THE ASTROPHYSICAL JOURNAL, 475:L65–L68, 1997 January 20

EXCESS ^{36}Ar IN THE EFREMOVKA METEORITE: A STRONG HINT FOR THE PRESENCE OF ^{36}Cl IN THE EARLY SOLAR SYSTEM

S. V. S. MURTY AND J. N. GOSWAMI
Physical Research Laboratory, Ahmedabad 380 009, India

AND

YU. A. SHUKOLYUKOV
Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow 117975, Russia
Received 1996 May 13; accepted 1996 November 7

ABSTRACT

Noble gas studies of fine-grained silicate material of the Efremovka carbonaceous chondrite revealed the presence of excess ^{36}Ar over and above the level expected due to contributions from the trapped and cosmic-ray–produced, both spallogenic and secondary neutron–induced, components. The observed excess in ^{36}Ar can be best explained as due to in situ decay of ^{36}Cl ($\tau = 0.43$ Ma) in the analyzed samples and provides a strong hint for the presence of this now-extinct nuclide in the early solar system. Additional experiments that will confirm our observation are proposed. A conservative estimate of an initial ^{36}Cl/^{35}Cl of $(1.4 \pm 0.2) \times 10^{-6}$ at the time of formation of Efremovka silicates can be made from our data. If we consider a nucleosynthetic origin of ^{36}Cl, the time interval between the last addition of freshly synthesized ^{36}Cl to the solar nebula and the formation of some of the first silicate grains in the nebula could be estimated to be approximately 1 Ma.

Subject headings: solar system: formation — solar system: general — nuclear reactions, nucleosynthesis, abundances

1. INTRODUCTION

The recent observation of fossil records of the extinct nuclide ^{41}Ca ($\tau = 0.15$ Ma) in Ca-Al–rich refractory inclusions (CAIs) from the Efremovka meteorite (Srinivasan, Ulyanov, & Goswami 1994; Srinivasan et al. 1996) strongly suggested the possibility that ^{36}Cl ($\tau = 0.43$ Ma) could also be present in it. This motivated us to analyze samples of this meteorite to look for excess ^{36}Ar that may be attributed to in situ decay of ^{36}Cl. Detection of extinct ^{36}Cl in meteorites will help us to further constrain the timescale for grain formation in the solar nebula (see, e.g., Cameron 1995) and also to pinpoint the source(s) of the short-lived nuclides that were present in the early solar system.

^{36}Ar present in any meteorite is a mixture of at least two components: a trapped component and a cosmic-ray–produced (cosmogenic) component. The cosmogenic component is again the sum of two components: the spallation component, produced by direct interaction of energetic cosmic-ray particles, and the neutron induced component, produced by cosmic-ray secondary neutrons via the reaction $^{35}\mathrm{Cl}(n, \gamma)^{36}\mathrm{Cl} \rightarrow {}^{36}\mathrm{Ar}$. Both the trapped and cosmogenic ^{36}Ar components are also accompanied by additional nuclides of Ar and other noble gases as well. If the now-extinct nuclide ^{36}Cl was also present in the meteorite, we have an additional component of pure ^{36}Ar. As Ar is effectively a two-isotope system (^{40}Ar is dominated by contribution from the deacy of the naturally occuring long-lived nuclide ^{40}K), it is not possible to decompose the total ^{36}Ar in to the various components from the Ar isotopic data alone. However, simultaneous measurement of other noble gas isotopes (e.g., Ne and Xe) that also have their characteristic trapped and cosmogenic components enables one to estimate the magnitude of the different ^{36}Ar components.

2. SAMPLE DETAILS AND EXPERIMENTAL APPROACH

We have analyzed two matrix samples, representing fine-grained silicate material, and two CAIs, one coarse-grained and another fine-grained, from the Efremovka meteorite. One matrix sample from the Allende meteorite was also analyzed. Since the volatile nature of Cl may preclude its presence in the refractory CAIs, we have included the matrix samples of Efremovka in this study. Petrographic studies of the CV3 group of meteorites, of which both Efremovka and Allende are members, suggest that Efremovka has suffered very little secondary alteration among the meteorites in this group (Sylvester, Simon, & Grossman 1993; Goswami, Srinivasan, & Ulyanov 1994), making samples of this meteorite extremely suitable for the present study. The sample of Allende was analyzed to cross-check earlier reports of absence of ^{36}Cl in this meteorite (Jordan & Pernicka 1981; Göbel, Begemann, & Ott 1982).

Ne, Ar, and Xe isotopic compositions were analyzed in these samples by stepwise pyrolysis using standard procedures (Murty & Goswami 1992) on a VG1200 mass spectrometer. Prior to pyrolysis, an initial combustion at 400°C in 2 torr O_2 was carried out to get rid of surficial contaminantion. Subsequently, pyrolysis was carried out in a molybdnum crucible. Air standards are used to assess sensitivity and mass discrimination of the mass spectrometer. Blanks are done at each temperature under identical conditions. Except for Xe in E40, where the blank contribution is greater than 10% and up to 25%, the level of blank correction is less than a few percent for all the noble gases in this and the other four samples. The data reported in this Letter are corrected for blanks and mass discrimination. Signals at masses 35 and 37 were monitored during both the blank and sample runs to check for possible interference from HCl at mass 36. In all the samples, the peak height at mass 35 was less than 1% of the observed peak height

TABLE 1

Ar and Xe Isotopic Data

Temperature (°C)	^{36}Ar[a] (10^{-8} cm^3 STP g^{-1})	$^{38}Ar/^{36}Ar$[b]	^{132}Xe[a] (10^{-10} cm^3 STP g^{-1})	$^{128}Xe/^{132}Xe$[b]	$^{129}Xe/^{132}Xe$[b]
Efremovka, Matrix (EF-1), 68.3 mg					
400.....	0.11	0.1906 ± .0009	0.10	...	...
900.....	23.73	0.1833 ± .0004	13.5	0.07906 ± .00088	1.094 ± .007
1200	150.0	0.1795 ± .0004	103.8	0.08130 ± .00057	1.082 ± .007
1500	0.69	0.2131 ± .0004	1.35	0.08567 ± .00092	1.204 ± .006
Total.....	174.5	0.1801 ± .0004	118.7	0.08100 ± .00060	1.083 ± .006
Efremovka, Matrix (EF-2), 51.73 mg					
400.....	0.04	0.2249 ± .0025	<0.1	...	...
800.....	0.69	0.2008 ± .0003	3.80	0.07605 ± .00091	1.002 ± .003
1000	30.17	0.1855 ± .0001	3.73	0.08290 ± .00028	1.141 ± .003
1200	188.2	0.1800 ± .0001	111.5	0.08188 ± .00026	1.079 ± .002
1400	18.1	0.1941 ± .0002	14.1	0.08348 ± .00033	1.082 ± .004
1600	0.13	0.2593 ± .0012	0.20	0.1184 ± .0027	1.146 ± .010
Total.....	237.4	0.1819 ± .0001	133.3	0.08196 ± .00029	1.079 ± .003
Efremovka, Fine-grained CAI (E42), 15.29 mg					
Total.....	54.30	0.2237 ± .0002	16.17	0.0879 ± .0007	1.389 ± .006
Efremovka, Coarse-grained CAI (E40), 10.44 mg					
Total.....	3.51	1.228 ± .004	0.46	...	...
Allende, Matrix (AL-1), 103.67 mg					
Total.....	15.63	0.1983 ± .0002	17.61	0.08488 ± .00056	1.942 ± .050

[a] Errors in concentration (2 σ) are ±10% for Ar and ±15% for Xe.
[b] Errors in isotopic composition represent 95% confidence limit.

at mass 36, and interference from $[H^{35}Cl]$ at mass 36 can be ruled out. In addition, the Ne data have been also corrected for $^{40}Ar^{2+}$ (at ^{20}Ne) and $^{44}[CO_2]^{2+}$ (at ^{22}Ne). These corrections are always less than 1%.

3. RESULTS AND DATA ANALYSIS

Ar and Xe isotopic compositions of the samples, relevant to the present study, are given in Table 1. Data for temperature release fractions as well as the totals are given for both of the matrix samples of Efremovka, while only totals are tabulated for the Efremovka CAIs and the matrix sample of Allende. In Figure 1 we show the $^{38}Ar/^{36}Ar$ ratios for different temperature fractions, plotted against cumulative ^{36}Ar released, for all the five samples. The trapped $^{38}Ar/^{36}Ar$ value of 0.188 measured in chondrites (see, e.g., Swindle 1988) is also shown in each of these plots. Measured ratios of $^{38}Ar/^{36}Ar$ less than the trapped value indicate the presence of a ^{36}Ar-rich component. The most likely source for this component is neutron-produced ^{36}Ar and/or the decay of ^{36}Cl of now-extinct origin that was initially present in the sample. On the other hand, $^{38}Ar/^{36}Ar$ ratios higher than the trapped value suggest the presence of a cosmic-ray–produced spallation component in which ^{38}Ar is favored over ^{36}Ar. The measured $^{38}Ar/^{36}Ar$ ratios are below the trapped value for the matrix samples of both Efremovka and Allende for some of the temperature steps (Figs. 1*a*–1*c*), while the data for Efremovka CAIs plot above this value (Figs. 1*d* and 1*e*). In the case of Allende, the decrease below the trapped value is seen only in the 800°C fraction, in which less than 10% of the total ^{36}Ar is released (Fig. 1*c*). In contrast, the matrix samples of Efremovka show such a decrease at both the 1000 and 1200°C fractions, where a total of approximately 80% of ^{36}Ar is released (Figs. 1*a* and 1*b*).

The measured $^{38}Ar/^{36}Ar$ ratio and the total ^{36}Ar in a sample can be written as the sum of the different components as follows:

$$(^{38}Ar/^{36}Ar)_m(^{36}Ar)_m = (^{38}Ar/^{36}Ar)_s(^{36}Ar)_s + (^{38}Ar/^{36}Ar)_t(^{36}Ar)_t + (^{38}Ar/^{36}Ar)_{cl}(^{36}Ar)_{cl}, \quad (1)$$

$$(^{36}Ar)_m = (^{36}Ar)_t + (^{36}Ar)_s + (^{36}Ar)_{cl}, \quad (2)$$

where m is the measured value, s and t represent the spallation and the trapped components, and cl represents the Cl-related component that could have contributions from both a neutron-induced and an extinct component. Although it is not possible to resolve the data for individual temperature fractions in terms of the different Ar components, it is possible to do this for the total Ar. Here we illustrate the data decomposition procedure for the Efremovka sample EF-1; we have followed a similar procedure in the other cases. We first evaluate the spallation Ar component based on the data for spallation ^{21}Ne, as the ratio of $(^{21}Ne/^{38}Ar)_s$ can be obtained from the average chemical composition of CV3 meteorites (Wasson & Kellymeyn 1988), and shielding depth–dependent production rate systematics for ^{21}Ne and ^{38}Ar (Eugster 1988). For the sample EF-1, we estimate a $(^{21}Ne/^{38}Ar)_s$ value of 5.42. Combining this value with the measured spallation ^{21}Ne content of 4.13×10^{-8} cm^3 STP g^{-1}, (where STP denotes standard temperature and pressure) and the expected $(^{36}Ar/^{38}Ar)_s = 0.67 \pm 0.05$ in this sample, we obtain a value of $(^{36}Ar)_s = 0.51 \times 10^{-8}$ cm^3

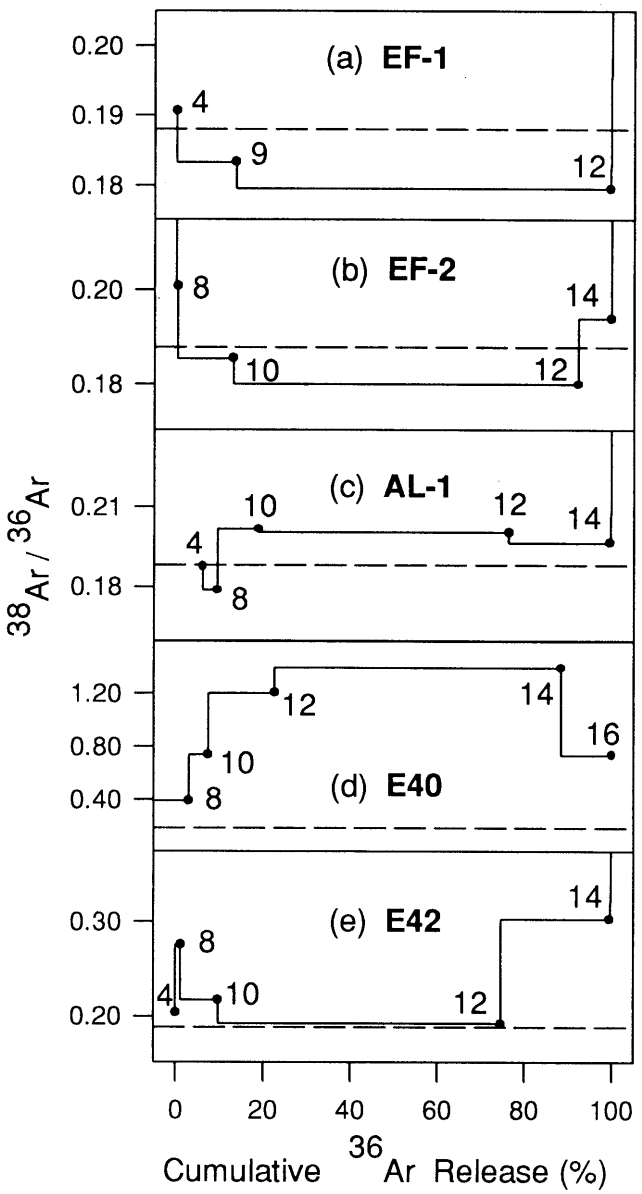

FIG. 1.—Release pattern of ^{38}Ar/^{36}Ar, plotted against cumulative ^{36}Ar released, for matrix samples of Efremovka (*a*, *b*) and Allende (*c*), as well as for the two Efremovka CAIs (*d*, *e*) analyzed in this study. The dotted line in all the panels represents the trapped ^{38}Ar/^{36}Ar ratio of 0.188. Release temperature in hundreds of degrees Celcius is indicated for all the data points.

STP g^{-1} in EF-1. We use these values to correct the measured total ^{36}Ar and (^{38}Ar/^{36}Ar) for the spallation component using relations (1) and (2). The corrected values then represent a mixture of the trapped and Cl-related (neutron-induced and extinct) components. For further decomposition of these components, we use a trapped (^{38}Ar/^{36}Ar) value of 0.188 measured in chondritic meteorites. Although a value of less than 0.188 for this ratio has been observed in solar wind and subsolar components (see, e.g., Swindle 1988), contributions from these components in Efremovka samples can be ruled out from the measured noble gas elemental ratios (^{20}Ne/^{36}Ar and ^{36}Ar/^{132}Xe) in them. The (^{38}Ar/^{36}Ar) ratio for the neutron-induced component depends on the effective energy of the neutrons, and we use a value of 0.003 (Mughabghab, Divadeenam, & Holden 1981) in our calculations.

TABLE 2

Ar AND Ne COMPONENTS

Sample	^{36}Ar(10^{-8} cm^3 STP g^{-1})[a]				^{21}Ne$_s$[a]
	t[b]	s[b]	(n, γ)[b]	^{36}Cl$_e$[b]	(10^{-8} cm^3 STP g^{-1})
EF-1.....	163.0	0.51	<0.14	10.8	4.13
EF-2.....	226.2	0.42	<0.28	10.2	3.26
E-40.....	0.87	2.64	~0	~0	2.28
E-42.....	53.4	~0.9	~0	~0	2.11
AL-1.....	14.7	0.23	0.70	~0	2.22

[a] The Ne and Ar amounts derived here have 2 σ errors of 10% and 15%, respectively, and include the systematic errors as well as the errors in the composition of the components.

[b] The terms are as follows: *t*, trapped; *s*, spallation; (n, γ), ^{35}Cl(n, γ) ^{36}Cl; and ^{36}Cl$_e$, extinct.

The values for the various ^{36}Ar components in EF-1 and the other samples, obtained following the above decomposition procedure, are given in Table 2, along with the data for spallation ^{21}Ne. The measured ^{36}Ar in both the Efremovka CAIs, E40, and E42 is dominated by the spallation component for which Ca is the main target element. Our data suggest the absence of a neutron-induced ^{36}Ar component (from Cl) in both the CAIs. In the case of E40, this is also consistent with the near absence of another halogen, iodine, as inferred from the absence of detectable iodine-related excess in Xe isotopes [either from ^{129}I decay (to ^{129}Xe) or from ^{127}I$(n, \gamma)^{128}$Xe reaction]. However, in E42 we do see ^{128}Xe and ^{129}Xe excesses, and the absence of a neutron-produced component of ^{36}Cl in it may be due to our use of the average value of 10% for its Ca content, typical for the fine-grained Efremovka CAIs (Nazarov et al. 1982).

The data obtained by us clearly suggest the presence of excess ^{36}Ar in the matrix samples of Allende and Efremovka that is related to Cl and could represent either a neutron-induced or an extinct component, or a mixture of both. The amount of neutron-produced ^{36}Ar can be estimated from the observed excess in ^{128}Xe resulting from the ^{127}I$(n, \gamma)^{128}$Xe reaction, if the Cl/I ratio of the analyzed sample is known. Excess ^{128}Xe is evident in both EF-1 and EF-2, from the increase in the ^{128}Xe/^{132}Xe ratio in the high-temperature release fractions that is also accompanied by an increase in the ^{129}Xe/^{132}Xe ratio (see Table 1). Since the increase in ^{129}Xe is from the in situ decay of ^{129}I, the observed correlation suggests that the increase in ^{128}Xe/^{132}Xe ratio at high temperature is in fact related to the presence of iodine. Although the observed ^{128}Xe could have a spallation component, we attribute the entire ^{128}Xe excess to neutron-induced reactions on ^{127}I to obtain the maximum amount of neutron-produced ^{36}Ar. Using appropriate cross sections (Mughabghab et al. 1981) and the measured Cl/I ratio of 690 for Efremovka (Dreibus 1996), we obtain upper limits of 0.14×10^{-8} and 0.26×10^{-8} cm^3 STP g^{-1} for the amounts of ^{36}Ar produced by neutron-induced reactions on Cl in EF-1 and EF-2, respectively. An independent assessment of this component, based on the measured cosmogenic ^{36}Cl in Efremovka, yielded a value of 0.1×10^{-8} cm^3 STP g^{-1} (Murty, Nishiizumi, & Goswami 1996), which suggests that our estimates are indeed upper limit estimates. Similar calculation for AL-1, using the measured Cl/I ratio of 1350 in the Allende meteorite (Dreibus, Spettel, & Wänke 1979), yielded a value of 0.7×10^{-8} cm^3 STP g^{-1} for this sample. After correcting for the neutron-induced component, we do not find any residual ^{36}Ar for the Allende sample AL-1, which is

consistent with the results obtained in earlier studies of this meteorite (Jordan & Pernicka 1981; Göbel et al. 1982). However, both the Efremovka matrix samples, EF-1 and EF-2, yield large amount of residual ^{36}Ar that can only be accounted for by invoking in situ decay of the now-extinct short-lived nuclide ^{36}Cl in these samples. In fact, the observed excess of approximately 10^{-7} cm^3 STP g^{-1} of ^{36}Ar represents about 4%–6% of the total ^{36}Ar measured in these samples and is almost an order of magnitude higher than the spallation and the neutron-induced components taken together. The extremely tightly bound value of 0.188 ± 0.001 for the trapped component (see, e.g., Swindle 1988) rules out the possibility that the observed excess is an artifact of our data decomposition procedure. Results obtained from a very recent collaborative experiment conducted at Max-Planck-Institut für Chemie, Mainz (Germany), following the submission of this paper, have also indicated the presence of excess ^{36}Ar in Efremovka (S. Murty, private communication). We conclude that the excess ^{36}Ar found in the samples of the Efremovka matrix can be best explained as due to in situ decay of the now-extinct nuclide ^{36}Cl.

4. DISCUSSION

The observed excess ^{36}Ar in the Efremovka matrix material provides a very strong hint for the presence of the short-lived nuclide ^{36}Cl in the early solar system. Further experiments are necessary to confirm our observation, particularly by establishing a correlation between the excess ^{36}Ar and Cl, the parent element. A recent study of a halogen-rich chondrule from the Allende meteorite did not reveal any excess ^{36}Ar in it (Murty & Wasserburg 1996); however, this may merely indicate a late formation of this halogen-rich chondrule compared to the Efremovka matrix material. Analysis of samples of the Efremovka matrix with varying Cl content, as well as studies of neutron-irradiated samples to look for correlated release of excess ^{36}Ar and ^{38}Ar [produced via $^{37}\mathrm{Cl}(n, \gamma)^{38}\mathrm{Cl} \rightarrow {}^{38}\mathrm{Ar}$ reaction] during the stepwise heating experiment, will be extremely useful in this regard. Nonetheless, we can use the data presented here to obtain a conservative estimate of the initial ^{36}Cl/^{35}Cl in the early solar system at the time of formation of the Efremovka matrix material. Using the measured Cl content of approximately 160 parts per million in Efremovka (Drebius 1996) and assuming that there was no remobilization and/or uptake of Cl following the formation of the matrix material and that all the Cl in the sample is correlated with the now-extinct ^{36}Cl initially present in it, we obtain an initial ^{36}Cl/^{35}Cl value of $(1.4 \pm 0.2) \times 10^{-6}$.

Several suggestions have been made to explain the presence of the short-lived nuclides ^{26}Al, ^{41}Ca, ^{53}Mn, ^{60}Fe, and ^{107}Pd in the early solar system (see, e.g., Srinivasan et al. 1996 and references therein). These include injection of freshly synthesized material from specific stellar site(s), production by energetic particles in different environments, and "fossil" remnants from an earlier epoch. If we consider the first alternative to be true, we can deduce the value of Δ, the time interval between the last injection of freshly synthesized material to the solar nebula and the formation of some of the first silicate grains in the nebula, from the value of initial ^{36}Cl/^{35}Cl inferred by us and appropriate stellar production rates. The production ratio of ^{36}Cl/^{35}Cl in a supernova is approximately 10^{-2} for stars of 15–40 $M_\odot$ (Woosley & Weaver 1995) and for a low-mass thermally pulsing asymptotic giant branch (TP-AGB) star this value is approximately 6.8×10^{-2} (Gallino et al. 1996). Assuming the mixing model of Cameron et al. (1995) for supernova ejecta and of Wasserburg et al. (1994, 1995) for material ejected from a TP-AGB star, we obtain a Δ value of approximately 1 Ma from our data. This is consistent with the value of less than 1 Ma derived earlier from the observation of ^{41}Ca in Efremovka CAIs (Srinivasan, et al. 1994; Srinivasan et al. 1996; Wasserburg et al. 1995).

We thank U. Ott for his permission to quote unpublished results from MPIC, Mainz, Germany. Constructive comments by an anonymous reviewer led to considerable improvement of the paper. This work is a part of an Indo-Russian collaborative program (ILTP B-2.11) supported by the Department of Science and Technology, India, and the Russian Academy of Sciences. Support from the Department of Space, India, is gratefully acknowledged.

REFERENCES

Cameron, A. G. W. 1995, Meteoritics, 30, 133
Cameron, A. G. W., Hoflich, P., Myers, P. C., & Clayton, D. D. 1995, ApJ, 447, L53
Dreibus, G. 1996, private communication
Dreibus, G., Spettel, B., & Wänke, H. 1979, in Origin and Distribution of the Elements, ed. L. H. Ahrens (London, Pergamon), 33
Eugster, O. 1988, Geochim. Cosmochim. Acta, 52, 1649
Gallino, R., Busso, M., Arlandini, M., & Straniero, D. 1996, Mem. Soc. Astron. Italiana, in press
Göbel, R., Begemann, F., & Ott, U. 1982, Geochim. Cosmochim. Acta, 46, 1777
Goswami, J. N., Srinivasan, G., & Ulyanov, A. A. 1994, Geochim. Cosmochim. Acta, 58, 431
Jordan, J., & Pernicka, E. 1981, Meteoritics, 16, 332
Mughabghab, S. F., Divadeenam, M., & Holden, N. F. 1981, Neutron Capture Cross Section, Vol. 1 (New York: Academic)
Murty, S. V. S., & Goswami, J. N. 1992, Proc. Lunar Planet. Sci. Conf., 22, 225
Murty, S. V. S., Nishiizumi, K., & Goswami, J. N. 1996, Lunar Planet. Sci., 27, 923
Murty, S. V. S., & Wasserburg, G. J. 1996, Meteorit. Planet. Sci., 31, A94
Nazarov, M. A., Ulyanov, A. A., Korina, M. I., & Kolesov, G. M. 1982, Lunar Planet. Sci., 13, 584
Srinivasan, G., Sahijpal, S., Ulyanov, A. A., & Goswami, J. N. 1996, Geochim. Cosmochim. Acta, 60, 1823
Srinivasan, G., Ulyanov, A. A., & Goswami, J. N. 1994, ApJ, 431, L67
Swindle, T. 1988, in Meteorites and the Early Solar System, ed. J. F. Kerridge & M. S. Matthews (Tucson: Univ. Arizona Press), 535
Sylvester, P. J., Simon, S. B., & Grossman, L. 1993, Geochim. Cosmochim. Acta, 57, 3763
Wasserburg, G. J., Busso, M., Gallino, R., & Raiteri, C. M. 1994, ApJ, 424, 412
Wasserburg, G. J., Gallino, R., Busso, M., Goswami, J. N., & Raiteri, C. M. 1995, ApJ, 440, L101
Wasson, J. T., & Kelleymeyn, G. W. 1988, Philos. Trans. R. Soc. London, A, 325, 535
Woosley, S. E., & Weaver, T. A. 1995, ApJS, 101, 181