times 10^{-4}$ for Run 2), computed using ^{36}Ar concentration data reported elsewhere is consistent with a mixture between implanted solar wind, primordial, and atmospheric noble gases. Most significantly, there is no evidence that IDPs are particularly enriched in primordial noble gases compared to chondritic meteorites, as implied by previous work.

INTRODUCTION

Interplanetary dust particles (IDPs) are rock fragments ~1 to 100 μm in diameter that comprise the zodiacal cloud. Unlike meteorites, which are mainly from asteroids (Wetherill and Chapman 1988; Farinella et al. 1998), IDPs are thought to come from a wide variety of parent objects, including comets (Bradley et al. 1992), asteroids (Kortenkamp and Dermott 1998), and possibly Kuiper belt objects (Flynn 1996). This broad sampling of parent objects occurs because of Poynting-Robertson (PR) light drag, which causes the orbits of IDPs to decay inward toward the Sun. In principle, this mechanism can deliver dust from throughout the solar system to Earth-crossing orbits at 1 AU.

Although ram pressure and frictional heating during atmospheric entry selectively alter or destroy IDPs depending on their Earth-approach speed, entry angle, density, and size (Brownlee 1985), a fraction survives the entry. NASA high-altitude aircraft are used to collect IDPs as they settle through the lower stratosphere.

Many IDPs have delicate, highly porous morphologies (Bradley and Brownlee 1986), unequilibrated textures (Fraundorf 1981), high abundances of volatile trace elements relative to chondritic meteorites (Flynn and Sutton 1990), and large concentrations of isotopically anomalous presolar material (McKeegan et al. 1985; Messenger et al. 2003). Together this evidence supports the expectation that IDPs come from a variety of primitive parent objects.

The results of noble gas measurements of individual IDPs are diagnostic of space exposure history (Kehm et al. 2006) and the severity of atmospheric entry heating (e.g., Nier and Schlutter 1993). The relative concentrations and isotopic compositions of He, Ne and Ar in individual IDPs reflect a dominant contribution from implanted solar-wind ions (Pepin et al. 2000; Kehm et al. 2002, 2006). Although no measurements of Kr and Xe have been reported for individual particles, Hudson et al. (1981) detected Xe in a set of 13 IDPs that were simultaneously degassed in a W resistance oven. Their results showed a non-solar $^{132}Xe/^{20}Ne$ ratio in IDPs, intermediate between the atmospheric and bulk carbonaceous chondrite values. Moreover, Hudson et al. (1981) inferred a ^{132}Xe concentration of $\sim 10^{-7}$ cc/g, which is a factor of 10 higher than the concentration typically measured in bulk carbonaceous chondrite meteorites.

Observation of Hudson et al. (1981) suggests that IDPs contain trapped primordial Xe, similar to primitive meteorites, but implies that the parent bodies of IDPs have larger concentrations of primordial trapped gases than the parent bodies of carbonaceous chondrites. The presence of primordial He, Ne, and Ar in IDPs is difficult to detect because of large solar wind concentrations. However, the chances of detecting heavy primordial noble gases in IDPs are improved by the fact that the relative elemental abundances of Kr and Xe are higher in primordial noble gases than in the solar wind. Primordial Xe in chondritic meteorites consists of multiple, isotopically distinct components, but is dominated by so-called Xe-Q, also referred to as Xe-P1 in the literature (see review by Ott [2002]). The abundances of Xe-Q in ordinary chondrites seem to partially reflect the degree of parent body metamorphism, with lower abundances in more metamorphosed meteorites (Huss et al. 1996). By analogy, Q-gases may be highly abundant in some IDPs, particularly those particles that appear to come from volatile-rich parent bodies like comets. This expectation is supported by observations of large concentrations of Q-like Ne in cometary matter captured by the Stardust spacecraft (Marty et al. 2008). If observable, measurements of primordial noble gases in IDPs could yield important insights into (1) the nature of the IDP parent objects, (2) the relationship between the parent bodies of IDPs and meteorites, (3) the metamorphic histories of IDP parent bodies, and (4) the origin of the Q noble gas component itself.

This paper reports our initial effort to measure Xe in individual IDPs in order to assess contributions from both implanted solar wind and primordial Xe, and to verify the observation of unusually high primordial ^{132}Xe concentrations in IDPs as reported by Hudson et al. (1981). The Xe compositions of individual IDPs were measured using noble gas mass spectrometers at the Laboratory for Space Science at Washington University in St. Louis and the School of Earth, Atmospheric and Environmental Sciences at the University of Manchester.

EXPERIMENTAL

Samples

The NASA stratospheric dust collection includes particles with roughly chondritic major element compositions (classified as "cosmic"), as well as particles that are presumed to be natural terrestrial contaminants (TCN) based on their compositions (Zolensky and MacKinnon 1985). Cosmic particles generally occur either as individual grains or so-called cluster particles, which are large IDPs that break into multiple fragments when they impact the collection surface. For this study, several individual cosmic particles and a smaller number of TCN grains from the NASA collection were allocated. Particles in the 20–30 µm size range were studied, which were presumed to be of sufficient size to

contain measurable noble gases, while small enough to escape relatively severe atmospheric entry heating. Photomicrographs of the analyzed IDPs suggest that they span a range of morphologies, from compact to porous (e.g., see Kehm et al. [2006] for descriptions of the particles analyzed at Washington University), and thus should be roughly representative of the general population of stratospheric IDPs in this size range. TCN particles were subjected to the same measurements as the cosmic particles in order to compare noble gas contents and assess the preliminary classifications of both particle types. Sample preparation and measurement procedures for the Washington University and University of Manchester analyses were somewhat different and are described in separate sections below.

Particle masses were estimated by assuming particles have a density of 2 g/cm^3 (Love et al. 1994) and are spherical with radii equal to the average of the longest and shortest dimensions visible on a photomicrograph (see Table 1). Note that masses for the IDPs analyzed at Washington University were previously reported by Kehm et al. (2002). The assumption that IDPs are spheres is arguably the simplest approach for making volume estimates for these particles, but can be inaccurate especially for particles with large differences between their longest and shortest dimensions (see section Upper Limit Xe Contents in the IDPs).

Washington University Analyses

Noble gas analyses were performed in two different measurement runs, labeled Run 1 and Run 2. Xenon analyses were performed using spectrometer "MS-North." This instrument shares gas extraction apparatus with spectrometer "MS-South," which was used to measure the light noble gas compositions of the same particles (He, Ne and Ar). The data from the light noble gas analyses were reported by Kehm et al. (2002).

The measurement procedures for each run were nearly identical. Particles were first analyzed for trace element content using synchrotron X-ray fluorescence (SXRF) at Brookhaven National Lab. The results of the trace element analyses were reported by Kehm et al. (2002). Subsequently the IDPs were shipped to Washington University and loaded onto gold foil-covered scanning electron microscopy (SEM) stubs. Secondary electron imaging and energy dispersive X-ray spectroscopy were used to photograph and verify the major element compositions of the particles before loading them into the laser extraction cell of the Washington University noble gas mass spectrometer. The laser gas extraction system was described by Nichols et al. (1995).

Samples were individually vaporized with a Nd-YAG laser. Helium, Ne, and Ar in the particles were measured using the protocol described by Kehm et al. (2002). Sample gases were purified by exposure to getter material consisting of a freshly deposited Ti film, which reacts with chemically

Table 1. Results of Xe analyses.

Particle ID	Analysis #[a]	^{132}Xe ($\times 10^3$ atoms)[b]	Mass ($\times 10^{-9}$ g)
Washington University Analyses Run 1			
TCN Particles			
L2008 T11	14	74 ± 8	2
L2008 T9	18	44 ± 8	
IDPs			
L2021 B1	7	70 ± 8	44
L2036 G13	9	48 ± 8	20
L2009 L20	10	49 ± 8	10
L2009 D10	11	44 ± 8	9
L2036 G2	12	53 ± 8	9
L2036 G14[‡]	13	40 ± 8	16
L2036 G11	15	55 ± 8	12
L2036 E15	16	53 ± 8	14
L2021 B9	17	78 ± 11	38
L2021 D3	19	59 ± 8	22
Ave. (S.D.[c])		55 (12)	
Blanks			
Cold blank	1	72 ± 11	
Hot blank	2	55 ± 11	
Hot blank	3	61 ± 11	
Hot blank	4	49 ± 15	
Hot blank	5	46 ± 11	
Hot blank	6	48 ± 8	
Hot blank	8	48 ± 8	
Hot blank	20	42 ± 4	
Ave. (S.D.)		53 (10)	
Washington University Analyses Run 2			
TCN Particles			
L2008 U4	3	55 ± 11	
IDPs			
L2036 G8	4	59 ± 11	8
L2009 F32	5	65 ± 11	10
L2008 F9	6	42 ± 8	6
L2021 C3	7	48 ± 8	9
L2008 O16	8	74 ± 11	8
L2009 I12	10	46 ± 11	18
L2021 C21	11	61 ± 8	26
L2036 H14	12	49 ± 8	30
Ave. (S.D.)		55 ± 11	
Blanks			
Cold blank	1	91 ± 15	
Hot blank	2	67 ± 11	
Hot blank	9	38 ± 8	
Hot blank	13	29 ± 8	
Ave. (S.D.)		56 (24)	
University of Manchester Analyses			
TCN Particles, Evidence of Heating Observed			
L2005 T6	3	5.5 ± 0.4	
L2005 T7	11	11.3 ± 0.3	
L2005 T8	13	7.2 ± 0.6	
Ave. (S.D.)		8.0 (3.0)	
TCN Particles, No Evidence of Heating Observed			
L2005 T7[d]	12	6.6 ± 0.2	

Table 1. *Continued.* Results of Xe analyses.

Particle ID	Analysis #[a]	^{132}Xe ($\times 10^3$ atoms)[b]	Mass ($\times 10^{-9}$ g)
IDPs Evidence of Heating Observed			
W7190 D25	5	4.1 ± 0.6	11
L2008 P14	4	9.0 ± 1.3	5
L2011 P14	8	7.0 ± 1.3	11
Ave. (S.D.)		6.7 (2.5)	
IDPs, No Evidence of Heating Observed			
W7190 D23	2	9.5 ± 2.3	6
L2036 G12	7	5.4 ± 0.4	10
L2011 P14[d]	9	3.2 ± 0.6	
L2009 G7	10	3.7 ± 0.3	6
W7190 D22	14	5.7 ± 0.5	17
W7190 D22	15	4.5 ± 0.4	
W7190 D23	16	6.1 ± 1.2	
L2036 G12	17	5.6 ± 1.1	
Ave. (S.D.)		5.5 (1.9)	
Blanks			
Cold Blank	1	8.3 ± 2.0	
Cold Blank	6	6.6 ± 1.6	

[‡]Pump valve accidently left open during this analysis, removing some or all of the Xe.
[a]Numerical order of analyses.
[b]Two-sigma uncertainties associated with counting statistics.
[c]S.D. is one standard deviation.
[d]Attempted repeat heating of previously analyzed sample.

active sample gases. During measurement of He and Ne, the heavy noble gases (Ar, Kr, and Xe) remained frozen on an activated charcoal surface maintained at liquid N$_2$ temperature. The charcoal finger was then heated for 15 min. (~200 °C) to liberate Ar and some fraction of the Kr and Xe. The same finger was then immersed in a mixture of methanol and dry ice (−81 °C) in order to re-adsorb Xe. After a 30-minute Xe sorption period, Ar was admitted into a mass spectrometer and measured. The Ar remaining in the sample system was pumped away for 4 min. During this period, the Ti getter was reactivated briefly, providing a fresh Ti surface to react with any residual active species that had survived the initial purification step by becoming frozen onto the surface of the activated charcoal. Subsequently the activated charcoal was reheated to ~200 °C for 40 min., releasing adsorbed Xe for measurement in the mass spectrometer.

The amount of Xe in the IDPs was expected to be quite small assuming implanted solar wind is the dominant source. Based on the ^{132}Xe concentration in IDPs determined by Hudson et al. (1981), ^{132}Xe signals occasionally exceeding a few sigma of the typical blank were expected. Though determining ratios of ^{124}Xe/^{132}Xe and ^{126}Xe/^{132}Xe, for example, might have been especially diagnostic of contributions from implanted solar wind, it was anticipated that only the most abundant isotopes might be detectable. Thus, isotope abundance measurements excluded ^{124}Xe and ^{126}Xe, as well as ^{128}Xe during Run 2.

Xenon-128 was measured in the particles from Run 1, but these data are not reported due to spectrometer memory associated with this isotope; MS-North is frequently used for studies of neutron-irradiated samples for I-Xe dating, which introduces Xe with artificially high ^{128}Xe amounts from neutron capture on ^{127}I. The abundance of the reference isotope, ^{132}Xe, was determined by extrapolating its signal back to the time of gas inlet into the spectrometer. Isotope ratios, ^{N}Xe/^{132}Xe, were determined using the average measured ratio (number of ratio determinations = ~15) during the measurement.

Calibrated quantities of atmospheric Xe were used to determine the procedural Xe sensitivity, which was ~19,000 atoms/count/second for MS-North. This value is considered accurate to within ±10%. Repeated, successive analyses of Xe from calibration volumes indicate a measurement-to-measurement reproducibility of the ^{132}Xe amounts of ~15–20%. Calibrations were also used to assess the degree of instrumental isotopic mass bias. A correction was applied to the final data, although the size of these corrections (a few per mil per amu), was insignificant compared to uncertainties associated with counting statistics.

Two types of "blank" measurements were performed to determine the procedural noble gas background. So-called "hot blanks" assessed the background by simulating the analysis of a sample grain; the laser was fired at a particle-free area of the sample stub and the evolved noble gases were analyzed. "Cold blanks," as the name implies, simulated the analysis of a grain without firing the heating laser at the sample stub.

University of Manchester Analyses

The analyses described here took place as part of an extended development program towards the analyses of individual SiC grains using RELAX (Refrigerator Enhanced Laser Analyser for Xenon—Gilmour et al. 1994). The technique was first tested on a series of grains of organic material isolated from the Murchison meteorite (dubbed "M grains"), then applied to the IDP and TCN particles and, finally, to presolar SiC grains. Results from the SiC analyses will be reported elsewhere (Crowther et al. 2008).

IDPs and TCN particles from the NASA Johnson Space Center (JSC) collection were sent to the University of Manchester on dimpled glass slides. Particles were washed in hexane at JSC prior to shipping to Manchester in order to minimize the amount of silicone oil on the particle surfaces. Subsequently, particles were individually washed in a drop of distilled methanol on a flow bench in the University of Manchester clean room facility in order to further reduce possible surface contaminants acquired during processing. The washed particles were picked with a W needle using a micromanipulator and placed in the etched glass particle mount (see below) for Xe analysis.

In order to minimize laser heating of the sample holder and thereby minimize the Xe background, the IDPs and TCN particles were mounted on a glass substrate with a reference grid etched on the surface. The grid was generated by covering the glass substrate with a mask and exposing it to dilute HF. Our hope was that the glass sample mount would absorb less heat from the laser and hence reduce procedural blank. The slide with mounted IDPs and TCN particles was placed inside the laser port of the RELAX mass spectrometer; the extraction system having been reconfigured for minimum volume to increase sensitivity. In contrast to M grains of similar size and to subsequent SiC grain analyses, both IDPs and TCN particles proved hard to locate using the viewing optics of our laser probe.

Heating was attempted using the output of a continuous wave Nd:YAG laser, which was focused to a spot size close to 5 μm. This was scanned around the location of the particle for 60 seconds during each analysis until a glow was observed, whereupon the position was held constant until the remainder of the 60 s extraction time had been completed. Three out of three TCN particles were observed to glow during this process, while glows were obtained from only three of the seven IDPs. Accordingly, we divide our data into three groups—TCN particles, IDP analyses during which a glow was observed, and attempted IDP analyses that produced no glow. No particle was observed to glow in more than one attempted analysis, and no particle residue could be identified when the mount was removed from the instrument, so we conclude that our analytical protocol completely destroyed and degassed any particle that glowed. Samples that were not observed to glow were either destroyed without visible heating by exposure to the laser or displaced before analysis was attempted.

Cold blanks were performed using the same protocol without allowing laser output to enter the extraction chamber. No systematic difference in Xe count rates was observed between cold blanks and regular analyses, which suggests that laser heating of surfaces inside the sample cell does not measurably affect the Xe blank.

Gas was admitted to the mass spectrometer immediately following the heating step and analysis commenced. RELAX is a resonance ionization mass spectrometer with an atom buncher (Gilmour et al. 1994). Xenon in the mass spectrometer continually condenses onto a localized cold spot in the ion source. Every tenth of a second the atoms that have condensed are released using an infrared laser pulse. The ionizing laser pulse passes through the plume at a delay chosen to optimize the ionization efficiency by maximizing the population of sample atoms in the ionization region. The ionization laser is tuned to a two-photon resonance in the Xe atom. Excited atoms are photoionized at the same wavelength. At high power densities this process ionizes Xe with high efficiency.

Sample analysis consisted of 30 mass spectra obtained over 5 min. by summing the response to 100 consecutive 10 Hz ionization laser shots. Ratios and signal intensities are
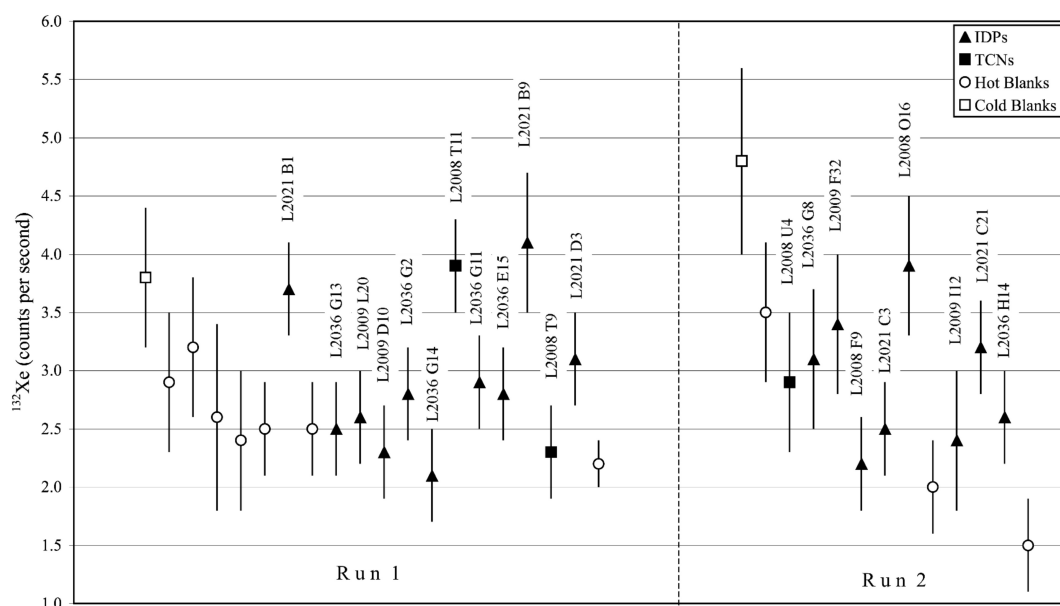
Fig. 1. ^{132}Xe count rates measured in blanks, TCN particles and IDPs for the Washington University measurements. Data are divided into two measurement runs and are shown in the sequence that the measurements were performed. Uncertainties are 2σ. In both Run 1 and Run 2, a general downward trend in blank levels is observed, consistent with gradual improvement in the blank over time.

obtained for each of the 30 time-of-flight mass spectra and extrapolated back to time zero to obtain definitive data. Sample spectra from RELAX are shown in our companion paper, Crowther et al. (2008).

The analytical program consisted of procedural blanks, particle analyses and interspersed air calibrations. Air calibrations are derived from a secondary reservoir filled from a primary reservoir of air Xe. Each extraction from the secondary volume depletes it by a factor of 0.94. Thus successive air calibrations yield an amount of gas that decreases by a known factor until the secondary reservoir is pumped out and refilled from the primary reservoir (at least daily). The ^{132}Xe signal from each air calibration was used to deduce a sensitivity factor, and the sensitivity factors deduced from bracketing air calibrations were used to convert measured signals in attempted sample analyses and blanks into equivalent numbers of atoms of ^{132}Xe. For air calibrations the instrument volume included the calibration inlet line which was valved off for sample analyses—sensitivity during analyses was ~15% higher during sample analyses and an appropriate adjustment has been made to the reported data. The sensitivity of RELAX can fluctuate within a day as a function of laser pulse energy and laser wavelength. Uncertainty in gas concentrations arising from this source has been included in data reported here.

RESULTS

Washington University Analyses

The results of the Washington University analyses are summarized in Table 1 and depicted in Fig. 1. The

uncertainties in the ^{132}Xe amounts reflect statistical uncertainties and do not include potential variations in the spectrometer sensitivity of 15–20% (see section Washington University Analyses). The ^{132}Xe abundance data in Fig. 1 are ordered in the sequence that the measurements were performed. Note that the initial cold blanks have somewhat higher ^{132}Xe count rates than the remainder of the analyses. Further, both runs show a gradual decline in ^{132}Xe blank amounts with time. This presumably reflects a gradual decrease in Xe background in the sample system with increasing numbers of analyses.

Accepting the general downward trend in blank levels with time, the ^{132}Xe amounts in a few of the IDPs (e.g., L2021 B1 in Run 1) appear to be elevated above the blank. However, the two TCN particles analyzed in Run 1 and the single TCN analyzed in Run 2 have ^{132}Xe amounts similar to the IDPs. During preliminary particle classification, TCN particles are distinguished from IDPs based on their major element chemistry (see section Samples). In addition, all of the IDPs represented in Fig. 1 were found to contain measurable quantities of He, Ne and Ar in solar-wind like abundances, while no measurable light gases were present in the TCN particles (Kehm et al. 2002). The difference in light noble gas content between TCNs and IDPs confirms the previous classification of these particles. The similarity in Xe count rates between the terrestrial particles and the IDPs depicted in Fig. 1 suggests that some amount of the apparent Xe "excesses" measured in the IDPs may not be extraterrestrial in origin, and may simply reflect an elevated background associated with degassing an ~20 μm particle in the sample system, which is not adequately simulated by the hot blanks. It is possible that polymerized silicone oil adhering to particle
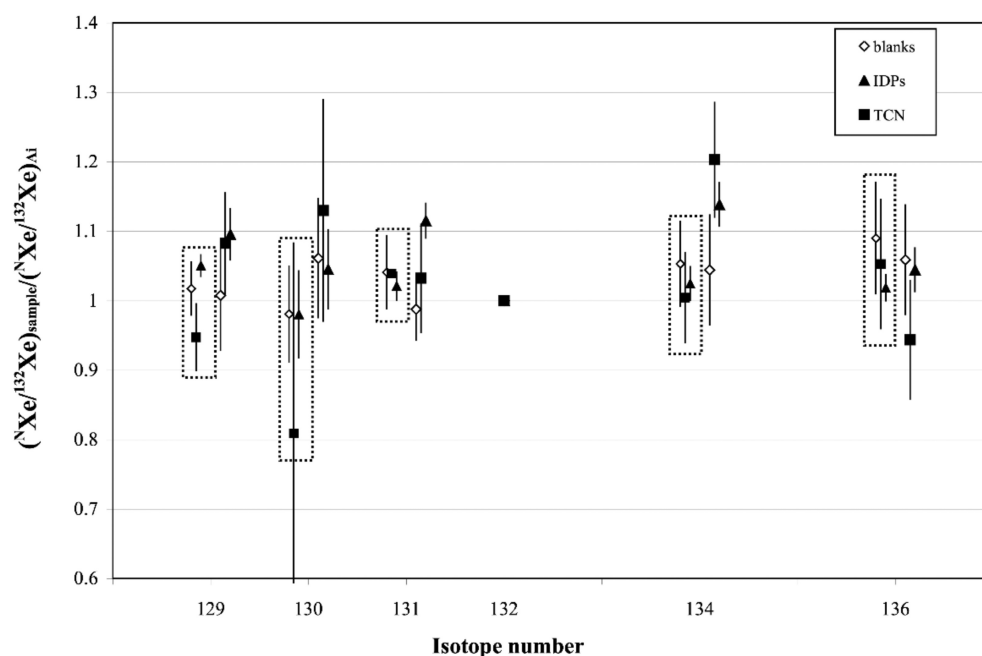
Fig. 2. A comparison of the average measured isotopic compositions in the blanks, IDP analyses, and TCN particle analyses for the Washington University measurements. Isotope ratios are normalized to the composition of the terrestrial atmosphere. Data for Run 1 are enclosed in a box to distinguish them from Run 2 data. Plotted error bars are 1σ and reflect standard errors in the mean values. An exception to this is the single TCN analyzed in Run 2 whose error bars correspond to uncertainties in the isotope ratio measurement. Within each run, the isotopic data are essentially indistinguishable from each other and close to the atmospheric composition.

surfaces following trace element analyses (see Kehm et al. 2002) retained trapped atmospheric Xe, which contributes to the signal when a particle is measured (either TCN or IDP). Indeed during preliminary Xe analyses, relatively high Xe count rates (~20 counts per second) were observed to be associated with ~50 μm TCNs possessing unusually thick polymerized silicone oil coatings.

Figure 2 shows the average isotopic compositions of the blank, TCN particles and the IDPs, normalized to the composition of atmospheric Xe, for each run. It is clear that the isotopic composition of the IDPs cannot be definitively distinguished from either the TCN particles or the blank. Furthermore, all three compositions are similar to atmospheric Xe.

Results of the University of Manchester Analyses

Figure 3 shows the number of ^{132}Xe atoms that entered the mass spectrometer in each RELAX analysis. Data are arranged according to sample type and analysis type (evidence of heating or not)—the sequence of analyses is reported in Table 1 where data are tabulated.

There is no significant difference in the amount of Xe detected in those analyses where an IDP was clearly heated and those in which an IDP analysis was attempted but no evidence of heating was observed. In addition, both are consistent with the blank and with all but one attempted TCN particle analysis. One TCN particle analysis (L2005

T8) released a significant amount of gas at the 3σ level (treating all the other analyses as repeated blank determinations).

Isotopic data are presented in Fig. 4. Once again, analyses have been separated into those in which an IDP was demonstrably heated, and the rest. Data are consistent with a Xe blank that includes a small amount of contamination from non-resonantly ionized hydrocarbons, which are observed because of the high power densities necessary to saturate the resonance ionization process for Xe. The contamination is most apparent in masses ^{128}Xe and ^{132}Xe, where its contribution amounts to ~10% (~500 atoms equivalent, though non-resonant ionization of hydrocarbons is expected to be a lot less efficient than resonant ionization of Xe). There is a hint of a higher hydrocarbon contribution to the IDP analyses, though this could be attributable to the statistics of small numbers.

DISCUSSION

Upper Limit Xe Contents in the IDPs

It is useful to compute the inferred ^{132}Xe concentrations in the particles to facilitate comparisons with other types of extraterrestrial matter.

Ignoring the initially higher blank levels in the Washington University measurements, there appears to be a significant difference between ^{132}Xe amounts associated with
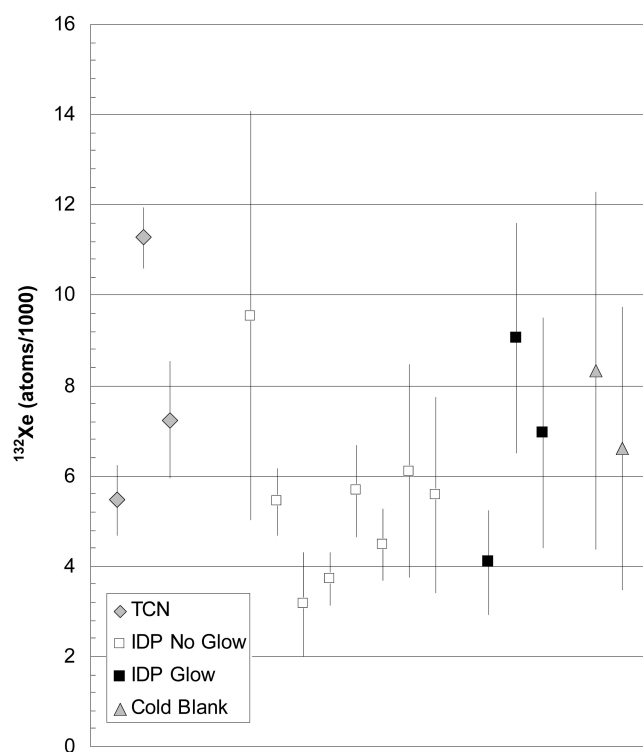
Fig. 3. Numbers of atoms of ^{132}Xe detected in each attempted RELAX analysis. Data are sorted according to analysis category and do not reflect the actual sequence in which analyses were performed. Errors are 2σ, and are dominated by variability in instrument sensitivity.
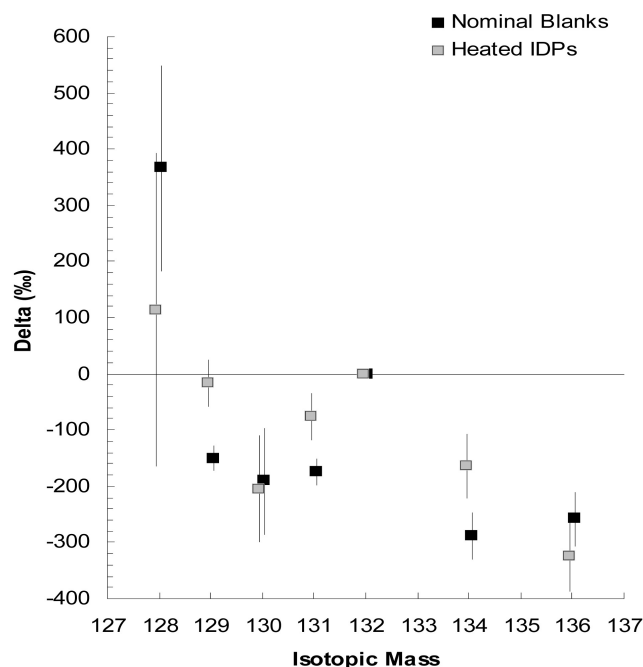

Fig. 4. Relative apparent composition at each Xe isotopic mass measured by RELAX. Values are expressed as delta values relative to atmospheric Xe. Errors are 1σ. A contribution from non-resonant ionization of hydrocarbons is apparent in the deviation from atmospheric composition of the blanks. There is evidence of a slightly different hydrocarbon composition (or a slightly greater contribution from Xe) in the analyses where IDPs were heated. Minor isotopes ^{124}Xe and ^{126}Xe are not shown.

the blank and particle analyses, respectively (Fig. 1). In view of this observation, upper limits on the ^{132}Xe contents in each particle measured at Washington University can be estimated by taking the difference between the measured ^{132}Xe amount in each IDP and the ^{132}Xe amount measured in the most Xe-poor blank for each measurement run. These values are reported in Table 2. Note that the final hot blank performed during Run 2, which was used to estimate upper limit gas concentrations for Run 2, was particularly Xe-poor (Fig. 1). Thus, the upper limit gas concentrations computed for Run 2 are correspondingly higher than those in Run 1 (Table 2), despite the fact that the average gas amounts for the IDPs in Run 1 and Run 2 are identical (Table 1). The corresponding upper-limit ^{132}Xe concentrations are determined by dividing the ^{132}Xe gas amounts by the estimated particle masses. The mass-weighted average in Table 2 is the sum of the upper limit ^{132}Xe amounts in the IDPs divided by the sum of the masses. Statistical uncertainties in the gas amounts yield 10–20% uncertainties in the mass-weighted average upper limit gas concentrations (Table 2). Not reflected in Table 2 are potential uncertainties in the particle masses, which are derived from uncertainties in the volumes and densities of the particles. A study by Love et al. (1994) showed that IDP densities exhibit a roughly symmetric distribution that extends

from ~0.75 g/cm^3 to ~4 g/cm^3 for chondritic particles, and is strongly peaked at ~2 g/cm^3. Thus, while our assumption of a common density of 2 g/cm^3 may generate substantial errors in the mass estimates for individual particles, the total mass of the analyzed IDPs should be more reliable. Uncertainties in the volume estimates are more difficult to quantify, but may be as large as ± 50%, as assumed by Kehm et al. (2002). Again, to the extent that errors in the volume estimates are statistical, the total mass of the particles should be more reliable than the estimated mass of any individual particle. However, as stated previously (see section Samples), the assumption that particles are spheres may systematically bias the volume estimates toward higher values especially for oblong particles. For example, an alternative estimate based on the assumption that these IDPs are oblate spheroids with equatorial radii equal to their shortest visible dimension on a photomicrograph yields particle volumes that are, on average, ~20% smaller than volumes based on the spherical estimate. This would lead to smaller mass estimates, which would shift the upper limit concentrations to somewhat higher values (~25% larger, on the average, if particles are oblate spheroids instead of spheres).

Variations in the upper limit gas concentrations among individual IDPs is less than a factor of 10. Uncertainties in the masses and statistical uncertainties in the gas amounts can

Table 2. Estimated upper limits on ^{132}Xe contents of IDPs analyzed at Washington University.

IDP	^{132}Xe per IDP ($\times 10^3$ atoms)[a]	^{132}Xe concentration ($\times 10^{-3}$ ccSTP/g)[b]
L2021 B1	27.7 ± 8.3	2.4
L2036 G13	5.6 ± 8.3	1.0
L2009 L20	7.5 ± 8.3	2.8
L2009 D10	1.9 ± 8.3	0.8
L2036 G2	11.0 ± 8.3	4.6
L2036 G11	12.9 ± 8.3	4.0
L2036 E15	11.0 ± 8.3	3.0
L2021 B9	35.2 ± 11.8	3.5
L2021 D3	16.7 ± 8.3	2.8
Run 1 mass-weighted average		2.7
L2036 G8	29.6 ± 13.4	13.8
L2009 F32	35.2 ± 13.4	13.1
L2008 F9	12.9 ± 10.5	8.1
L2021 C3	18.5 ± 10.5	7.8
L2008 O16	44.6 ± 13.4	20.7
L2009 I12	16.7 ± 13.4	3.5
L2021 C21	31.4 ± 10.5	4.5
L2036 H14	20.4 ± 10.5	2.5
Run 2 mass-weighted average		6.8

[a]Upper limit estimated as ^{132}Xe(sample)-^{132}Xe(lowest blank) with 2σ uncertainties.

[b]Using particle masses estimated by Kehm et al. (2002).

presumably account for some of the apparent differences between particles. It should also be noted that He, Ne, and Ar amounts in individual IDPs are highly variable, resulting from differing particle sizes, variable solar wind exposure times and differing degrees of gas loss during atmospheric entry (Kehm et al. 2002). Xenon concentrations may also be variable, which could account for some of the apparent differences in upper limit ^{132}Xe concentrations in Table 2.

No significant differences between blank and particle analyses are apparent in the University of Manchester measurements (Fig. 3). To place an upper limit on the ^{132}Xe content of the IDPs that were definitely heated in the University of Manchester analyses, all other analyses with the exception of L2005 T8 were identified as blank determinations. This leads to a blank of 6100 ± 1800 atoms and a detection limit of 5500 atoms ^{132}Xe (3σ of the blank). This value is adopted as the upper limit on the number of ^{132}Xe present in any of the "successful" University of Manchester IDP analyses.

The upper limit gas concentrations for the IDPs analyzed at Manchester, computed by dividing the upper limit gas concentration by the individual particle masses (Table 1), range from ~1 to 4×10^{-8} ccSTP/g of ^{132}Xe with a mass-weighted average of ~2.2×10^{-8} ccSTP/g of ^{132}Xe.

The upper limits on the ^{132}Xe concentrations in the IDPs estimated from the Washington University and University of Manchester measurements are consistent and remarkably similar despite the fact that the measurements were conducted

Table 3. Comparisons between the upper limit ^{132}Xe concentrations in IDPs and other types of extraterrestrial matter.

	^{132}Xe ($\times 10^{-8}$ ccSTP/g)
IDPs, average, Wash. Univ., Run 1	<2.7
IDPs, average, Wash. Univ., Run 2	<6.8
IDPs, average, Univ. of Manchester analyses	<2.2
IDPs, Hudson et al. (1981)	~10
16–37 µm bulk lunar soil (70181), Pepin et al. (1975)	2.22 ± 0.06
20 µm bulk lunar soil (12001), Eberhardt et al. (1972)	2.8 ± 0.5
20–30 µm bulk lunar soil (14163), Bogard and Nyquist (1972)	6.0 ± 0.6
^{132}Xe-Q in bulk Orgueil (CI), Huss et al. (1996)	1.31 ± 0.03

in different labs with different types of instruments, and using differing sample preparation and sample mounting techniques. In Table 3, these values are compared with ^{132}Xe concentrations in different extraterrestrial materials.

The mass-weighted upper limit ^{132}Xe concentrations estimated from the Washington University (Run 1 and Run 2) and the University of Manchester analyses are similar to the concentrations measured in three different bulk lunar soils with similar grain sizes as the IDPs (Table 3). These soils acquired their ^{132}Xe from exposure to the solar wind on the lunar surface. Variations in Xe concentrations among soils probably represent differences in average solar wind exposure times, small variations in grain size and soil composition, and differing degrees of diffusive gas loss. The Orgueil (CI) meteorite contains one of the highest concentrations of primordial Xe among chondrites that have been studied so far (Huss et al. 1996; Busemann et al. 2000). Xenon-Q dominates the Xe content in Orgueil and its concentration is shown in Table 3 for comparison with the IDPs. The ^{132}Xe concentration determined by Hudson et al. (1981) for a group of 13 IDPs is more than a factor of five higher than the upper limits established by the University of Manchester analyses. However, potential uncertainties in the mass estimates (as large as a factor of 2) for the Hudson et al. (1981) data, may account for part of this difference. It should also be noted that Hudson et al. (1981) blank-corrected their data using a series of particle-free analyses performed prior to their IDP measurements. These Xe blanks were particularly low (<10^{-16} ccSTP ^{132}Xe) and may not reflect the actual blank level associated with the IDP analysis. For example atmospheric Xe trapped in residual silicone oil on the IDPs may have contributed to the blank associated with the IDP analyses. Thus, it is possible that the ^{132}Xe amounts reported by Hudson et al. (1981) are relatively elevated due to under correction for blank Xe.

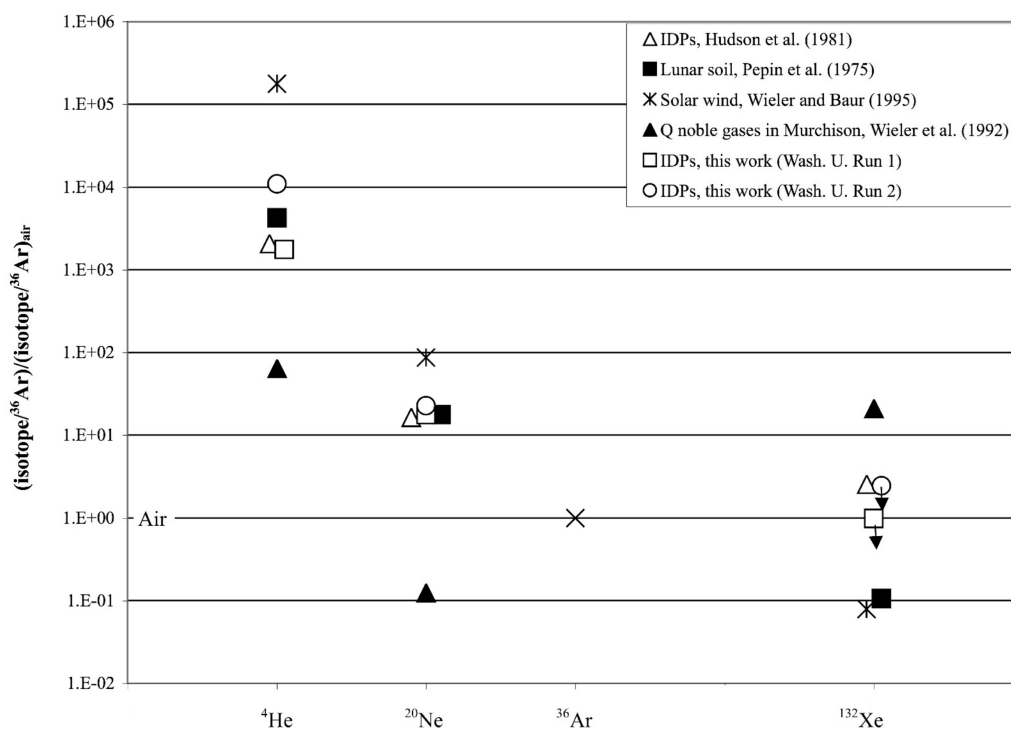Figure 5 shows a comparison between the elemental ratios in the IDPs and other extraterrestrial materials.

Fig. 5. Noble gas elemental ratios in the IDPs at Washington University are compared to the composition of solar wind (Wieler and Baur 1995), bulk lunar soil with grain sizes similar to the IDPs (see Table 3; Pepin et al. 1975), Q noble gases as measured in the Murchison (CM2) meteorite (average of 2C1a/III, KB1/I, and II; Wieler et al. 1992), and IDPs as measured by Hudson et al. (1981). The ^{4}He/^{36}Ar concentration reported by Hudson et al. (1981) were derived using data from Rajan et al. (1977). Ratios are given with respect to ^{36}Ar and normalized to the composition of the terrestrial atmosphere. Light noble gas data for the IDPs in Runs 1 and 2 were reported by Kehm et al. (2002). The arrows on the ^{132}Xe/^{36}Ar compositions indicate that these are upper limits on the actual ratio. Uncertainties in the data from Runs 1 and 2 are the size of the plotted points or smaller.

Elemental ratios are normalized to ^{36}Ar and the composition of the terrestrial atmosphere. Data for the Washington University measurements (Runs 1 and 2) are computed by summing the total gas in all IDPs using the ^{4}He, ^{20}Ne, and ^{36}Ar amounts that were reported previously (Kehm et al. 2002). Data from IDP L20^{36} G14 was not included because of the unreliability of the Xe results for this particle (see Table 1). The overall abundance patterns for the IDPs analyzed in this work and those analyzed by Hudson et al. (1981) are similar. The IDPs plot near the lunar soil composition for the light noble gases. Like lunar soils, IDPs receive large doses of solar wind during exposure to the solar wind stream in space. Noble gas isotopic evidence reinforces this conclusion (e.g., Kehm et al. 2006). Elemental fractionation of the light gases relative to solar wind values (Fig. 5), presumably reflects incomplete retention of incident solar wind particles during implantation, diffusive gas losses in space, and/or fractionating gas losses during atmospheric entry heating (Kehm et al. 2002). The upper limit ^{132}Xe/^{36}Ar ratios computed from Run 1 (^{132}Xe/^{36}Ar < ~8 × 10^{-4}) and Run 2 (^{132}Xe/^{36}Ar < ~19 × 10^{-4}) are similar to the Hudson et al. (1981) ratio (~20 × 10^{-4}). These values may reflect a mixture between Q noble gases (represented by data from the CM2 meteorite Murchison in Fig. 5), solar wind and atmospheric

noble gases. Like the light noble gases, the ^{132}Xe/^{36}Ar ratio may be modified by elemental mass fractionation. Fractionating gas loss would shift values of ^{132}Xe/^{36}Ar upward in Fig. 5.

CONCLUSIONS

Measurements of the Xe contents of 25 stratospheric IDPs were conducted in two different laboratories, using gas extraction by focused laser heating and (1) a conventional low-blank magnetic sector mass spectrometer (Washington University-St. Louis) and (2) a resonance ionization time of flight mass spectrometer (RELAX-University of Manchester). For both sets of observations, the measured gas concentrations and Xe isotopic compositions were found to be consistent with blank levels in the spectrometer and/or with the gas compositions of individual terrestrial stratospheric "test" particles (so-called TCN grains). However data from both labs yielded a similar upper-limit ^{132}Xe concentration in the IDPs, which is up to a factor of five smaller than the previous ^{132}Xe concentration estimated for a group of thirteen simultaneously degassed IDPs (Hudson et al. 1981). The upper limit cumulative ^{132}Xe/^{36}Ar ratio in the IDPs was computed using ^{36}Ar concentration data reported

previously (Kehm et al. 2002). This ratio was found to be consistent with a possible mixture between implanted solar-wind, primordial, and atmospheric noble gases possibly modified by elemental fractionation.

Among other things, this work has demonstrated the importance of TCN particles in providing perhaps the best possible way to assess procedural blank for laser noble gas micro-analysis. Results showed that Xe associated with the vaporization of a TCN particle in the sample cell sometimes exceeded the "blank" and mimicked or exceeded the amounts detected during analyses of IDPs. The reason for the apparently elevated Xe concentrations in some TCN particles is unknown. One possibility is that heating of TCN particles and IDPs releases Xe atoms from the sample chamber in a non-reproducible way. Coupling between particle and sample substrate could depend on particle composition and/or density in such a way that IDPs (mostly silicates) are less prone to the effect than TCN particles.

Ultimately, isotopic analysis may be required to distinguish extraterrestrial Xe in IDPs from "background" Xe. Improvements in detection limits for Xe of the RELAX mass spectrometer accomplished after the completion of this work (Crowther et al. 2008) may allow the issue of the composition and concentration of Xe in IDPs to be revisited.

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REFERENCES

Bogard D. D. and Nyquist L. E. 1972. Noble gas studies on regolith materials from Apollo 14 and 15. Proceedings, 3rd Lunar Planetary Science Conference, vol. 2. pp. 1797–1819.

Bradley J. P. and Brownlee D. E. 1986. Cometary particles: Thin sectioning and electron beam analysis. *Science* 231:1542–1544.

Bradley J. P., Humecki H. J., and Germani M. S. 1992. Combined infrared and analytical electron microscope studies of interplanetary dust particles. *The Astrophysical Journal* 394: 643–651.

Brownlee D. E. 1985. Cosmic dust: Collection and research. *Annual Review of Earth and Planetary Science* 15:147–173.

Busemann H., Baur H., and Wieler R. 2000. Primordial noble gases in "phase Q" in carbonaceous and ordinary chondrites studied by closed-system stepped etching. *Meteoritics & Planetary Science* 35:949–973.

Crowther S. A., Mohapatra R. K., Turner G. Blagburn D. J., Kehm K., and Gilmour J. D. 2008. Characteristics and applications of RELAX, an ultrasensitive resonance ionization mass spectrometer for xenon. *Journal of Analytical Atomic Spectrometry* 23:938–947.

Eberhardt P., Geiss J., Graf H., Grögler N., Mendia M. D., Mörgeli M., Schwaller H., Stettler A., Krähenbühl U., and Gunten H. R. von. 1972. Trapped solar wind noble gases in Apollo 12 lunar fines 12001 and Apollo 11 breccia 10046. Proceedings, 3rd Lunar Science Conference, vol. 2. pp. 1821–1856.

Farinella P., Vokrouhlicky D., and Hartmann W. K. 1998. Meteorite delivery via Yarkovsky orbital drift. *Icarus* 132:378–387.

Flynn G. J. 1996. Sources of 10 micron interplanetary dust: The contribution from the Kuiper belt. In *Physics, chemistry, and dynamics of interplanetary dust*, edited by Gustafson B. Å. S. and Hanner M. S. ASP Conference Series, vol. 104. Woodbury, NY: American Institute of Physics. pp. 171–175.

Flynn G. J. and Sutton S. R. 1990. Synchrotron X-ray fluorescence analyses of stratospheric cosmic dust: New results for chondritic and low-nickel particles. Proceedings, 20th Lunar and Planetary Science Conference. pp. 335–342.

Fraundorf P. 1981. Interplanetary dust in the transmission electron microscope: Diverse materials from the early solar system. *Geochimica et Cosmochimica Acta* 45:915–943.

Gilmour J. D., Lyon I. C., Johnston W. A., and Turner G. 1994. RELAX: An ultrasensitive, resonance ionization mass spectrometer for xenon. *Review of Scientific Instruments* 65:617–625.

Hudson B., Flynn G. J., Fraundorf P., Hohenberg C. M., and Shirck J. 1981. Noble gases in stratospheric dust particles: Confirmation of extraterrestrial origin. *Science* 211:383–386.

Huss G. R., Lewis R. S., and Hemkin S. 1996. The "normal planetary" noble gas component in primitive chondrites: Compositions, carrier and metamorphic history. *Geochimica et Cosmochimica Acta* 60:3311–3340.

Kehm K., Flynn G. J., Sutton S. R., and Hohenberg C. M. 2002. Combined noble gas and trace element measurements on individual stratospheric interplanetary dust particles. *Meteoritics & Planetary Science* 37:1323–1335.

Kehm K., Flynn G. J., and Hohenberg C. M. 2006. Noble gas space exposure ages of individual interplanetary dust particles. *Meteoritics & Planetary Science* 41:1199–1217.

Kortenkamp S. J. and Dermott S. F. 1998. Accretion of interplanetary dust particles by the Earth. *Icarus* 135:469–495.

Love S. G., Joswiak D. J., and Brownlee D. E. 1994. Densities of stratospheric micrometeorites. *Icarus* 111:227–236.

Marty B., Palma R. L., Pepin R. O., Zimmermann L., Schlutter D. J., Burnard P. G., Westphal A. J., Snead C. J., Bajt S., Becker R. H., and Simones J. E. 2008. Helium and neon abundances and compositions in cometary matter. *Science* 319:75–78.

McKeegan K. D., Walker R. M., and Zinner E. 1985. Ion microprobe isotopic measurements of individual interplanetary dust particles. *Geochimica et Cosmochimica Acta* 49:1971–1987.

Messenger S., Keller L. P., Stadermann F. J., Walker R. M., and Zinner E. 2003. Samples of stars beyond the solar system: Silicate grains in interplanetary dust. *Science* 300:105–108.

Nichols R. H. Jr., Kehm K., and Hohenberg C. M. 1995.

Microanalytical laser extraction of noble gases: Techniques and applications. In *Advances in analytical geochemistry,* vol. 2, edited by Hyman M. and Rowe M. W. Greenwich, CT: JAI Press Inc. pp. 119–140.

Nier A. O. and Schlutter D. J. 1993. The thermal history of interplanetary dust particles collected in the Earth's stratosphere. *Meteoritics* 28:675–681.

Ott U. 2002. Noble gases in meteorites—Trapped components. *Review of Scientific Instruments* 47:71–100.

Pepin R. O., Dragon J. C., Johnson N. L., Bates A., Coscio M. R. Jr., and Murthy V. R. 1975. Rare gases and Ca, Sr, and Ba in Apollo 17 drill-core fines. Proceedings, 6th Lunar Science Conference, vol. 2. pp. 2027–2055.

Pepin R. O., Palma R. L., and Schlutter D. J. 2000. Noble gases in interplanetary dust particles, I: The excess helium-3 problem and estimates of the relative fluxes of solar wind and solar energetic particles in interplanetary space. *Meteoritics & Planetary Science* 35:495–504.

Rajan R. S., Brownlee D. E., Tomandl D., Hodge P. W., Farrar H., and Britten R. A. 1977. Detection of ^{4}He in stratospheric particles gives evidence of extraterrestrial origin. *Nature* 267:133–134.

Wieler R. and Baur H. 1995. Fractionation of Xe, Kr and Ar in the solar corpuscular radiation deduced by closed system etching of lunar soils. *The Astrophysical Journal* 453:987–997.

Wieler R., Anders E., Baur H., Lewis R. S., and Signer P. 1992. Characterisation of Q-gases and other noble gas components in the Murchison meteorite. *Geochimica et Cosmochimica Acta* 40: 2907–2921.

Wetherill G. W. and Chapman C. R. 1988. Asteroids and meteorites. In *Meteorites and the early solar system*, edited by Kerridge J. F. and Matthews M. S. Tucson, Arizona: The University of Arizona Press. pp. 41–44.

Zolensky M. E. and MacKinnon I. D. R. 1985. Accurate stratospheric particle size distributions from a flat-plate collection surface. *Journal of Geophysical Research* 90:5801–5808.