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^{40}Ar-^{39}Ar ANALYSES OF JUVINAS FRAGMENTS

Ichiro Kaneoka[1], Keisuke Nagao[2], Akira Yamaguchi[3]* and Hiroshi Takeda[3]

[1]*Earthquake Research Institute, University of Tokyo,*
1–1, Yayoi 1-chome, Bunkyo-ku, Tokyo 113
[2]*Institute for Study of the Earth's Interior, Okayama University,*
Misasa, Tottori, 981–01
[3]*Mineralogical Institute, Graduate School of Sciences, University of Tokyo,*
3–1, Hongo 7-chome, Bunkyo-ku, Tokyo 113

Abstract: Three fragments of the Juvinas (eucrite) taken from the main mass with a size of about 30 cm were analyzed by the ^{40}Ar-^{39}Ar method in order to examine differences of secondary thermal effects.

The brecciated matrix shows a scattered pattern in the ^{40}Ar-^{39}Ar age spectrum, indicating excess ^{40}Ar in the higher temperature fractions. Two other fragments show no definite plateau ages but indicate similar age patterns. A probable disturbance event(s) around 4–4.1 Ga is indicated in the 975–1050°C fractions. Thus, Juvinas shows evidence of secondary thermal events, probably due to impacts.

1. Introduction

Juvinas is a monomict eucrite which fell near the village of Libonnes, France in 1821. Its original weight has been estimated to be over 91 kg (Graham *et al.*, 1985). About half of the meteorite has been kept in the National Museum of Natural History, Paris. We have investigated samples from this specimen.

For Juvinas, Rb-Sr, Pb-Pb and Sm-Nd ages have been reported to be 4.50–4.56 Ga (Allègre *et al.*, 1975; Lugmair *et al.*, 1976; Manhes *et al.*, 1984), but no ^{40}Ar-^{39}Ar ages have been reported. In the case of achondrites, they often show secondary disturbance(s), which are characteristically reflected in comparatively low ^{40}Ar-^{39}Ar ages (*e.g.*, Kaneoka, 1981; Kunz *et al.*, 1994). For example, in Pasamonte, Pb-Pb and Sm-Nd ages of 4.53 and 4.58 Ga are reported (Unruh *et al.*, 1977), whereas its ^{40}Ar-^{39}Ar age is only about 4.1 Ga (Kunz *et al.*, 1994; Podosek and Huneke, 1973), reflecting a later thermal disturbance.

Juvinas is a monomict breccia and its texture is rather heterogeneous. Some portions of Juvinas show signs of a shock, but other portions do not. As mentioned before, Rb-Sr, Pb-Pb and Sm-Nd ages for Juvinas so far reported range from 4.50 to 4.56 Ga, but it is not clear whether Juvinas was also affected later by secondary disturbance as observed in other eucrites. In order to clarify this point, ^{40}Ar-^{39}Ar analyses were performed on three fragments of Juvinas with apparently different textures.

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*Present address: Department of Geology and Geophysics, University of Hawaii at Manoa, 2525 Correa Road, Honolulu, Hawaii 96822, U.S.A.

2. Samples

Three fragments (40E1(a), 40E2, 40E4) were prepared from the main mass of Juvinas (about 42 kg) which is kept at the National Museum of Natural History of Paris. They were sampled from completely different locations of the stone for which ALLÈGRE and his colleagues analyzed Rb-Sr and Pb-Pb ages (ALLÈGRE *et al.*, 1975; MANHES *et al.*, 1984).

These three fragments have different textures, though they are located within a rather limited region (not more apart than 10 cm from each other). The sample 40E1(a) is a brecciated matrix, indicating partial melting due to shock. Sample 40E2 has a crystalline texture, showing no sign of partial melt. On the other hand, sample 40E4 is a fragment with an intermediate texture between 40E1(a) and 40E2. All samples were prepared as chips with dimensions of a few mm in size. Powders were carefully removed in order to avoid Ar loss from small grains and/or atmospheric contamination during the sample preparation process.

3. Experimental

The samples (0.14–0.17 g each) were wrapped in Al-foil and each sample was sandwiched between standard samples (MMhb-1 hornblende, K-Ar age: 519.5±2.5 Ma; ALEXANDER, Jr. *et al.*, 1978). They were stacked together in a quartz vial (diameter: 10mm; length: about 70mm) with Cd-shielding. CaF_2 and K_2SO_4 wrapped in Al-foil were also included in the same vial to monitor the production rate of Ar isotopes derived from Ca and K by the neutron irradiation.

The quartz vial was irradiated with a total fast neutron flux of about 1×10^{18} nvt/cm^2 in the Japan Material Test Reactor (JMTR). After cooling for about two months, Ar was extracted and purified by conventional procedures at the Radioisotope Center, University of Tokyo, and stored in pyrex glass tubes (*e.g.*, KANEOKA, 1981). The Ar isotopic composition was analyzed at the Institute for Study of the Earth's Interior, Okayama University using a VG-5400 mass spectrometer with a mass resolution of about 700 (NAGAO *et al.*, 1991). The mass resolution was sufficient enough to separate the Ar isotopes from the hydrocarbon background.

Blanks and K- and Ca-derived interfering Ar isotopes were corrected to calculate ^{40}Ar-^{39}Ar ages. Blank levels were $(2\text{–}3)\times10^{-9}$cm^{3}STP^{40}Ar below 1300°C extraction temperatures, but increase up to 1×10^{-8} cm^{3}STP^{40}Ar at the highest temperature fraction (1600°C) during degassing times of 45 min. The factors used to correct for K- and Ca-derived Ar isotopes are indicated in the footnote of Table 1. The amounts of Ca- and K-derived Ar isotopes formed by the neutron irradiation can be calculated on the basis of these values. To give a rough idea of the order of these components, an example is shown in the case of sample E2. For Ca-derived components, the total amounts of each Ar isotope are as follows: ^{36}Ar, 0.214; ^{37}Ar, 79.4; ^{38}Ar, 0.0746; ^{39}Ar, 0.0929 (unit: 10^{-8}cm^{3}STP/g). K-derived Ar isotopes are as follows: ^{38}Ar, 0.189; ^{39}Ar, 2.91; ^{40}Ar, 0.074 (unit: 10^{-8}cm^{3}STP/g).

To calculate ^{40}Ar-^{39}Ar ages, the following values were assumed: Trapped Ar: ^{40}Ar/^{36}Ar=0.50, ^{38}Ar/^{36}Ar=0.187; cosmogenic Ar: ^{40}Ar/^{38}Ar=0.15, ^{38}Ar/^{36}Ar=1.5

Table 1. Ar isotopes in neutron-irradiated fragments of Juvinas (eucrite).

40El(a) 0.1355 g $J=0.004007\pm0.000047$

T(°C)	[^{40}Ar] (×10^{-8} cm^3 STP/g)	^{36}Ar/^{40}Ar (×10^{-4})	^{37}Ar/^{40}Ar (×10^{-4})	^{38}Ar/^{40}Ar (×10^{-4})	^{39}Ar/^{40}Ar (×10^{-4})	^{40}Ar*/^{39}Ar*	Age (Ma)
600	12.5	11.44	490.6	11.13	40.16	252.6	1261
		±0.05	±0.6	±0.05	±0.08	±0.5	±11
675	49.7	5.967	567.0	11.90	69.46	145.4	828.0
		±0.022	±0.4	±0.03	±0.05	±0.1	±7.8
750	166	10.59	485.1	9.894	39.42	257.4	1278
		±0.02	±0.4	±0.039	±0.03	±0.2	±11
825	147	5.605	500.4	7.108	8.501	1263	3251
		±0.012	±0.5	±0.055	±0.012	±2	±18
875	128	6.339	416.2	6.155	5.250	2099	4045
		±0.007	±0.4	±0.027	±0.007	±3	±19
925	109	9.608	339.7	5.864	4.320	2549	4360
		±0.006	±0.3	±0.033	±0.002	±2	±19
975	81.0	4.485	430.0	5.809	5.052	2198	4119
		±0.008	±0.2	±0.041	±0.007	±3	±19
1050	160	4.986	434.8	6.127	4.628	2427	4280
		±0.012	±0.4	±0.032	±0.011	±6	±20
1135	151	15.29	319.0	6.985	3.406	3297	4788
		±0.02	±0.3	±0.023	±0.006	±7	±20
1200	136	29.70	803.7	16.98	2.500	6408	5924
		±0.05	±0.7	±0.02	±0.006	±25	±21
1275	97.2	29.52	786.8	16.18	2.213	7732	6251
		±0.01	±0.4	±0.05	±0.007	±42	±23
1350	129	19.84	1018	17.51	3.712	3965	5099
		±0.01	±1	±0.01	±0.007	±11	±20
1425	37.0	28.36	274.1	9.300	1.225	11055	6879
		±0.01	±0.4	±0.022	±0.009	±110	±27
1500	84.2	10.40	625.3	10.16	3.787	3272	4775
		±0.01	±0.2	±0.01	±0.006	±6	±20
1600	11.8	3.206	1530	10.56	4.772	3352	4816
		±0.003	±2	±0.03	±0.023	±26	±24
Total	1499.4	13.19	553.1	9.880	10.02	1066	2999

N.B. 1) All tabulated data have been corrected for the blanks and mass discrimination effect during the analyses, but do not include other corrections except for ^{40}Ar*/^{39}Ar* ratios and calculated ages.

2) ^{40}Ar*/^{39}Ar* indicates a ratio of the radiogenic ^{40}Ar from the decay of ^{40}K(^{40}Ar*) to the K-derived ^{39}Ar by a reaction of ^{39}K(n, p)^{39}Ar(^{39}Ar*).

3) To calculate an age, the following correction factors were used for K- and Ca-derived interference Ar isotopes.
$(^{39}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}}=(1.17\pm0.01)\times10^{-3}$, $(^{38}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}}=(9.39\pm0.47)\times10^{-4}$, $(^{36}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}}=(2.69\pm0.31)\times10^{-3}$, $(^{40}\mathrm{Ar}/^{39}\mathrm{Ar})_{\mathrm{K}}=(2.54\pm0.01)\times10^{-2}$, $(^{38}\mathrm{Ar}/^{39}\mathrm{Ar})_{\mathrm{K}}=(6.44\pm0.12)\times10^{-2}$.

4) Uncertainties in the measured ratio represent those of the mass spectrometric analyses. For the ^{40}Ar*/^{39}Ar* ratios and calculated ages, however, uncertainties in J values are included.

Table 1. (Continued)

40E2 0.1741 g $J = 0.004007 \pm 0.000047$

T(°C)	[^{40}Ar] ($\times 10^{-8}$cm^3 STP/g)	^{36}Ar/^{40}Ar ($\times 10^{-4}$)	^{37}Ar/^{40}Ar ($\times 10^{-4}$)	^{38}Ar/^{40}Ar ($\times 10^{-4}$)	^{39}Ar/^{40}Ar ($\times 10^{-4}$)	^{40}Ar*/^{39}Ar*	Age (Ma)
600	8.71	24.99 ±0.03	225.3 ±0.6	12.91 ±0.04	65.52 ±0.09	153.2 ±0.2	863.6 ±8.1
675	22.8	6.266 ±0.012	511.8 ±0.3	20.59 ±0.07	212.1 ±0.1	47.26 ±0.02	312.8 ±3.4
750	42.1	5.642 ±0.009	560.2 ±0.2	23.31 ±0.02	249.3 ±0.1	40.19 ±0.02	269.4 ±2.9
825	134	9.285 ±0.012	485.9 ±0.4	10.88 ±0.03	58.00 ±0.04	174.1 ±0.1	954.8 ±8.7
875	127	4.431 ±0.013	434.4 ±0.3	6.851 ±0.029	15.54 ±0.02	665.2 ±0.9	2343 ±15
925	116	3.575 ±0.008	378.8 ±0.3	5.533 ±0.031	6.601 ±0.017	1624 ±4	3637 ±19
975	123	4.097 ±0.019	371.6 ±0.3	5.420 ±0.028	5.111 ±0.010	2138 ±5	4074 ±19
1050	162	3.621 ±0.005	382.2 ±0.2	5.455 ±0.026	5.025 ±0.005	2184 ±2	4108 ±19
1125	137	3.609 ±0.005	355.7 ±0.2	5.311 ±0.040	5.578 ±0.014	1937 ±5	3915 ±19
1200	51.8	6.345 ±0.006	413.9 ±0.4	7.493 ±0.028	7.621 ±0.015	1401 ±3	3408 ±18
1275	166	14.19 ±0.02	1191 ±1	19.40 ±0.05	5.108 ±0.006	2691 ±4	4450 ±20
1350	159	10.35 ±0.01	870.1 ±0.6	14.13 ±0.02	4.486 ±0.005	2882 ±4	4564 ±20
1425	37.8	4.857 ±0.005	682.5 ±0.5	10.37 ±0.03	4.639 ±0.012	2603 ±8	4395 ±20
1500	86.3	5.153 ±0.007	462.3 ±0.2	7.031 ±0.021	4.070 ±0.014	2833 ±11	4535 ±20
1600	26.1	4.706 ±0.006	503.4 ±0.4	7.309 ±0.029	4.139 ±0.009	2816 ±7	4525 ±20
Total	1399.61	6.778	567.5	9.903	21.48	480.4	1936

(PODOSEK and HUNEKE, 1973). For present samples, it has been revealed that the contributions of cosmogenic components are essential and no significant amounts of trapped components can be identified in most temperature fractions. The amounts of ^{40}Ar were calculated by comparing the peak heights with a calibrated air standard. An uncertainty of about 20% is estimated based on the reproducibility of the mass spectrometer sensitivity.

4. Results and Discussion

The observed Ar isotopic ratios and the amount of ^{40}Ar are summarized in Table

Table 1. (Continued)

40E4 0.1572 g $J = 0.004007 \pm 0.000047$

T(°C)	[^{40}Ar] ($\times 10^{-8}$cm^3 STP/g)	^{36}Ar/^{40}Ar ($\times 10^{-4}$)	^{37}Ar/^{40}Ar ($\times 10^{-4}$)	^{38}Ar/^{40}Ar ($\times 10^{-4}$)	^{39}Ar/^{40}Ar ($\times 10^{-4}$)	^{40}Ar*/^{39}Ar*	Age (Ma)
600	7.53	29.14 ±0.06	173.8 ±0.5	10.61 ±0.07	41.00 ±0.09	245.1 ±0.5	1234 ±11
675	21.0	8.454 ±0.012	711.3 ±1.1	23.49 ±0.05	208.7 ±0.1	48.08 ±0.02	317.8 ±3.4
750	61.2	7.586 ±0.011	743.3 ±0.4	19.58 ±0.03	148.0 ±0.1	67.94 ±0.05	434.4 ±4.5
825	144	10.29 ±0.01	630.0 ±0.5	12.47 ±0.05	52.08 ±0.04	194.7 ±0.2	1040 ±49
875	99.0	5.484 ±0.010	567.8 ±0.4	8.190 ±0.045	9.188 ±0.005	1173 ±1	3140 ±17
925	51.5	5.980 ±0.007	520.3 ±0.4	7.628 ±0.025	6.249 ±0.012	1773 ±4	3774 ±19
975	78.7	5.709 ±0.011	575.2 ±0.2	8.130 ±0.027	5.456 ±0.008	2090 ±3	4037 ±19
1050	139	6.468 ±0.013	607.7 ±0.5	8.711 ±0.045	5.245 ±0.018	2205 ±9	4124 ±20
1125	98.9	6.369 ±0.012	633.6 ±0.8	9.129 ±0.027	5.550 ±0.009	2079 ±4	4029 ±19
1200	44.1	6.984 ±0.131	684.9 ±2.6	10.58 ±0.05	7.976 ±0.049	1394 ±10	3400 ±21
1275	58.0	27.23 ±0.02	2053 ±2	34.60 ±0.02	7.771 ±0.007	1862 ±3	3852 ±19
1350	160	19.63 ±0.02	1538 ±1	26.24 ±0.03	4.850 ±0.011	3276 ±12	4777 ±21
1425	16.3	5.113 ±0.009	867.8 ±0.7	12.86 ±0.03	4.944 ±0.014	2545 ±9	4358 ±20
1500	3.29	22.59 ±0.07	1401 ±3	14.40 ±0.11	8.978 ±0.044	1363 ±8	3366 ±20
1600	1.32	−68.28 ±0.12	2187 ±3	15.52 ±0.08	15.34 ±0.13	782.3 ±8.0	2560 ±21
Total	983.84	10.46	858.9	14.72	25.57	407.1	1745

1 together with the calculated ^{40}Ar-^{39}Ar ages for each temperature step. The results indicate possible K contamination of the samples in the lower temperature fractions (less than 875°C). This is demonstrated by the observed ^{39}Ar release patterns in these samples (Figs. 1–3) as well as by the total K concentrations calculated from the amounts of ^{39}Ar. K contents of 660 ppm (40E1(a)), 1420 ppm (40E2) and 1110 ppm (40E4) are observed. These K contents are much higher than those reported for Juvinas (230–480 ppm) using instrumental chemical analyses (*e.g.*, KIRSTEN *et al.*, 1963; MEGRUE, 1966; TERA *et al.*, 1970). Because the high mass resolution of the mass spectrometer can resolve ^{39}Ar from hydrocarbon peaks, a background problem can be excluded. Hence, it is concluded that the high ^{39}Ar in the lower temperature

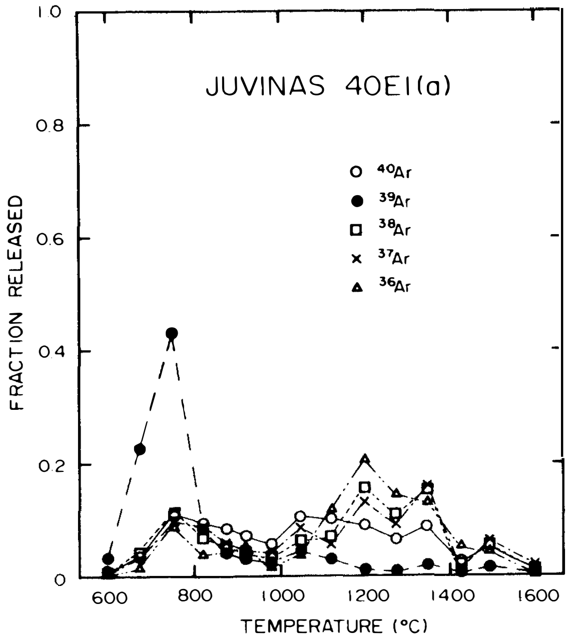

Fig. 1. Release patterns of Ar isotopes for Juvinas 40E1(a).

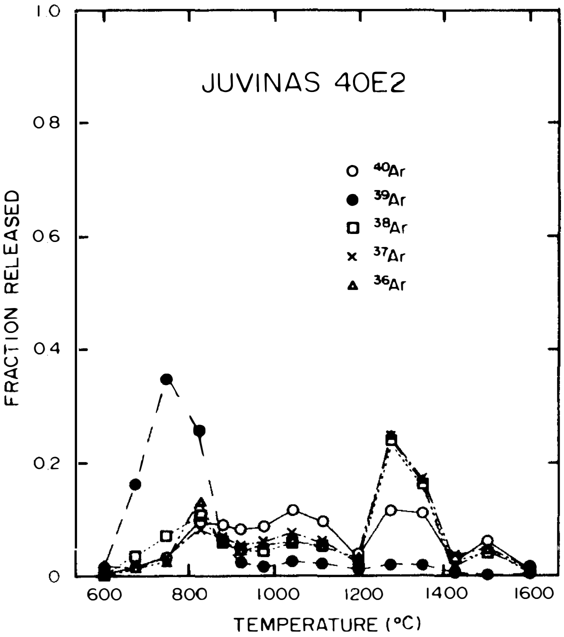

Fig. 2. Release patterns of Ar isotopes for Juvinas 40E2.

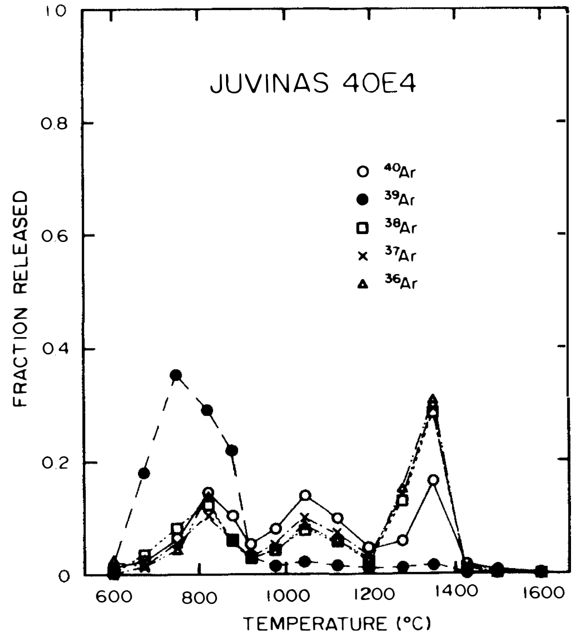

Fig. 3. Release patterns of Ar isotopes for Juvinas 40E4.

fractions is probably caused by addition of K to the meteorite surface. We have applied the same sample preparation procedure before to other samples but we have never observed such K addition (*e.g.*, Kaneoka and Nagao, 1993). Thus, it must be concluded that Juvinas has been contaminated with K before analysis.

For this reason, we have excluded the low temperature fractions of less than 875°C for discussing the age spectra. In Figs. 4–6, ^{40}Ar-^{39}Ar age patterns are shown. Although total amounts of ^{39}Ar from each sample may include some ambiguities due

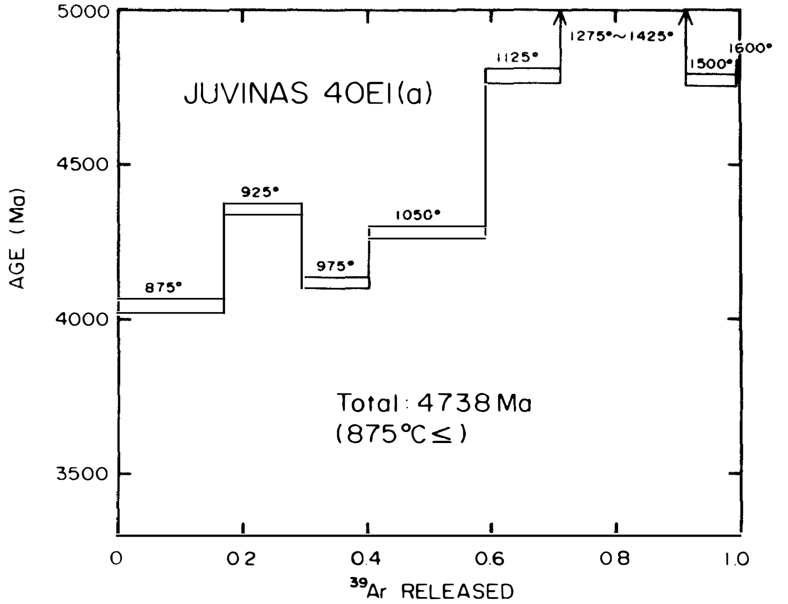

Fig. 4. *^{40}Ar-^{39}Ar age spectrum for Juvinas 40E1(a). The number at each increment indicates the degassing temperature in degrees Celsius. The uncertainty is indicated by 1σ. "Total" represents a total ^{40}Ar-^{39}Ar age. Only the temperature fractions of more than 875°C are shown due to possible K contamination for the lower temperature fractions. See text for discussion.*

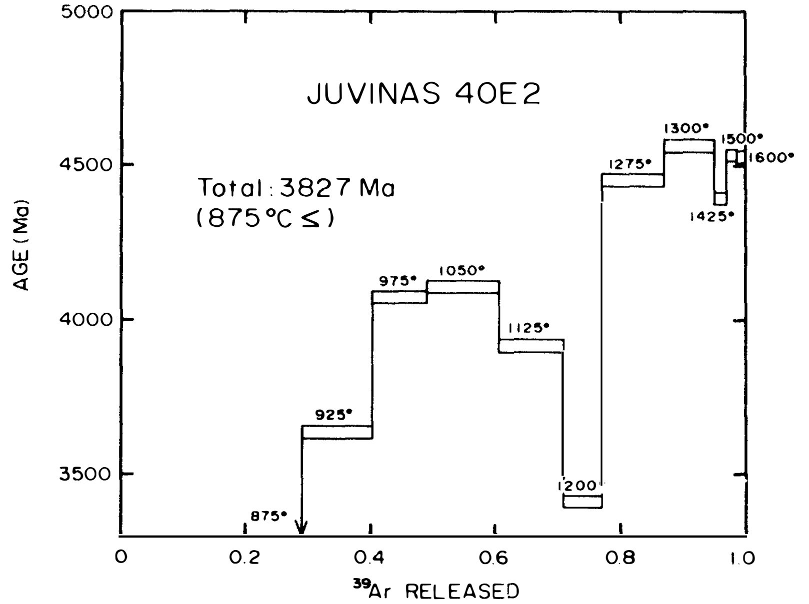

Fig. 5. *^{40}Ar-^{39}Ar age spectrum for Juvinas 40E2.*

to contamination, the age pattern would not be affected in its essential characteristics.

In the case of the sample 40E1(a) (Fig. 4), the age pattern is scattered and some values exceed 4.6 Ga for fractions with temperatures of more than 1125°C. Such high values could be caused by redistribution of radiogenic ^{40}Ar from less retentive sites to more retentive sites due to shock or some other secondary disturbances. Similar cases

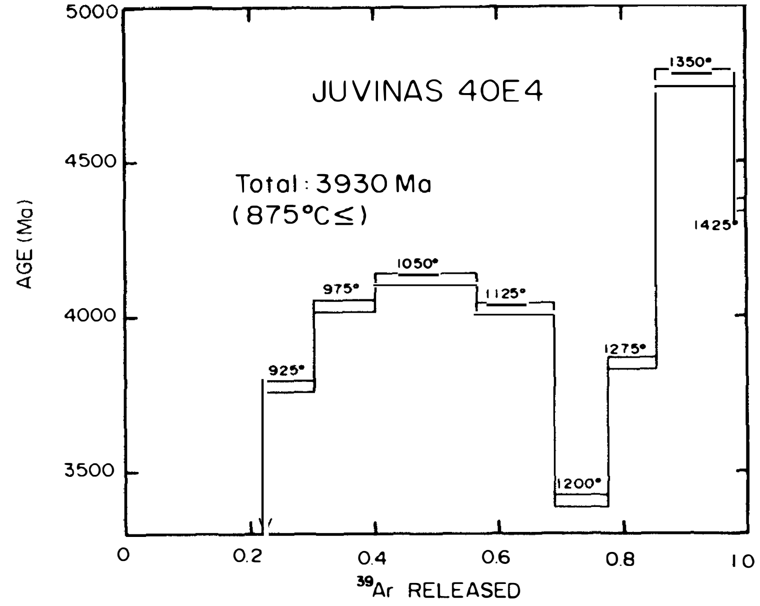

Fig. 6. ^{40}Ar-^{39}Ar age spectrum for Juvinas 40E4.

have been sometimes observed in a shocked lunar sample (*e.g.*, Kirsten *et al.*, 1972). In effect, sample 40E1(a) shows partial melting, indicating shock effects. The age pattern would surely reflect this. Further, the total age of this sample integrated for the temperature fractions of more than 875°C exceeds 4600 Ma. However, the total age for temperature fractions including lower temperature fractions decreases to 3000 Ma. Since the lower temperature fractions would probably include some amounts of in-situ Ar components, the high total ^{40}Ar-^{39}Ar age for the fractions of more than 875°C might be caused due to artificial selection of temperature fractions for this sample.

Both samples 40E2 and 40E4 show similar age patterns: intermediate temperature fractions (975–1050°C) indicate an event of around 4.0–4.1 Ga and expose for higher temperature fractions higher ^{40}Ar-^{39}Ar ages of about 4.5 Ga. Both samples show ^{40}Ar-^{39}Ar ages of less than 3.5 Ga in the 1200°C fraction. Such an age drop might reflect some common features for present samples. The reason is not always clear for this decrease in age, but may reflect some movement of ^{39}Ar due to the recoil effect from a more retentive site to a less retentive site. Since this condition reflects the kind of coexisting minerals including glass phase and their grain sizes and present samples are heterogeneous in these respects, it is not easy to evaluate the effect in a quantitative way. As another possibility, the occurrence of secondary recrystallized minerals formed slowly from shock-produced glass might be raised. The recrystallized phase might be degassed at a temperature of around 1200°C. In effect, similar age drops in the 1200–1300°C fractions have been observed in a shocked LL-chondrite (Takigami and Kaneoka, 1987). In such a case, the apparent age gap between the time of a shock event and observed age in the 1200°C fraction might correspond to the time to form secondary minerals until they can keep radiogenic ^{40}Ar after the shock event. We have no definite criteria to decide which possibility is more probable for the present case.

Although no plateau ages are obtained for the present samples, the age patterns suggest the possibility of a later thermal event at around 4.0–4.1 Ga as revealed in the ages of 40E2 and 40E4 (Figs. 5, 6). The event was probably an impact, because some parts of Juvinas have a brecciated texture. Furthermore, as shown in Figs. 4–6, the ^{40}Ar-^{39}Ar age spectrum for the sample 40E1(a) is definitely different from those of the other two samples. This means that the thermal effect due to an impact on the parent body of Juvinas might be rather heterogeneous, compatible with the observation of their apparently different textures. Further, higher temperature fractions of the sample 40E2 indicate ages of around 4.5 Ga, which probably reflects the radiogenic components which were present since the formation of the meteorite.

In the case of eucrites, late thermal events around 4.0–4.2 Ga have been reported for Pasamonte, Y-74159 and Y-74450 (KANEOKA, 1981; KUNZ *et al.*, 1994; PODOSEK and HUNEKE, 1973). In this respect, Juvinas is also possibly thermally disturbed. As mentioned before, Rb-Sr, Pb-Pb and Sm-Nd ages do not indicate such an event for Juvinas. Hence, the effect would not be so intense as to reset all chronological systematics. As a similar case, Pasamonte also indicates internal isochron ages of 4.53±0.03 Ga by the Pb-Pb method and 4.58±0.12 Ga by the Sm-Nd method (UNRUH *et al.*, 1977), though Rb-Sr age indicates a disturbed signature. For eucrites, ages of less than 4.3 Ga have been identified by the Rb-Sr method for Bereba (4.08±0.25 Ga) (BIRCK and ALLÈGRE, 1978), by the Pb-Pb method for Stannern (about 4.13 Ga), by the Sm-Nd method for Cachari (about 4.02 Ga) (TERA *et al.*, 1987) and those obtained by the ^{40}Ar-^{39}Ar method (BOGARD *et al.*, 1993; KANEOKA, 1981; KANEOKA *et al.*, 1979; KUNZ *et al.*, 1994; PODOSEK and HUNEKE, 1973). This would imply that an impact event might have caused the disturbance visible mostly in the ^{40}Ar-^{39}Ar systematics. The Rb-Sr systematics are also sometimes affected by impact events, but the Pb-Pb and Sm-Nd systematics are more resistant against such an effect.

One inference from the present study is that like other eucrites Juvinas might have also been affected by a later impact event(s) around 4.0–4.1 Ga, though the age(s) might include large uncertainties. This could only be identified in the ^{40}Ar-^{39}Ar systematics. Late impacts by small meteorites on the parent body of eucrites might be quite common. Since HED meteorites show similar data with regard to this point (*e.g.*, KUNZ *et al.*, 1994), such an inference might also be extended to the parent body of HED meteorites.

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