Antarct. Meteorite Res., **16**, 196–219, 2003

Remnant extraterrestrial noble gases in Antarctic cosmic spherules

Takahito Osawa[1], Keisuke Nagao[1], Takaaki Noguchi[2],
Ayako Nakazawa[2] and Jyun-ichi Mikada[2]

[1] *Laboratory for Earthquake Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113–0033*
[2] *Department of Materials and Biological Sciences, Ibaraki University, Bunkyo 2–1–1, Mito 310–8512*

Abstract: Noble gas abundances in Antarctic cosmic spherules collected from the Tottuki Point on the Sôya Coast, Antarctica, are considerably lower than those reported in unmelted micrometeorites, indicating severe heating of the cosmic spherules during atmospheric entry. Although ^{3}He was below detection limits (2×10^{-15} cm^3 STP) in most spherules, ^{3}He was detectable in three spherules and their ^{3}He/^{4}He ratios were close to those of unmelted micrometeorites. Ne and Ar abundances and isotopic compositions were determined for more than half of the spherules. Thirteen samples had high ^{21}Ne/^{22}Ne ratios, possibly reflecting the presence of cosmogenic ^{21}Ne, although blank corrections could not be made for most samples due to the low Ne concentrations. Eight particles had ^{40}Ar/^{36}Ar ratios lower than the atmospheric value of 296, and five of them also had SEP (solar energetic particles)-like Ne, confirming their extraterrestrial origin. These spherules apparently preserve extraterrestrial noble gases in their interiors in spite of severe heating. Sample To440080 has ^{40}Ar/^{36}Ar ratio (566.3 ± 14.8) higher than that of terrestrial atmosphere in spite of the presence of SEP-like Ne, indicating different source material from some spherules and micrometeorites. Extraterrestrial Ne and Ar were not identified in 22 of 31 analyzed spherules, although relative noble gas abundances of fifteen spherules were similar to those of unmelted micrometeorites and clearly distinguishable from terrestrial materials such as terrestrial basalt, air, and water, reflecting their extraterrestrial origin. Since noble gas abundances in Antarctic spherules can be explained as mixtures of solar and Q-components and the contribution of adsorption air is insignificant, a majority of these Antarctic spherules represent accreted extraterrestrial material and are not volcanic products.

key words: cosmic spherule, micrometeorite, noble gas, laser extraction, solar energetic particles

1. Introduction

Micrometeorites are a major source of extraterrestrial material on Earth, which has accumulated ~10^{20} kg of accreted dust since its formation (Kortenkamp and Dermott, 1998). The oldest description of extraterrestrial dust goes back to the beginning of the 19th century. Cosari, for example, found blackish-gray particles that fell in hail at Padua, Italy, on August 26, 1834 (Cosari, 1835) and concluded that the dust was a combination of iron or nickel. The same month of that year also saw the discovery of the source of the Perseid meteors.

Cosmic spherules were discovered by Murray (1876), during the H.M.S. Challenger Expedition of 1873–1876. Spherical particles in red clay from deeper parts of the central and southern Pacific Ocean were separated and were interpreted to be solidified drops of molten materials swept off meteors during their passage through the Earth's atmosphere (Murray and Renard, 1884, 1891). These cosmic spherules were generally round and their surfaces were covered with a shiny black coating having all the properties of magnetic iron oxide, which was evidence of their cosmic origin.

Cosmic spherules have been systematically collected since the middle of the 20th century in various places (*e.g.*, Buddhue, 1950; Bruun *et al.*, 1955; Parkin and Hunter, 1959; Hunter and Parkin, 1961; Murrell *et al.*, 1980; Czajkowski *et al.*, 1983; Peng and Lui, 1989; Taylor and Brownlee, 1991). Despite the many reports on cosmic dust collection, it was extremely difficult to distinguish between terrestrial and extraterrestrial material before the 1980s.

To identify spherules as extraterrestrial, cosmic-ray-produced nuclides, *i.e.*, ^{53}Mn, ^{59}Ni, ^{10}Be, and ^{26}Al, were measured (*e.g.*, Nishiizumi, 1983; Yamakoshi, 1991; Nishiizumi *et al.*, 1991, 1995; Zoppi *et al.*, 1997; Matsuzaki *et al.*, 2000). Noble gas analyses of unmelted cosmic dust particles were done to clarify their extraterrestrial origin, since noble gas isotopic compositions in extraterrestrial materials differ greatly from those of terrestrial materials (*e.g.*, Olinger *et al.*, 1990; Maurette *et al.*, 1991; Pepin *et al.*, 2000, 2001; Osawa and Nagao, 2002a). No comprehensive noble gas measurement exists, however, for individual cosmic spherules, because they generally have lost most of their noble gases due to severe heating, making it difficult to analyze single spherules (Stuart *et al.*, 1999; Osawa *et al.*, 2000). Highly sensitive mass spectrometers with ultra low blank levels are required for determining noble gas isotopic compositions in cosmic spherules. In the present work, we determined noble gas compositions for individual cosmic spherules using laser gas extraction.

2. Samples

Since the first recovery of Antarctic micrometeorites (AMMs) near Japan's Syowa Station in Antarctica from February 1957 to February 1958 (Nishibori and Ishizaki, 1959), several collections have recovered a large number of AMMs (*e.g.*, Maurette *et al.*, 1991; Nakamura *et al.*, 1999a; Yada and Kojima, 2000; Taylor *et al.*, 2000). A large-scale micrometeorite collection was conducted by the 41st Japanese Antarctic Research Expedition (JARE). Micrometeorites were collected by filtering Antarctic ice melted by a heated radiator in which warmed nonfreezing liquid was circulated. AMMs in melted ice were collected by four different filters (openings of 10, 40, 100, and 238 μm). Collection was done at sixteen points for twenty-one days (Iwata and Imae, 2002).

Spherules analyzed in this work were collected from a bare ice field near the Tottuki Point on the Sôya Coast in northeastern Lützow-Holm Bay (Iwata and Imae, 2002). Samples measured in this study are listed in Table 1. All spherules were extracted from the 100 μm filter of Tottuki #4. A majority of the particles adhering to the filter were removed by washing in clear water and residual particles were removed by ultrasonic washing. In the present study, twenty water-washed spherules and eleven ultrasonically washed spherules were analyzed. Ultrasonically washed samples are smaller than water-washed samples. Cosmic spherules are roughly classified into three groups—Stony (S), Glassy (G), and Iron (I) type—following the method of Blanchard *et al.* (1980). Among the spherules studied here, twenty-four were classified as S-type, three as I-type, and four as G-type based on texture and chemical composition determined by EDS (energy dispersive spectrometer) analysis. Transparency and color of spherules were determined by optical microscopy.

Table 1. List of spherules studied in this work.

Sample*	Type†	Size	Weight (μg)	Transparency‡	Color	Shape	Remarks
T004uTC003	S	70 × 60	1.5	Opaque	Black	Sphere	
T004uTC004	S	65 × 60	1.0	Opaque	Black	Sphere	
T004uTC005	S	75 × 60	1.0	Opaque	Black	Oval	Barred Olivine type
T004uTC006	S	80 × 80	2.0	Opaque	Black	Sphere	
T004uTC010	S	80 × 70	1.0	Opaque	Black	Sphere	
T004uTC011	I	65 × 60	0.8	Opaque	Black	Sphere	
T004uTC012	G	50 × 45	0.5	Trans.	Dark yellow	Sphere	
T004uTC013	S	55 × 50	0.5	Opaque	Black	Not spherical	Dendritic Magnetite type
T004uTC016	S	45 × 40	0.3	Opaque	Black	Sphere	
T004uTC018	S	38 × 35	<0.3	Opaque	Black	Sphere	
T004uTC020	I	95 × 90	1.8	Opaque	Black	Sphere	
T004TC002	S	170 × 170	12.1	Opaque	Black	Sphere	
T004TC003	S	250 × 250	10	Opaque	Black	Oval	Barred Olivine type
T004TC005	S	140 × 130	5.1	Opaque	Black	Sphere	
T004TC006	S	150 × 160	4.4	Opaque	Black	Sphere	
T004TC007	S	180 × 180	10.2	Opaque	Black	Sphere	Barred Olivine type
T004TC008	I	90 × 90	3.9	Opaque	Black	Sphere	Ni bearing
T004TC009	G	170 × 160	11.4	Trans.	Green	Sphere	
T004TC010	G	140 × 130	2.1	Trans.	Green	Hemisphere	
To440065	G	85 × 85	0.8	Trans.	Gray	Sphere	
To440066	S	100 × 100	1.4	Opaque	Black	Not spherical	
To440070	S	110 × 100	1.7	Opaque	Black	Not spherical	
To440072	S	95 × 95	1.6	Opaque	Black	Sphere	Dendritic Magnetite type
To440077	S	105 × 90	1.0	Opaque	Black	Not spherical	
To440078	S	95 × 70	0.5	Opaque	Black	Oval	
To440080	S	95 × 80	0.7	Opaque	Gray	Not spherical	
To440081	S	115 × 105	1.8	Opaque	Black	Sphere	
To440084	S	100 × 95	1.9	Opaque	Black	Sphere	
To440085	S	100 × 70	1.3	Opaque	Dark Brown	Hemisphere	
To440088	S	105 × 100	1.9	Opaque	Black	Sphere	
To440089	S	115 × 105	2.1	Opaque	Black	Sphere	Ni bearing

* A small letter 'u' in the sample name shows ultrasonic washing.

† Spherules are classified to three groups: Stony (S), Glassy (G), and Iron (I) type based on a microscopic investigation and EDS analyses.

‡ Transparency is determined by optical microscopy to opaque and transparent (Trans.).

3. Experimental procedure

Samples were loaded into a tantalum sample holder and covered by a thin glass. The sample holder was connected to an ultrahigh vacuum chamber with a purification line. The ultra-high vacuum line pressure was approximately 2×10^{-10} Torr. Noble gases in spherules were extracted by laser heating using a Nd-YAG continuous wave laser with an output power of 2.5–3.5 W. Extracted gas was purified by a heated Ti-Zr getter and noble gases other than He were trapped in a cryogenically cooled trap at 15K. The isotopic composition of He was analyzed on a modified VG-5400 mass spectrometer (MS-III). Ne, Ar, Kr, and Xe were released from the trap at 45, 110, 135, and 160 K, respectively, and successively measured. All noble gas isotopes were measured by a secondary electron multiplier using an ion counting system. Sensitivity and mass discrimination effects were calibrated using an atmospheric noble gas standard, and a helium standard gas with $^{3}He/^{4}He=1.71\times10^{-4}$, which was prepared by mixing pure ^{3}He and ^{4}He. Neon mass interferences caused by $^{40}Ar^{++}$ and CO_2^{++} were corrected using experimentally determined $^{40}Ar^{++}/^{40}Ar^{+}$ and CO_2^{++}/CO_2^{++} ratios precisely determined as 0.39 and 0.004, respectively, before the inlet of gases into the mass spectrometer. During Ne analysis, argon and carbon dioxide were removed by a liquid-nitrogen-cooled trap. Blanks were determined by laser-heating of an empty crucible. The weight of each AMM was determined by averaging several measurements using a precision balance.

4. Results and discussions

4.1. *Noble gas concentrations*

Released amounts and concentrations of noble gases are listed in Table 2 and indicate that the light noble gas concentrations in spherules are extremely low. Figure 1 displays histograms of ^{4}He and ^{20}Ne contents. The spherules clearly have lower concentrations of He and Ne than those of unmelted micrometeorites, indicating loss of noble gases during atmospheric entry heating. Unmelted micrometeorites generally have solar-derived He in the range of 1.5×10^{-5} cm^3 STP/g to 1×10^{-2} cm^3 STP/g and Ne in the range of 5×10^{-7} cm^3 STP/g to 1×10^{-4} cm^3 STP/g (*e.g.*, Osawa *et al.*, 2000). If the spherules originally contained solar-He and Ne, these gases must have been lost during their atmospheric entry, which removes the surface layers of the cosmic particles. Note that even solar energetic particles (SEP) with larger energies compared to solar wind gases penetrate only a few tens of microns into exposed silicate material (Wieler *et al.*, 1987).

The low Ne concentrations cannot be explained by depletion due to aqueous alteration in Antarctic ice because no systematic Ne loss was found in jarosite-bearing AMMs, although significant He loss was found in these AMMs (Osawa and Nagao, 2002a). The result shows that aqueous alteration does not control Ne concentration and, hence, the systematic Ne loss found in the spherules is not caused by aqueous alteration. Therefore, low He and Ne concentrations in the cosmic spherules are probably caused by atmospheric entry heating.

^{36}Ar and ^{40}Ar contents of spherules are also lower than those of unmelted microme-

Table 2. Released amounts of noble gases and calculated concentrations per gram.

Sample	Weight (μ g)*	Run	^{4}He†	^{20}Ne†	^{36}Ar†	^{40}Ar†	^{84}Kr†	^{132}Xe†	^{4}He‡	^{20}Ne‡	^{36}Ar‡	^{40}Ar‡	^{84}Kr‡	^{132}Xe‡
			(10^{-12}cm^{3}STP)						(10^{-6}cm^{3}STP/g)					
T004uTC003	1.5	1	23.0	8.29	0.56	34.5	0.0039	0.0010	4.54	5.38	0.34	12.0	0.0012	0.0007
T004uTC004	1.0	1	26.6	0.45	0.10	29.4	0.0011	n.d.§	10.4	0.23	0.046	12.9	n.d.#	n.d.
T004uTC005	1.0	1	18.9	0.30	0.062	19.4	0.0013	n.d.§	2.70	0.08	0.010	2.9	n.d.#	n.d.
T004uTC006	2.0	1	17.7	0.32	0.10	31.7	0.0012	0.0005	0.75	0.05	0.025	7.6	n.d.#	0.0002
T004uTC010	1.0	1	17.8	0.38	0.082	24.3	0.0028	0.0004	1.60	0.16	0.029	7.8	0.0007	0.0004
T004uTC011	0.8	1	19.1	0.83	0.06	17.6	0.0023	0.0003	3.59	0.76	0.007	1.4	0.0002	0.0004
T004uTC012	0.5	1	18.0	0.31	0.12	35.9	0.0027	0.0003	3.55	0.17	0.13	38.8	0.0012	0.0006
T004uTC013	0.5	1	20.0	2.15	0.21	30.1	0.0059	0.0015	7.65	3.85	0.32	27.3	0.0076	0.0030
T004uTC016	0.3	2	9.9	0.27	0.04	11.6	0.0015	0.0008	0.20	n.d.#	n.d.#	n.d.#	0.0018	0.0010
T004uTC018	<0.3	2	30.6	1.50	0.16	28.0	n.d.$	0.0008	>69.3	>3.96	>0.40	>47.7	n.d.	>0.001
T004uTC020	1.8	2	10.0	0.29	0.05	15.0	0.0017	0.0006	0.14	n.d.#	0.0020	0.73	0.0004	0.0001
T004TC002	12.1	1	16.9	0.25	0.10	33.5	0.0033	0.0023	0.06	0.002	0.0043	1.4	0.0001	0.0002
T004TC003	10	1	16.5	0.32	0.12	35.9	0.0030	0.0002	0.03	0.01	0.0064	1.9	0.0001	0.00002
T004TC005	5.1	1	15.3	0.27	0.075	22.8	0.0041	0.0005	n.d.#	0.01	0.0044	1.2	0.0004	0.0001
T004TC006	4.4	1	16.9	0.35	0.74	29.6	0.0048	0.0003	0.16	0.03	0.16	3.0	0.0006	0.00008
T004TC007	10.2	1	15.2	0.28	0.043	13.3	0.0010	0.0003	n.d.#	0.01	n.d.	n.d.#	n.d.#	0.00003
T004TC008	3.9	1	16.1	1.86	0.074	23.4	0.0039	0.0003	n.d.#	0.42	0.0055	1.8	0.0005	0.00009
T004TC009	11.4	1	16.8	0.34	0.049	15.3	0.0041	n.d.§	0.05	0.010	n.d.	n.d.#	0.0002	n.d.
T004TC010	2.1	1	18.1	0.27	0.037	11.3	0.0025	n.d.§	0.89	0.02	n.d.	n.d.#	0.0002	n.d.
To440065	0.8	2	12.4	8.31	1.073	73.5	0.0003	n.d.§	3.29	10.00	1.29	74.8	n.d.	n.d.
To440066	1.4	2	11.5	0.36	0.066	20.3	0.0026	0.0007	1.19	0.03	0.015	4.7	0.0012	0.0001
To440070	1.7	2	12.3	0.29	0.029	10.2	0.0013	0.0008	1.48	n.d.	n.d.	n.d.#	0.0002	0.0002
To440072	1.6	2	10.5	0.37	0.060	18.9	0.0014	0.0004	0.47	0.04	0.010	3.2	0.0003	n.d.#
To440077	1.0	2	77.2	4.95	0.40	35.2	0.0019	0.0008	67.4	4.64	0.36	21.5	0.0010	0.0003
To440078	0.5	2	10.0	0.37	0.045	14.1	0.0022	0.0006	0.37	0.11	0.0016	0.78	0.0025	0.0002
To440080	0.7	2	236	11.0	0.50	271.9	0.0021	0.0007	323	15.3	0.65	368.8	0.0017	0.0003
To440081	1.8	2	11.8	2.84	0.32	23.3	0.0021	0.0011	1.09	1.41	0.15	5.4	0.0006	0.0003
To440084	1.9	2	11.0	0.37	0.11	31.9	0.0026	0.0010	0.64	0.03	0.034	9.6	0.0008	0.0003
To440085	1.3	2	10.0	0.30	0.060	18.2	0.0019	0.0006	0.15	n.d.	0.012	3.5	0.0007	0.0001
To440088	1.9	2	18.8	3.48	0.16	7.2	0.0020	0.0006	4.75	1.67	0.061	n.d.#	0.0006	0.0001
To440089	2.1	2	10.5	0.33	0.054	15.6	0.0011	0.0008	0.31	0.01	0.0046	0.89	0.0001	0.0001
blank (run 1)	---		16.2	0.22	0.052	16.5	0.0021	n.d.§	---	---	---	---	---	---
blank (run 2)	---		9.8	0.31	0.044	13.8	0.0010	0.0005	---	---	---	---	---	---

* Weights have 10-30 percent errors.
† Measured abundances without blank corrections. Uncertainties about 15%
‡ Blank corrections were carried out.
§ Xe concentrations were lower than the detection limit, which is about 1 10^{-16} cm^3.
# Concentrations cannot be determined due to the low abundance of noble gases comparable to blank values.
$ Cannot detected due to experimental trouble.

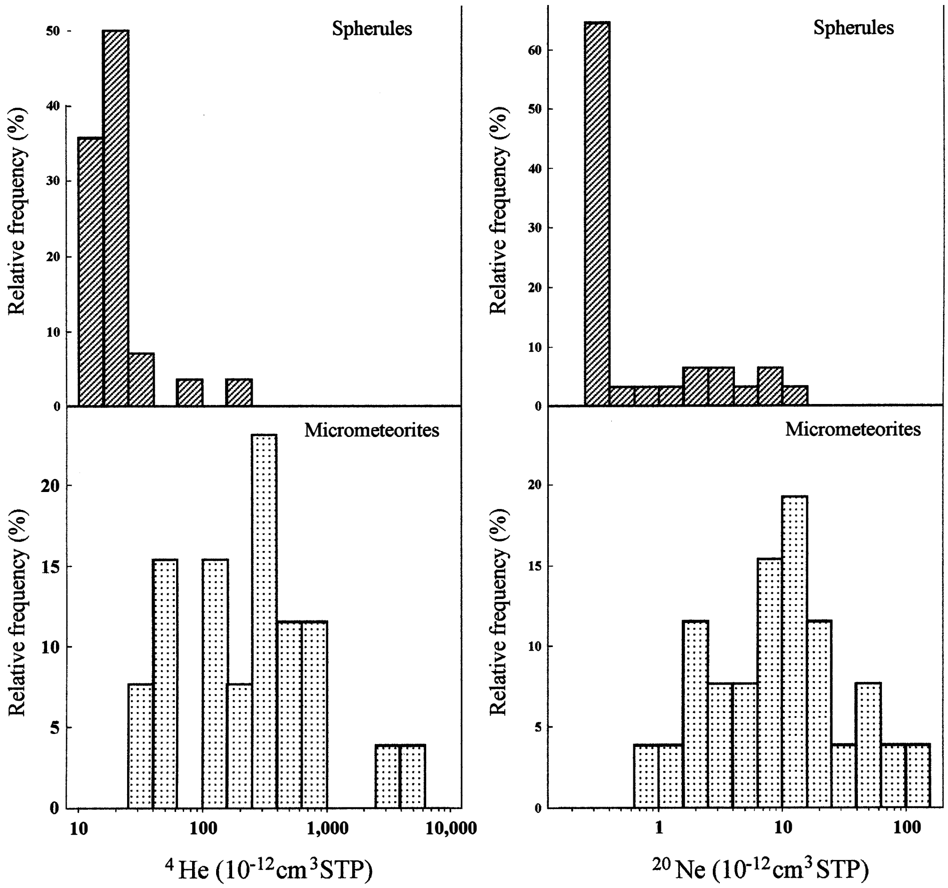

Fig. 1. Histograms of ^{4}He and ^{20}Ne contents in Antarctic cosmic spherules and micrometeorites. Data on unmelted micrometeorites is from Osawa and Nagao (2002b). Contents of ^{4}He and ^{20}Ne of spherules are dramatically lower than those in micrometeorites, showing the escape of light noble gases.

teorites (Fig. 2). Osawa and Nagao (2002b) reported that ^{36}Ar in unmelted AMMs contains a significant primordial trapped component. Hence the low ^{36}Ar concentrations in the spherules presumably indicate loss of trapped ^{36}Ar and SEP-Ar if these particles are extraterrestrial. The noble gas loss presumably took place during atmospheric entry heating.

4.2. Light noble gases

Unmelted micrometeorites generally have SEP-like He, with ^{3}He/^{4}He ratio of 2–4 $\times 10^{-4}$ (*e.g.*, Stuart *et al.*, 1999; Osawa and Nagao, 2002b). Most spherules, however, have very low ^{3}He/^{4}He ratios (Table 3). Released amounts of ^{3}He in most spherules were comparable to the detection limit of the mass spectrometer, 2×10^{-15} cm^3 STP. Therefore, accurate ^{3}He/^{4}He ratios could not be determined in fifteen samples and only

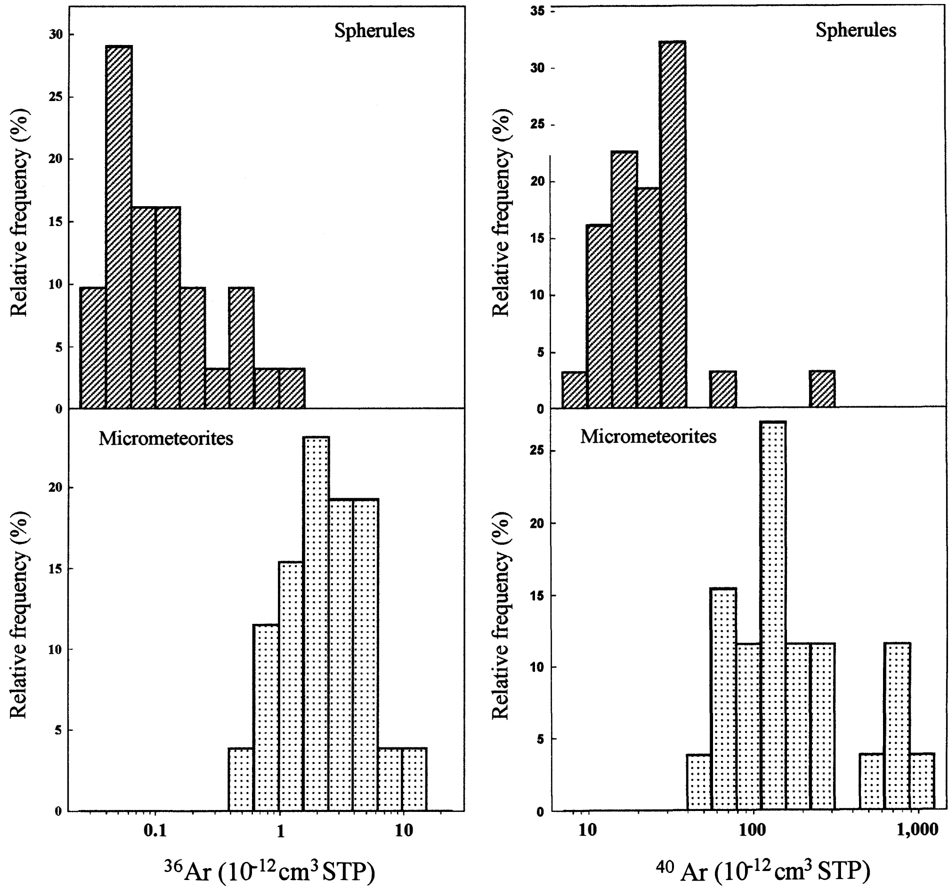

Fig. 2. Histograms of ^{36}Ar and ^{40}Ar contents in Antarctic cosmic spherules and micrometeorites. Data on unmelted micrometeorites is after Osawa and Nagao (2002b). Ar contents of spherules are clearly lower than those in the micrometeorites.

upper limits could be estimated in thirteen samples. Although these thirteen spherules may preserve solar-He, we cannot prove extraterrestrial origin from He data due to large ambiguities. Clearly, the majority of He gases in most samples was lost by heating, even if they originally had solar-derived He.

Three spherules (T004uTC018, To440077, and To440080) have detectable ^{3}He and their ^{3}He/^{4}He ratios were determined. Figure 3 shows He composition of spherules and unmelted Antarctic micrometeorites. Since ^{3}He/^{4}He ratios of these three spherules clearly indicate the presence of solar-derived He, their extraterrestrial origin is confirmed by the He data. ^{3}He/^{4}He ratios for To440077 and T004uTC018 are close to the solar wind (SW) (^{3}He/^{4}He$=4.57\times10^{-4}$; Benkert *et al.*, 1993), and To440080 is between SW and SEP (^{3}He/^{4}He$=2.17\times10^{-4}$; Benkert *et al.*, 1993). He concentrations of these three spherules (6.7–32×10^{-5} cm^{3}STP/g) are comparable to unmelted micrometeorites, showing relatively mild atmospheric entry heating. This conjecture

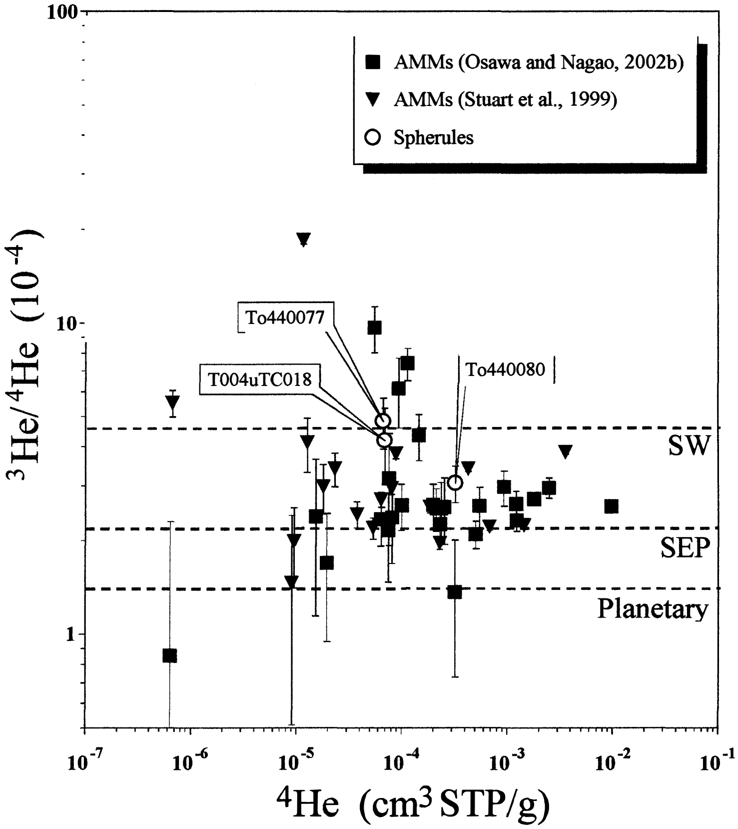

Fig. 3. Relationship between ^4He concentration and $^3He/^4He$ ratio. Errors are one sigma. Unmelted AMMs are after Osawa and Nagao (2002b) and Stuart et al. (1999). SW-He, SEP-He (Benkert et al., 1993) and planetary-He (Reynolds et al., 1978). $^3He/^4He$ ratios of three spherules show the presence of solar He.

agrees with non-spherical shapes of To440077 and To440080 (Table 1). T004TC018 is, however, spherical particle, showing severe heating during atmospheric entry. Since these spherules clearly preserve solar He in spite of low retention of He, relic grains may exist in them and their inner portions barely avoided complete He loss.

Since neon concentrations for most spherules are also low as shown in Fig. 1, blank corrections could not be carried out for Ne in half of the particles (Table 3). The data with and without blank corrections are shown separately (Fig. 4). Ne isotopic compositions of ten samples (Fig. 4 upper panel) are consistent with the atmospheric value within experimental uncertainties. These particles did not preserve their solar-derived neon component, in contrast with the micrometeorites, which generally have SEP-Ne (Olinger *et al.,* 1990; Maurette *et al.*, 1991; Osawa *et al.*, 2000; Osawa and Nagao, 2002 a, b). On the other hand, thirteen samples have relatively high $^{21}Ne/^{22}Ne$ ratios, which indicate the presence of cosmogenic nuclides. Unmelted micrometeorites generally have very short cosmic ray exposure ages (<1 Ma) compared to normal meteorites, and

Table 3. Helium and neon in spherules.

Sample	not corrected for blank ^{4}He (10^{-12}cm^{3}STP)	not corrected for blank ^{3}He/^{4}He (10^{-4})	corrected for blank ^{4}He (10^{-12}cm^{3}STP)	corrected for blank ^{3}He/^{4}He (10^{-4})	not corrected for blank ^{20}Ne (10^{-12}cm^{3}STP)	not corrected for blank ^{20}Ne/^{22}Ne	not corrected for blank ^{21}Ne/^{22}Ne	corrected for blank* ^{20}Ne (10^{-12}cm^{3}STP)	corrected for blank* ^{20}Ne/^{22}Ne	corrected for blank* ^{21}Ne/^{22}Ne
T004uTC003	23.0	<2.93	6.81	<9.99	8.29	11.89 ±0.465	0.030 ±0.0072	8.07	11.94 ±0.48	0.030 ±0.007
T004uTC004	26.6	<2.34	10.4	<6.02	0.45	9.60 ±1.05	0.090 ±0.056	0.23	9.07 ±2.09	0.136 ±0.111
T004uTC005	18.9	n.d.*	2.70	n.d.	0.30	10.77 ±1.94	0.041 ±0.028	0.08	n.d.	n.d.
T004uTC006	17.7	n.d.*	1.49	n.d.	0.32	9.84 ±1.49	0.047 ±0.031	0.09	n.d.	n.d.
T004uTC010	17.8	n.d.*	1.60	n.d.	0.38	10.09 ±0.92	0.027 ±0.021	0.16	10.03 ±2.22	(0.005) (±0.053)
T004uTC011	19.1	n.d.*	2.88	n.d.	0.83	9.95 ±0.92	0.034 ±0.011	0.61	9.88 ±1.26	0.031 ±0.015
T004uTC012	18.0	n.d.*	1.77	n.d.	0.31	9.88 ±1.00	0.043 ±0.011	0.09	n.d.	n.d.
T004uTC013	20.0	<2.00	3.83	<11.1	2.15	11.02 ±0.46	0.035 ±0.010	1.92	11.12 ±0.51	0.035 ±0.011
T004uTC016	9.9	n.d.*	0.06	n.d.	0.27	7.41 ±1.13	0.033 ±0.022	n.d.	n.d.	n.d.
T004uTC018	30.6	2.85 ±0.76	20.8	4.18 ±1.15	1.50	10.76 ±0.53	0.024 ±0.008	1.19	10.99 ±0.70	0.022 ±0.010
T004uTC020	10.0	<1.32	0.2	<126	0.29	10.08 ±2.42	0.107 ±0.070	n.d.	n.d.	n.d.
T004TC002	16.9	n.d.*	0.70	n.d.	0.25	9.88 ±1.36	0.051 ±0.017	0.03	n.d.	n.d.
T004TC003	16.5	n.d.*	0.31	n.d.	0.32	10.78 ±1.63	0.159 ±0.066	0.10	n.d.	n.d.
T004TC005	15.3	n.d.*	n.d.	n.d.	0.27	9.67 ±1.34	0.142 ±0.038	0.05	n.d.	n.d.
T004TC006	16.9	<1.79	0.72	<47.6	0.35	9.70 ±0.90	0.028 ±0.021	0.13	8.96 ±2.46	(0.004) (±0.061)
T004TC007	15.2	n.d.*	n.d.	n.d.	0.28	9.40 ±0.98	0.125 ±0.058	0.06	n.d.	n.d.

T004TC008	16.1	<1.33	n.d.	n.d.	1.86	9.79 ±0.76	0.019 ±0.009	1.63	9.74 ±0.87	0.016 ±0.011
T004TC009	16.8	n.d.*	0.54	n.d.	0.34	10.18 ±0.81	0.045 ±0.022	0.12	10.26 ±2.36	0.049 ±0.066
T004TC010	18.1	n.d.*	1.88	n.d.	0.27	9.74 ±1.38	0.033 ±0.017	0.04	n.d.	n.d.
To440065	12.4	<0.55	2.6	<2.59	8.31	11.01 ±0.26	0.029 ±0.007	8.00	11.05 ±0.27	0.029 ±0.007
To440066	11.5	<0.23	1.7	<1.49	0.36	7.28 ±1.15	0.147 ±0.061	0.05	n.d.	n.d.
To440070	12.3	<0.78	2.5	<3.82	0.29	7.22 ±1.50	0.059 ±0.030	n.d.	n.d.	n.d.
To440072	10.5	<1.00	0.75	<17.1	0.37	10.02 ±2.14	0.035 ±0.021	0.06	n.d.	n.d.
To440077	77.2	4.22 ±0.79	67.4	4.83 ±0.90	4.95	10.60 ±0.50	0.049 ±0.020	4.64	10.65 ±0.54	0.050 ±0.021
To440078	10.0	n.d.*	0.19	n.d.	0.37	10.22 ±1.89	0.055 ±0.036	0.05	n.d.	n.d.
To440080	236	2.94 ±0.40	226	3.06 ±0.41	11.0	11.01 ±0.36	0.029 ±0.008	10.69	11.04 ±0.38	0.029 ±0.008
To440081	11.8	<2.29	2.0	<14.4	2.84	9.55 ±0.49	0.075 ±0.010	2.53	9.51 ±0.55	0.081 ±0.011
To440084	11.0	n.d.*	1.2	n.d.	0.37	10.71 ±1.63	0.084 ±0.053	0.05	n.d.	n.d.
To440085	10.0	<1.32	0.19	<197	0.30	9.49 ±2.01	0.093 ±0.052	n.d.	n.d.	n.d.
To440088	18.8	<2.90	9.0	<6.06	3.48	11.30 ±0.56	0.029 ±0.009	3.17	11.44 ±0.62	0.028 ±0.010
To440089	10.5	<1.59	0.66	<33.7	0.33	9.30 ±1.70	0.019 ±0.011	0.01	n.d.	n.d.
blank (run 1)	16.2	n.d.*	---	---	0.22	9.94 ±0.67	0.045 ±0.020	---	---	---
blank (run 2)	9.8	n.d.*	---	---	0.31	9.86 ±0.70	0.031 ±0.012	---	---	---

All errors are one sigma

* ^{3}He abundances were lower than the detection limit of 2 $10^{-15} cm^{3}$.

† Blank corrections were carried out for the samples with ^{20}Ne contents higher than the 150% of the blank value.

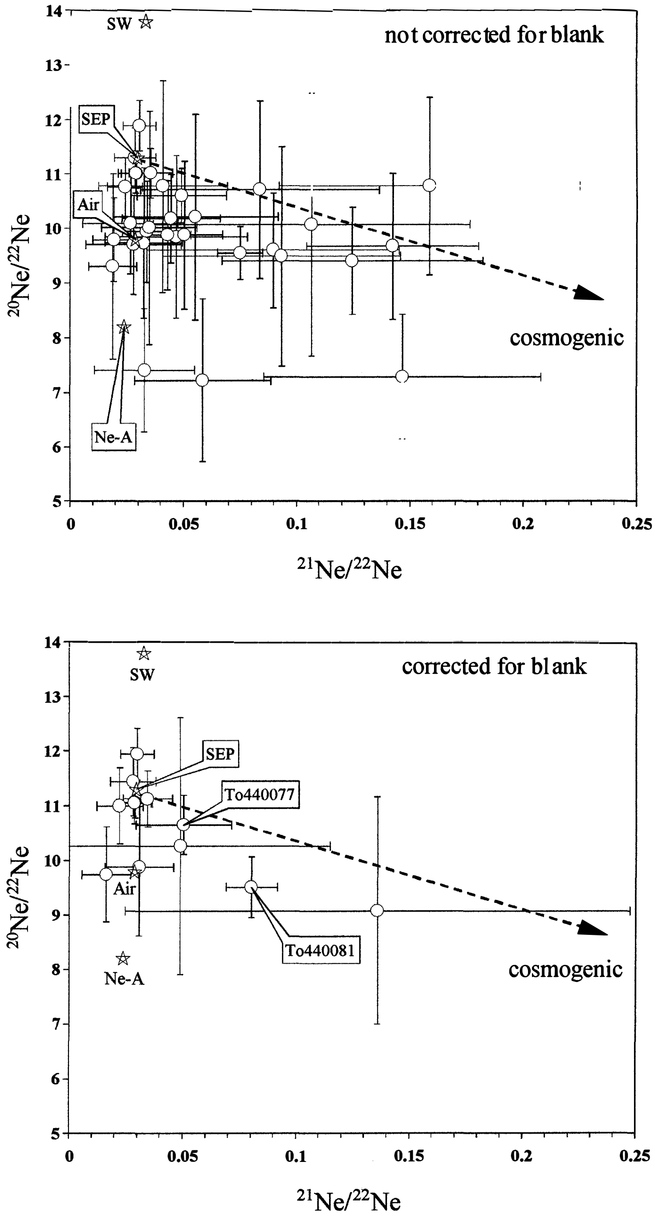

Fig. 4. Three-isotope plot of Ne. Errors are one sigma. Above is a diagram without blank correction. Blank corrected values of twelve samples are shown in the diagram below. Solar wind (SW) and solar energetic particle (SEP)-Ne are after Benkert et al. (1993), Ne-A after Black and Pepin (1969), and Air-Ne after Eberhardt et al. (1965). Thirteen particles have high $^{21}Ne/^{22}Ne$ ratios, possibly indicating the presence of cosmogenic nuclides, although blank correction cannot be carried out for most of these samples. Six spherules clearly preserve SEP-Ne, and have $^{20}Ne/^{22}Ne$ ratios higher than that of terrestrial air.

their $^{21}Ne/^{22}Ne$ ratios are low (Osawa and Nagao, 2002b). However, some micrometeorites have extremely long exposure ages, and their excess ^{21}Ne concentrations are $0.2–1.3 \times 10^{-7}$ cm^{3}STP/g (Osawa and Nagao, 2002b). The excess ^{21}Ne in these spherules is calculated to be $0.3–9.0 \times 10^{-9}$ cm^{3}STP/g, much lower than those of the micrometeorites with excess ^{21}Ne. Although the concentration of excess ^{21}Ne is lower than those of the micrometeorites, the high $^{21}Ne/^{22}Ne$ ratios of these spherules might represent some cosmogenic ^{21}Ne. However, the presence of cosmogenic Ne was surely unequivocally proven only for T0440081, which has relatively high Ne concentration ($^{20}Ne = 1.41 \times 10^{-6}$ cm^{3}STP/g) and high $^{21}Ne/^{22}Ne$ (0.081 ± 0.011). This spherule also has extraterrestrial Ar (described below).

SEP-like Ne was detected in six spherules (T004uTC003, T004uTC013, T004uTC 018, To440065, To440080, and To440088). Their blank-corrected $^{20}Ne/^{22}Ne$ ratios are higher than the atmospheric value of 9.8. They have relatively high Ne concentrations compared with other spherules (Table 2). The relationship between ^{20}Ne concentrations and $^{20}Ne/^{22}Ne$ ratios is shown in Fig. 5. These spherules have ^{20}Ne concentrations comparable to those of unmelted AMMs and their $^{20}Ne/^{22}Ne$ ratios are close to SEP-Ne ($^{20}Ne/^{22}Ne = 11.2$; Benkert *et al.*, 1993), reflecting surviving solar-derived Ne. Although To440077 has high ^{20}Ne concentration, its $^{20}Ne/^{22}Ne$ ratio is slightly lower than SEP. On the other hand, other particles have ^{20}Ne concentrations lower than 1.5

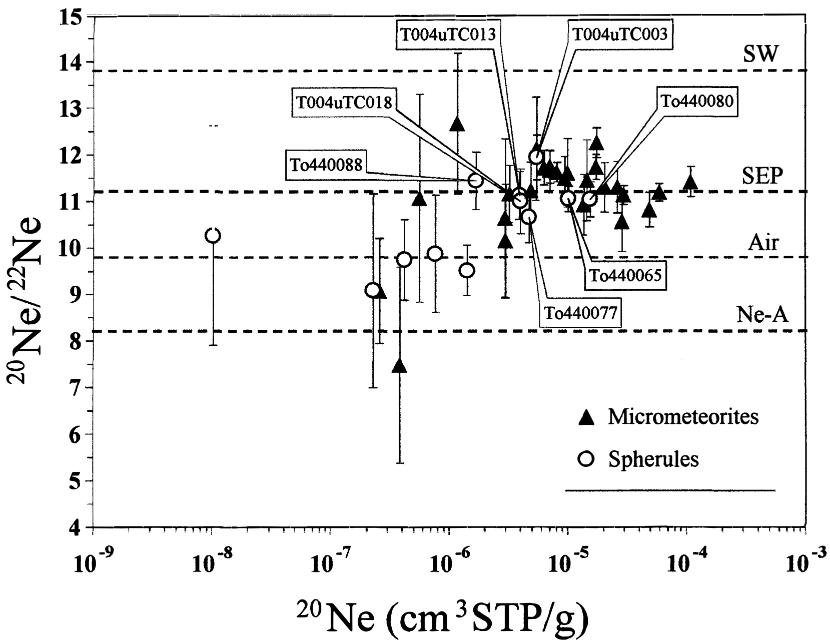

Fig. 5. ^{20}Ne concentrations versus $^{20}Ne/^{22}Ne$ ratios. Data on unmelted micrometeorites is after Osawa and Nagao (2002b). Errors are one sigma. Six spherules with SEP-like Ne have high ^{20}Ne concentrations comparable to those of unmelted AMMs, reflecting in complete degassing. $^{20}Ne/^{22}Ne$ ratio of sample To440077 is slightly lower than SEP, although its ^{20}Ne concentration is comparable to unmelted micrometeorites.

Table 4. Contents and isotopic ratios of heavy noble gases in spherules.

T004TC008	0.074	0.186 ±0.037	316.9 ±12.1	0.02	0.187 ±0.129	338 ±44.2	3.94	0.35	0.0011	0.00021
T004TC009	0.049	0.173 ±0.018	313.2 ±22.2	n.d.	n.d.	n.d.	4.13	n.d.	0.017	n.d.
T004TC010	0.037	0.175 ±0.015	309.6 ±15.9	n.d.	n.d.	n.d.	2.50	n.d.	0.010	n.d.
To440065	1.07	0.193 ±0.012	68.5 ±1.9	1.03	0.193 ±0.012	58.1 ±2.4	0.33	n.d.	n.d.	n.d.
To440066	0.07	0.194 ±0.041	309.2 ±8.5	0.02	0.201 ±0.126	307.0 ±30.3	2.59	0.69	0.035	0.0043
To440070	0.03	0.202 ±0.041	344.8 ±13.9	n.d.	n.d.	n.d.	1.31	0.79	n.d.	n.d.
To440072	0.06	0.185 ±0.021	315.1 ±15.1	0.02	0.169 ±0.085	328.8 ±61.7	1.44	0.39	0.0082	n.d.
To440077	0.40	0.202 ±0.010	87.2 ±1.9	0.36	0.204 ±0.011	59.8 ±4.4	1.94	0.79	0.0002	0.00006
To440078	0.04	0.179 ±0.039	313.3 ±31.5	0.001	n.d.	n.d.	2.19	0.59	0.0231	0.0018
To440080	0.50	0.191 ±0.012	543.7 ±13.2	0.46	0.191 ±0.014	566.3 ±14.8	2.13	0.69	0.0001	0.00002
To440081	0.32	0.199 ±0.013	73.8 ±1.5	0.27	0.200 ±0.015	35.4 ±5.9	2.06	1.08	0.0004	0.0002
To440084	0.11	0.195 ±0.014	294.3 ±3.0	0.06	0.197 ±0.025	283.3 ±7.7	2.56	0.98	0.0301	0.0092
To440085	0.06	0.185 ±0.034	304.9 ±8.6	0.02	0.167 ±0.132	289.5 ±40.1	1.88	0.59	n.d.	n.d.
To440088	0.16	0.208 ±0.039	44.6 ±4.6	0.12	0.215 ±0.054	<1	2.00	0.59	0.0003	0.000031
To440089	0.05	0.164 ±0.021	289.4 ±20.3	0.01	n.d.	n.d.	1.06	0.79	0.0079	0.0213
blank (run 1)	0.052	0.186 ±0.011	308.3 ±5.21	---	---	---	2.10	n.d.	0.0093	---
blank (run 2)	0.044	0.191 ±0.010	310.3 ±7.6	---	---	---	0.95	0.49	0.0031	0.0016

All errors are one sigma

* Blank corrections were carried out for the samples with ^{36}Ar contents higher than the 140% of the blank value.

† Blank corrections were carried out.

$\times 10^{-6}$ cm^3 STP/g and isotopic ratios close to atmospheric Ne, presumably representing exchanges with terrestrial atmospheric gases.

The six spherules with SEP-like Ne also have no ^{21}Ne excess (Fig. 3 lower panel), showing short exposure ages. Since a majority of unmelted micrometeorites have no ^{21}Ne excess, Ne compositions of the six particles correspond to micrometeorite compositions, proving their extraterrestrial origin. Sample To440077 has slightly high $^{21}Ne/^{22}Ne$ ratio (0.050 ± 0.021) and the calculated ^{21}Ne excess is 9.0×10^{-9} cm^3 STP/g if $^{21}Ne/^{22}Ne$ is assumed to be 0.050. Although the calculated excess ^{21}Ne concentration is the higher in the measured spherules, it is much lower than unmelted micrometeorites with excess ^{21}Ne (Osawa and Nagao, 2002b). Since the $^{20}Ne/^{22}Ne$ ratio of this spherule corresponds to Q-Ne (10.70; Wieler *et al.*, 1992) rather than SEP, this spherule may preserve a primordial Ne component, although this cannot be proven from this Ne data.

We obtained extraterrestrial evidence from Ne composition for only the seven spherules because other spherules did not have detectable solar-derived Ne.

4.3. Argon

Argon isotopic compositions of the spherules are listed in Table 4. Twenty-one samples released enough Ar gas to determine their compositions. Ten other particles have Ar contents comparable to the blank level and blank corrections could not be applied. Unmelted micrometeorites have lower $^{40}Ar/^{36}Ar$ ratios than the atmospheric value of 296 (Osawa *et al.*, 2000; Osawa and Nagao, 2002b) and extraterrestrial particles originally have chondritic Ar compositions (Osawa and Nagao, 2002b). Figure 6 shows the relationship between the ^{36}Ar concentrations and $^{40}Ar/^{36}Ar$ ratios. On the basis of their $^{40}Ar/^{36}Ar$ ratios and ^{36}Ar concentrations, spherules can be divided into three groups. The high $^{40}Ar/^{36}Ar$ group consists of fourteen spherules. They have lower ^{36}Ar concentrations (4.4×10^{-9} ~ 1.3×10^{-7} cm^3 STP/g) compared with other spherules and unmelted micrometeorites. $^{40}Ar/^{36}Ar$ ratios of this group correspond to the atmospheric value within errors, indicating absence of a chondritic or solar-Ar component. Even if they are extraterrestrial materials, primitive Ar components have been lost and exchange has taken place with atmospheric Ar. Therefore, we did not obtain extraterrestrial evidence for these spherules from Ar data.

Eight particles in another group having low $^{40}Ar/^{36}Ar$ ratios clearly show extraterrestrial origin. Since they preserve extraterrestrial Ar, their ^{36}Ar concentrations are clearly higher than the high $^{40}Ar/^{36}Ar$ group. Five of these particles also preserve SEP-like Ne. Samples 004TC006 and To440081 have extraterrestrial Ar in spite of a dearth of detectable extraterrestrial Ne. Since ^{36}Ar concentrations for these two spherules are lower than those of other spherules in the low $^{40}Ar/^{36}Ar$ group, SEP-Ne was removed by severe heating during atmospheric entry. Sample To440077 with Q-like Ne and excess ^{21}Ne has low $^{40}Ar/^{36}Ar$ ratio (59.8 ± 4.4), indicating its extraterrestrial origin. In Fig. 6, the eight spherules of this group are distributed in the left side of the area where unmelted micrometeorites are distributed, presumably indicating a systematic loss of Ar, but extraterrestrial Ar was not completely lost. Only sample To 440065 has high ^{36}Ar concentration comparable to unmelted micrometeorites, and its ^{20}Ne concentration is also comparable to those of micrometeorites (Fig. 5).

From the $^{40}Ar/^{36}Ar$ ratios, we cannot judge whether the source of the extraterres-

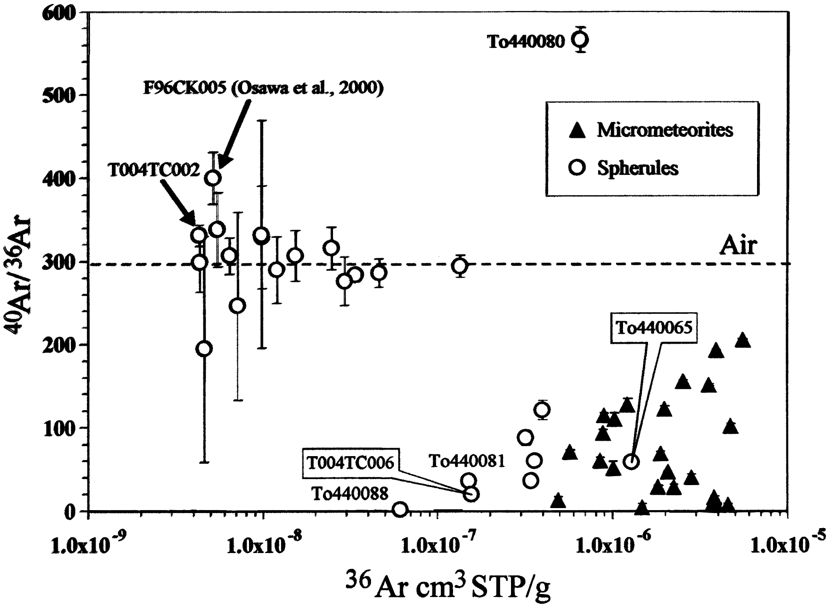

Fig. 6. *^{36}Ar concentrations versus ^{40}Ar/^{36}Ar ratios. Unmelted micrometeorites are after Osawa and Nagao (2002b). The broken line shows an atmospheric ^{40}Ar/^{36}Ar ratio of 296. ^{40}Ar/^{36}Ar ratios of fourteen spherules correspond to that of the atmosphere. Only sample To440080 has high ^{40}Ar/^{36}Ar ratio and high ^{36}Ar concentration possibly reflecting its distinctive origin (see text). Sample T004TC002 also has ^{40}Ar/^{36}Ar ratio higher than that of air and its Ar composition is similar to sample F96CK005, which is a spherule reported by Osawa et al. (2000). Eight spherules evidently preserve extraterrestrial Ar, although their ^{36}Ar concentrations are lower than unmelted micrometeorites.*

trial Ar component trapped in these spherules originated in a solar or a primordial component, because both components have very low ^{40}Ar/^{36}Ar ratios. The ^{38}Ar/^{36}Ar ratios are generally more diagnostic of solar and primordial component. However, the ^{38}Ar/^{36}Ar ratios of spherules have large ambiguities due to low concentration of ^{38}Ar and we cannot separate solar and primordial component.

It may be important that these two groups are mutually exclusive. Backscattered images of the nine particles with extraterrestrial Ne or Ar are shown in Fig. 7. Samples T004uTC013, To440077, and To440080 are nonspherical, possibly indicating that they underwent relatively mild heating and did not melt totally. However, dendritic magnetite appears on the surface of sample T004uTC013, similar to the texture observed in heated CM chondrite (Toppani *et al.*, 2001). Heating simulation of carbonaceous chondrites by Toppani *et al.* (2001) provides insights into the spherule formation process. Flash heating above 1000°C for 20 s led to the crystallization of spinels on the surface of the chondrite particle. Sample T004uTC013 was presumably heated to approximately 1500°C, since the chondrite fragment is completely melted with the quenched dendritic spinels at 1500°C (Toppani *et al.*, 2001). Samples T004uTC003, T004TC006, T004uTC018, To440081, and To440088 are typical spherules with globular

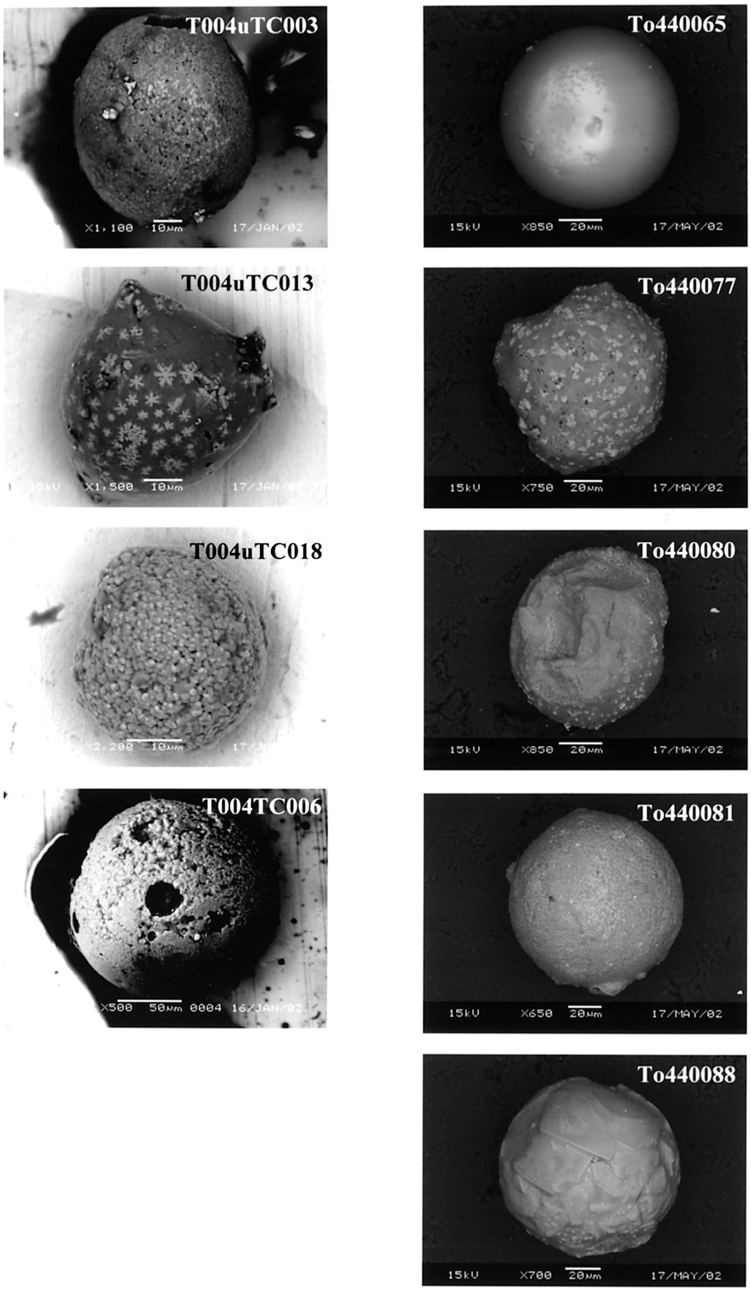

Fig. 7. Backscattered electron images of nine particles with extraterrestrial Ne or Ar. Three of them are non-spherical, showing relatively mild heating. Sample T004uTC013 has snow-like dendritic magnetite crystals on its surface. Five spherules are classified as porphyritic or relic-grain-bearing spherules. Only sample To440065 is a transparent spherule and should be classified as cryptocrystalline type (see text).

shapes. These particles match the description of porphyritic or relic-grain-bearing spherules judging from their surface textures (Blanchard *et al.*, 1980; Taylor *et al.*, 2000; Yada, 2001). Porphyritic spherules have equidimensional olivine and magnetite crystals in interstitial glass, and relic-grain-bearing spherules contain relic olivine, metal, or sulfide grains that have not been totally melted (Taylor *et al.*, 2000). If these spherules have relic grains in their interior, noble gases may be trapped in them. However, the melted portions of these spherules loose their extraterrestrial noble gases. We cannot confirm as yet whether they contain relic grains in their interiors.

Only sample To440065 is a glassy spherule. Although the spherule seems to be completely melted and is amorphous glass, it has a high concentration of Ne and Ar. Therefore, the spherule should be classified as the cryptocrystalline type. Cryptocrystalline-type spherules are similar to glassy-type spherules in their appearance and systematic Fe loss is observed in both types (Yada, 2001). Extraterrestrial noble gases might be trapped in relict crystals in sample To440065.

Sample To440080 and T004TC002 have higher $^{40}Ar/^{36}Ar$ ratios than that of the that of the atmosphere. There is no unmelted micrometeorite with $^{40}Ar/^{36}Ar$ higher than atmosphere, indicating the absence of ordinary-chondrite-like micrometeorites (Osawa *et al.*, 2000; Osawa and Nagao, 2000b). Sample To440080 has an exceptionally high $^{40}Ar/^{36}Ar$ ratio (566.3 ± 14.8), showing definite difference from unmelted micrometeorites. This spherule is evidently extraterrestrial material because it has SEP-Ne (Table 3). Judging from the Ar composition of this spherule, it has quite different source material from conventional extraterrestrial dust. It is very curious that this spherule has a high ^{36}Ar concentration (6.5×10^{-7} cm^{3}STP/g) in spite of a high $^{40}Ar/^{36}Ar$ ratios. Meteorites with such high ^{36}Ar concentrations generally has lower $^{40}Ar/^{36}Ar$ ratio than this spherule. Therefore, SEP-Ar may contribute the high ^{36}Ar concentration, although we cannot determine from the $^{38}Ar/^{36}Ar$ ratio due to uncertainty. Approximately 50% SEP-^{36}Ar contribution is calculated from the concentration of ^{20}Ne, if $^{20}Ne/^{36}Ar$ ratio of 47 is adopted as the SEP ratio (Murer *et al.*, 1997). If this estimation is correct, the original $^{40}Ar/^{36}Ar$ of this spherule was over 1000. Although we cannot identify the source material of this exceptional spherule based on the present data, this spherule undoubtedly originated in a different type of the parent body from other extraterrestrial dust particles.

Osawa *et al.* (2000) reported an S-type spherule (F96CK005) with a high $^{40}Ar/^{36}Ar$ ratio of 399 ± 31. This spherule is similar to sample T004TC002 in size, weight, $^{40}Ar/^{36}Ar$ ratio, and ^{36}Ar concentration (Fig. 6) (F96CK005 being 250 μm in diameter and weighing 21.5 μg and T004TC002 170 μm in diameter and weighing 12.1 μg). As well as sample To440080, these two spherules may have source materials or histories different from conventional extraterrestrial dust. These spherules, however, have significantly lower ^{36}Ar concentration than To440080 and have no detectable SEP-Ne. If these spherules are cosmic materials, they originated on parent bodies of ordinary chondrites, which have relatively higher $^{40}Ar/^{36}Ar$ ratios than those of CM chondrites, which are the most plausible source materials of micrometeorites (Kurat *et al.*, 1994; Genge *et al.*, 1997; Osawa and Nagao, 2002b).

In the present stage, we cannot completely clarify the origins of these three spherules from the Ar isotopic composition, but the existence of such exceptional

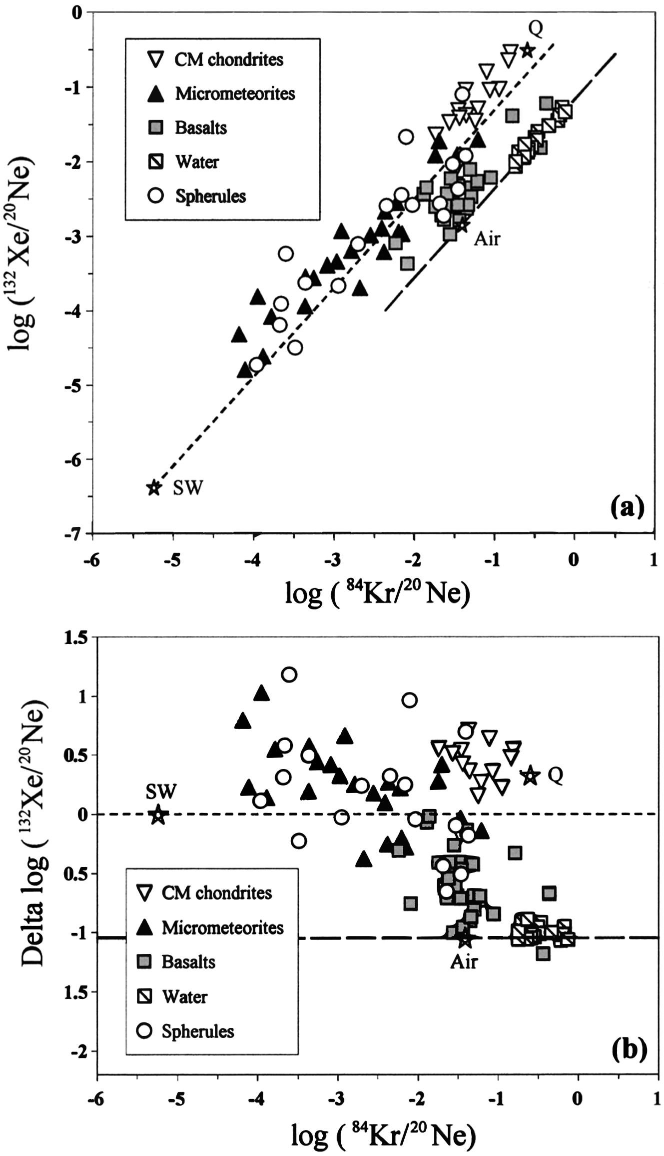

Fig. 8. Noble gas abundances of cosmic spherules and other extraterrestrial and terrestrial materials. (a): Relationship between ^{84}Kr/^{20}Ne and ^{132}Xe/^{20}Ne. The dotted and broken lines show theoretical fractionation established by mass-dependent Rayleigh distillation. (b): The abscissa is the same as for (a). The ordinate is defined as the distance from the dotted line in (a). CM chondrites: Y-791198 and Murchison (Nakamura et al., 1999b). Micrometeorites: Dome Fuji unmelted micrometeorites (Osawa and Nagao, 2002b). Basalt: Loihi and Kilauea (Honda et al., 1993a), Lau Backarc Basin (Honda et al., 1993b) and Indian Ocean (Kumagai and Kaneoka, 1998). Air: Ozima and Podosek (1983). Water: Groundwater and air-saturated water (Mazor, 1986). SW: Low temperature regime of L71501 in Becker et al. (1989) is represented. Q: Busemann et al. (2000).

particles may reflect the variety of extraterrestrial dust.

4.4. Elemental abundances as extraterrestrial evidence

Evidence for an extraterrestrial origin of twenty-two of the thirty-one spherules was not obtained by the Ne and Ar isotopic compositions, which are consistent with that of the terrestrial atmosphere within error, except for sample T004TC002 with its relatively high $^{40}Ar/^{36}Ar$ ratio.

Noble gas elemental abundances are allow determination of whether material is terrestrial or extraterrestrial, because terrestrial materials have characteristic noble gas compositions caused by a systematic deficit of Xe (called "missing Xe"). Figure 8 illustrated the relationship between $^{132}Xe/^{20}Ne$ and $^{84}Kr/^{20}Ne$ ratios. Only eighteen spherules are plotted because ^{84}Kr or ^{132}Xe concentrations for the other thirteen samples could not be determined. The dotted line indicates theoretical mass fractionation of SW. Mass dependent fractionation processes generate elemental compositions that lie on a line parallel to the dotted line with an inclination of 1.19. Terrestrial air is plotted below the dotted line, indicating the low abundance of Xe. Terrestrial materials, basalt and terrestrial water, are also distributed below the line. CM chondrites are mainly distributed above the line, although they have $^{84}Kr/^{20}Ne$ ratios similar to terrestrial basalt. The broken line represents theoretical atmospheric mass fractionation. Water lies on the line, indicating that the noble gas elemental compositions evolved from the atmospheric composition by solution. On the other hand, unmelted micrometeorites are distributed in an area, that is inconsistent with terrestrial materials and CM chondrites due to a high abundance of Ne derived from solar-Ne implantation. Most spherules are distributed in an area that closely corresponds to that of micrometeorites in spite of severe heating, indicating that spherules are not terrestrial.

Heavy noble gases are concentrated by adsorption on the rock surface. Therefore, $^{84}Kr/^{20}Ne$ or $^{132}Xe/^{20}Ne$ ratios of the adsorbed atmosphere should be larger than those of the terrestrial atmosphere. Although unmelted micrometeorites have adsorbed noble gases (Osawa and Nagao, 2002b), most micrometeorites have lower $^{84}Kr/^{20}Ne$ ratios than the atmosphere, showing that the contribution of adsorbed terrestrial atmosphere is negligible in these micrometeorites. The compositions of the micrometeorites mainly reflect two components, presumably solar and Q-components. Indeed, both unmelted particles and spherules are distributed between SW and Q compositions. Their compositions are not affected by noble gases dissolved in water, although these particles were trapped in Antarctic snow or ice.

Although several spherules have noble gas compositions similar to terrestrial materials due to atmospheric contamination (Fig. 8), most spherules found in Antarctic ice are presumably extraterrestrial and not mantle materials. If these granules were produced by volcanic eruption, they would have noble gas compositions similar to basalt. Indeed, Kr and Xe concentrations of the spherules (Kr $=5\times10^{-11}$ to 8×10^{-9} STP/g, Xe $=2\times10^{-11}$ to 3×10^{-9} STP/g) are one or two orders of magnitude higher than basalt glasses (Kr $=10^{-13}$ to 2×10^{-10} STP/g, Xe $=10^{-13}$ to 10^{-11} STP/g, Honda *et al.*, 1993), inconsistent with a terrestrial origin. It is important that the compositions of the spherules cannot be explained without contribution of a solar component.

Why were extraterrestrial Ne and Ar not detected in more than nine spherules, even though their noble gas elemental abundance patterns are distinguishable from terrestrial materials in Fig. 8? As for Ne, this is due to extremely low ^{22}Ne and ^{21}Ne contents. Therefore, Ne isotopic ratios could not be determined accurately for most particles, even if the ^{20}Ne concentration was determined. As for Ar, this is due to the high contribution of atmospheric Ar adsorbed on the particle surface or Ar dissolved in the melted phases presumably controlling the Ar isotopic compositions.

5. Conclusions

We measured noble gases in Antarctic cosmic spherules using laser gas extraction. Concentrations of He, Ne, and Ar in these spherules were clearly lower than those of unmelted micrometeorites, indicating systematic noble gas loss, presumably due to atmospheric deceleration heating. Concentrations of He were very low and only three of thirty-one spherules have detectable solar-He. As for other samples, $^{3}He/^{4}He$ ratios were not determined due to low ^{3}He concentrations comparable to blank level.

High $^{21}Ne/^{22}Ne$ ratios were detected in thirteen samples, possibly indicating the presence of cosmogenic nuclides, although blank corrections could not be applied for most of these samples due to low Ne contents comparable to the blank level.

Six spherules preserve SEP-like Ne with relatively high Ne concentrations, and five of them preserve their extraterrestrial Ar compositions. The $^{40}Ar/^{36}Ar$ ratios of these five spherules are clearly lower than the atmospheric value. An exceptional spherule To440080 has a high $^{40}Ar/^{36}Ar$ ratio (566.3 ± 14.8) and high ^{36}Ar concentration in spite of the presence of SEP-Ne, indicating different source material from other spherules and micrometeorites. Two spherules have extraterrestrial Ar, in spite of a deficit of SEP-Ne.

No extraterrestrial Ne and Ar were detected in other particles, although evidence of their extraterrestrial origin was indicated by the relative abundance of noble gases, distinguishable from those of terrestrial materials such as air, water, and basalt. Most spherules are presumably of extraterrestrial origin rather than terrestrially volcanic.

Although we detected extraterrestrial noble gases remaining in the Tottuki spherules, we could not determine where noble gases are preserved in the spherules and which types of spherules retained chondritic or solar noble gases. To answer these questions, we plan X-ray computed tomography to obtain three-dimensional microstructures before noble gas measurements (Tsuchiyama *et al.*, 2001a, b).

Acknowledgments

We thank the National Institute of Polar Research (NIPR) for providing Antarctic cosmic spherules. We also thank T. Yada for his invaluable advice. We are grateful to K.J. Mathew and an anonymous reviewer for their constructive reviews. We also grateful to P. Buchanan for his critical reading.

References

Becker, R.H. and Pepin, R.O. (1989): Long-term changes in solar wind elemental and isotopic ratios: A

comparison of two lunar ilmenites of different antiquities. Geochim. Cosmochim. Acta, **53**, 1135–1146.
Benkert, J.P., Baur, H., Signer, P. and Wieler, R. (1993): He, Ne, and Ar from the solar wind and solar energetic particles in lunar ilmenites and pyroxenes. J. Geophys. Res., **98**, E7, 13147–13162.
Black, D.C. and Pepin, R.O. (1969): Trapped neon in meteorites-II. Earth Planet Sci. Lett., **6**, 395–405.
Blanchard, M.B., Brownlee, D.E., Bunch, T.E., Hodge, P.W. and Kyte, F.T. (1980): Meteoroid ablation spheres from deep-sea sediments. Earth Planet. Sci. Lett., **46**, 178–190.
Bruun, A.F., Langer, E. and Pauly, H. (1955): Magnetic particles found by raking the deep sea bottom. Deep-Sea Res., **2**, 230–246.
Buddhue, J.D. (1950): Meteoritic Dust. Albuquerque, University of New Mexico Press.
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. Meteorit. Planet. Sci., **35**, 949–973.
Cosari, D.L. (1835): Account of some remarkable Hailstones which fell at Padua, on the 26th of August 1834. New Edinburgh Philos. J., **XIX**, 83–88.
Czaikowski, J., Englert, P., Bosellini, A. and Ogg, J.G. (1983): Cobalt enriched hardgrounds—New sources of ancient extraterrestrial materials. Meteoritics, **18**, 286–287.
Eberhardt, P., Eugster, O. and Marti, K. (1965): A redetermination of the isotopic composition of atmospheric neon. Z. Naturforsch., **20a**, 623–624.
Genge, M.J., Grady, M.M. and Hutchison, R. (1997): The textures and compositions of fine-grained Antarctic micrometeorites: Implications for comparisons with meteorites. Geochim. Cosmochim. Acta, **61**, 5149–5162.
Honda, M., Mcdougall, I., Patterson, D.B., Doulgeris, A. and Clague, D.A. (1993a): Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: A solar component in the Earth. Geochim. Cosmochim. Acta, **57**, 859–874.
Honda, M., Patterson, D.B., Mcdougall, I. and Falloon, T.J. (1993b): Noble gases in submarine pillow basalt glasses from Lau Basin: Detection of a solar component in backarc basin basalts. Earth Planet. Sci. Lett., **120**, 135–148.
Hunter, W. and Parkin, D.W. (1961): Cosmic dust in Tertiary rock and the lunar surface. Geochim. Cosmochim. Acta, **24**, 32–40.
Iwata, N. and Imae, N. (2002): Antarctic micrometeorite collection at a bare ice region near Syowa Station by JARE-41 in 2000. Antarct. Meteorite Res., **15**, 25–37.
Kortenkamp, S.J. and Dermott, S.F. (1998): Accretion of interplanetary dust particles by the Earth. Icarus, **135**, 469–495.
Kumagai, H. and Kaneoka, I. (1998): Variations of noble gas abundances and isotope ratios in a single MORB pillow. Geophys. Res. Lett., **25**, 3891–3894.
Kurat, G., Koeberl, C., Presper, T., Brandstatter, F. and Maurette, M. (1994): Petrology and geochemistry of Antarctic micrometeorites. Geochim. Cosmochim. Acta, **58**, 3879–3904.
Matsuzaki, H., Tanikawa, M., Kobayashi, K. and Hatori, S. (2000): Development of a gas counter for AMS measurement of ^{10}Be and ^{26}Al of cosmic spherules. Nucl. Instrum. Methods, B, **172**, 218–223.
Maurette, M., Olinger, C., Michel-Levy, M.C., Kurat, G., Pourchet, M., Brandstatter, F. and Bourot-Denise, M. (1991): A collection of diverse micrometeorites recovered from 100 tonnes of Antarctic blue ice. Nature, **351**, 44–47.
Mazor, E. (1986): Tritium corrected ^{14}C and atmospheric noble gas corrected 4He applied to deduce ages of mixed groundwaters: Examples from the Baden region, Switzerland. Geochim. Cosmochim. Acta, **50**, 1611–1618.
Murer, C.A., Baur, H., Signer, P. and Wieler, R. (1997): Helium, Neon, and Argon abundances in the solar wind: In vacuo etching of meteoritic iron-nickel. Geochim. Cosmochim. Acta, **61**, 1303–1314.
Murray, J. (1876): On the distribution of volcanic debris over the floor of the ocean. Proc. R. Soc. Edinburgh, **9**, 247–261.
Murray, J. and Renard, A.F. (1884): On the microscopic characters of volcanic ashes and cosmic dust, and their distribution in deep-sea deposits. Proc. R. Soc. Edinburgh, **12**, 474–495.
Murray, J. and Renard, A.F. (1891): Report on the scientific results of the voyage of H.M.S. Challenger during the years 1873–76. Deep-Sea Deposits.

Murrell, M.T., Davis, P.A., Nishiizumi, K. and Millard, H.T. (1980): Deep-sea spherules from Pacific clay: Mass distribution and influx rate. Geochim. Cosmochim. Acta, **44**, 2067–2074.

Nakamura, T., Imae, N., Nakai, I., Noguchi, T., Yano, H., Terada, K., Murakami, T., Fukuoka, T., Nogami, K., Ohashi, H., Nozaki, W., Hashimoto, M., Kondo, N., Matsuzaki, H., Ichikawa, O. and Ohmori, R. (1999a): Antarctic micrometeorites collected at the Dome Fuji Station. Antarct. Meteorite Res., **12**, 183–198.

Nakamura, T., Nagao, K. and Takaoka, N. (1999b): Microdistribution of primordial noble gases in CM chondrites determined by in situ laser microprobe analysis: Decipherment of nebular processes. Geochim. Cosmochim. Acta, **63**, 241–255.

Nishibori, E. and Ishizaki, M. (1959): Meteoritic dust collected at Syowa Base, Ongul island, east coast of Lützow-Holm Bay, Antarctica. Nankyoku Shiryô (Antarct. Rec.), **7**, 35–38 (in Japanese with English abstract).

Nishiizumi, K. (1983): Measurement of ^{53}Mn in deep-sea iron and stony spherules. Earth Planet. Sci. Lett., **63**, 223–228.

Nishiizumi, K., Arnold, J.R., Fink, D., Klein, J., Middleton, R., Brownlee, D.E. and Maurette, M. (1991): Exposure history of individual cosmic particles. Earth Planet. Sci. Lett., **104**, 315–324.

Nishiizumi, K., Arnold, J.R., Brownlee, D.E., Caffee, M.W., Finkel, R.C. and Harvey, R.P. (1995): Beryllium-10 and aluminum-26 in individual cosmic spherules from Antarctica. Meteoritics, **30**, 728–732.

Olinger, C.T., Maurette, M., Walker, R.M. and Hohenberg, C.M. (1990): Neon measurements of individual Greenland sediment particles: proof of an extraterrestrial origin and comparison with EDX and morphological analyses. Earth Planet. Sci. Lett., **100**, 77–93.

Osawa, T. and Nagao, K. (2002a): On low noble gas concentrations in Antarctic micrometeorites collected from Kuwagata Nunatak in the Yamato Meteorite Ice Field. Antarct. Meteorite Res., **15**, 165–177.

Osawa, T. and Nagao, K. (2002b): Noble Gas Compositions of Antarctic Micrometeorites Collected at the Dome Fuji Station in 1996 and 1997. Meteorit. Planet. Sci., **37**, 911–936.

Osawa, T., Nagao, K., Nakamura, T. and Takaoka, N. (2000): Noble gas measurement in individual micrometeorites using laser gas-extraction system. Antarct. Meteorite Res., **13**, 322–341.

Ozima, M. and Podosek, F.A. (1983): Noble Gas Geochemistry. Cambridge, Cambridge University Press, 12–14.

Parkin, D.W. and Hunter, W. (1959): Cosmic dust in the atmosphere. Nature, **183**, 732–734.

Peng, H. and Lui, Z. (1989): Measurement of the annual flux of cosmic dust in deep-sea sediments (abstract). Meteoritics, **24**, 315.

Pepin, R.O., Palma, R.L. and Schlutter, D.J. (2000): Noble gases in interplanetary dust particles, I: The excess herium-3 problem and estimates of the relative fluxes of solar wind and solar energetic particles in interplanetary space. Meteorit. Planet. Sci., **35**, 495–504.

Pepin, R.O., Palma, R.L. and Schlutter, D.J. (2001): Noble gases in interplanetary dust particles, II: Excess helium-3 in cluster particles and modeling constraints on interplanetary dust particles exposures to cosmic-ray irradiation. Meteorit. Planet. Sci., **36**, 1515–1534.

Reynolds J.H., Frick, U., Niel, J.M. and Phinney, D.L. (1978) Rare-gas-rich separates from carbonaceous chondrites. Geochim. Cosmochim. Acta, **42**, 1775–1797.

Stuart, F.M., Harrop, P.J., Knot, S. and Turner, G. (1999): Laser extraction of helium isotopes from Antarctic micrometeorites: Source of He and implications for the flux of extraterrestrial ^{3}He to earth. Geochim. Cosmochim. Acta, **63**, 2653–2665.

Taylor, S. and Brownlee, D.E. (1991): Cosmic spherules in the geologic record. Meteoritics, **26**, 203–211.

Taylor, S., Lever, J.H. and Harvey, R.P. (2000): Numbers, types, and composition of an unbiased collection of cosmic spherules. Meteorit. Planet. Sci., **35**, 651–666.

Toppani, A., Libourel, G.., Engrand, C. and Maurette, M. (2001): Experimental simulation of atmospheric entry micrometeorites. Meteorit. Planet. Sci., **36**, 1377–1396.

Tsuchiyama, A., Uesugi, K., Nakano, T., Suzuki, Y. and Yagi, N. (2001a): X-ray microtomography system using SR at SPring-8 for studies of three-dimensional microstructures of meteorites. Antarctic Meteorites XXVI. Tokyo, Natl Inst. Polar Res., 151–153.

Tsuchiyama, A., Uesugi, K., Noguchi, T., Yano, H., Nakano, T. and Suzuki, Y. (2001b): Three-dimensional microstructures of Antarctic micrometeorites by X-ray computed microtomography using synchrotron radiation at SPring-8. Meteorit. Planet. Sci., **36**, A210.

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. Astrophys. J., **453**, 987–997.

Wieler, R., Baur, H., Benkert, J.P., Pedroni, A. and Signer, P. (1987): Noble gases in the meteorite Fayetteville and in lunar ilmenite originating from solar energetic particles. Lunar and Planetary Science XVIII. Houston, Lunar Planet. Inst., 1080–1081.

Wieler, R., Anders, E., Baur, H., Lewis, R.S. and Signer, P. (1992): Characterization of Q-gases and other noble gas components in the Murchison meteorite. Geochim. Cosmochim. Acta, **56**, 2907–2921.

Yada, T. (2001): A comprehensive study of Antarctic micrometeorites collected at Yamato Mountains in 1998. Ph.D. thesis, Kyushu University, Fukuoka, Japan.

Yada, T. and Kojima, H. (2000): The collection of micrometeorites in the Yamato Meteorite Ice Field of Antarctica in 1998. Antarct. Meteorite Res., **13**, 9–18.

Yamakoshi, K. (1991): Cosmic ray exposure ages of meteoroids. J. Phys. G: Nucl. Part. Phys., **17**, S505–511.

Zoppi, U., Matsuzaki, H., Kobayashi, K., Imamura, M., Nagai, H., Hatori, S., Nakano, C. and Sunohara, Y. (1997): New interpretation of the 10Be and 26Al content in cosmic spherules. Nucl. Instrum. Methods B, **123**, 319–323.

(Received July 31, 2002; Revised manuscript accepted February 12, 2003)