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New crucible for noble gas extraction

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Abstract

Traditional Crucibles for noble gas extraction made of refractory metals are not suitable for metallic samples because these are easily alloyed with liquid metals. To obtain elemental and isotopic compositions of noble gases from metallic samples, new materials, i.e., single crystal MgO and hot-pressed BN have been carefully examined. Low background was achieved using these new crucibles. The MgO crucible is not suitable for materials with high temperature because MgO actively evaporates about 1700°C. Inertness to metallic materials and complete degassing from metallic materials were also achieved using the BN crucible. Based on noble gas data obtained using the BN crucible, we determined the cosmic exposure age of the Mundrabilla iron meteorite as 350 ± 90 Ma.

Keywords: Crucibles; Noble gas extraction; Molybdenum

1. Introduction

Noble gases generally are extracted from solid samples by stepwise pyrolysis, using temperatures up to 2000°C. A schematic diagram of a common design for a gas extraction furnace is shown in Fig. 1. The oven is composed of an outer Ta furnace and inner part crucible, and is connected to the vacuum line. The inner crucible has to be replaced after several sample runs because residual materials form previous samples occasionally prevent extracting gases from a new sample. Refractory metals such as molybdenum are conventionally used for the inner crucible, but these are unsuitable for metallic samples like iron meteorites because they are alloyed with liquid metal and release the gases dissolved within them (Fisher, 1981; Matsuda et al., 1995). Fisher (1981) used a molybdenum crucible with an inner lining of well-degassed silicate glass. He succeeded in protecting the Mo crucible from being alloyed with metal samples. However, his method cannot be applied for large samples with high density. For such samples, the gravity of the sample may overcome the surface tension of the melting silicate and, then, the sample will sink through the melting silicate and arrive at the bottom of the Mo crucible. This would be serious for samples with low concentrations of noble gases because a large quantity of the sample need to be prepared in order to determine elemental and isotopic compositions of the noble gases accurately. In this report, we have examined whether new materials, i.e., BN and MgO, are suit-

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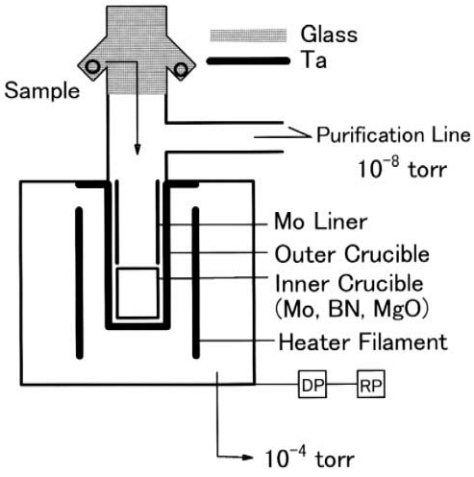

Fig. 1. Schematic diagram of a Ta furnace for noble gas extraction. "DP" represents an oil diffusion pump, and "RP" represents a rotary pump.

able or not as a crucible for noble gas extraction from metallic samples.

2. Experimental procedures

Amounts of noble gases in "hot blanks", which were performed by the same procedure as sample runs but without a sample in the furnace, are given in Table 1. Amounts of noble gases in the "cold blank", which were performed by the same procedures as that of a hot-blank run but without heating the crucible, are also given in Table 1.

Before each run, the crucible was pre-heated in vacuum for above the maximum temperature for gas extraction (i.e., >1600°C or >1800°C in this study). For gas extraction, the crucible was heated to

Table 1
Gas amounts of hot-blank measurements

Crucible	Temperature (°C)	Time (min)	^{4}He ($\times10^{-9}$)	^{22}Ne ($\times10^{-12}$)	^{36}Ar ($\times10^{-12}$)	^{84}Kr ($\times10^{-12}$)	^{132}Xe ($\times10^{-12}$) cm^3 STP
MgO	800	30	1.44	0.17	2.01	0.21	0.068
MgO	1600	30	1.47	0.62	17.05	0.46	0.083
MgO	1600	30	1.49	0.89	25.43	0.71	0.240
BN	800	20		0.81	17.94	0.66	0.048
BN	1600	20		1.02	32.81	1.19	0.084
BN	600	30		1.99	38.83	1.14	0.061
BN	800	30		0.17	2.46	0.17	0.032
BN	800	30		0.13	5.34	0.31	0.038
BN	1600	30		1.25	30.40	1.10	0.076
BN	1600	30		0.58	10.86	0.62	0.074
BN	1600	30	1.08	0.38	23.87	1.69	0.172
BN	1800	30	3.62	0.86	37.50	0.83	0.122
BN	1800	30	3.32	0.99	34.50	0.91	0.111
Mo	800	20			2.33	0.21	0.101
Mo	800	20		2.70	5.84	0.43	0.131
Mo	800	20		2.48	4.68	0.22	0.082
Mo	1600	20	0.96	0.19	31.57	0.70	0.401
Mo	1600	20		0.48	40.06	3.26	0.678
Mo	1600	20	1.07	1.51	6.47	0.18	
Mo	1600	20	5.22	0.16	2.27	0.23	
Mo	1600	20			14.03	0.66	0.237
Mo	1600	20		4.23	16.60	0.63	0.127
Mo	1800	20	2.93	0.28	4.57	0.28	0.150
Mo	1800	20		3.93	14.69	0.41	0.112
Mo	1600	30	0.07	0.16	5.35	0.13	
Mo	1600	30	1.13	0.47	18.03	0.71	0.123
Mo	Cold	20			4.05	0.13	0.090

the required temperature in 20 min and kept at that temperature for 20 or 30 min. Extracted gases were purified twice by Ti–Zr getters heated at 700°C for 15 min. After purification, the extracted noble gases were separated into four fractions (He + Ne, Ar, Kr, and Xe) by using cold traps (Maruoka and Matsuda, 1995). Each noble gas fraction was analyzed with a VG5400 sector-type mass spectrometer (e.g., Matsuda et al., 1995). The isotopic ratios of all detectable isotopes in hot blank runs were atmospheric within uncertainties.

3. MgO crucible

The first new crucible used for metallic samples was made of a MgO single crystal. This crucible achieved low-background measurements similar to the measurements by a traditional Mo crucible (Fig. 2). However, the MgO crucible cannot be heated in vacuum up to 1700°C because MgO actively evaporates above 1700°C and MgO vapor reacts with the tantalum from which the outer crucible is composed. Small holes connected to the outside of the gas extraction line were formed by this reaction. Al-

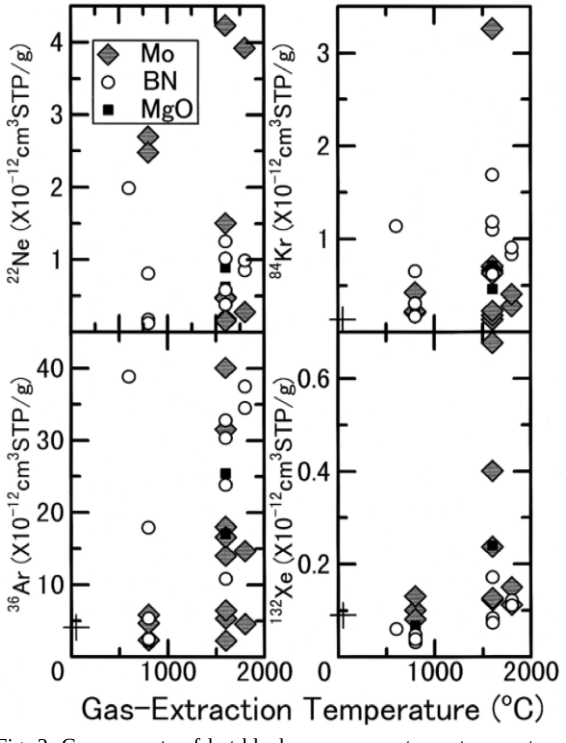

Fig. 2. Gas amounts of hot-blank measurements vs. temperatures for gas extraction. Gray diamonds, open circles, and closed squares represent data of hot-blank measurements extracted from Mo, BN and MgO crucibles, respectively. Cross symbols represent data of cold-blank measurements.

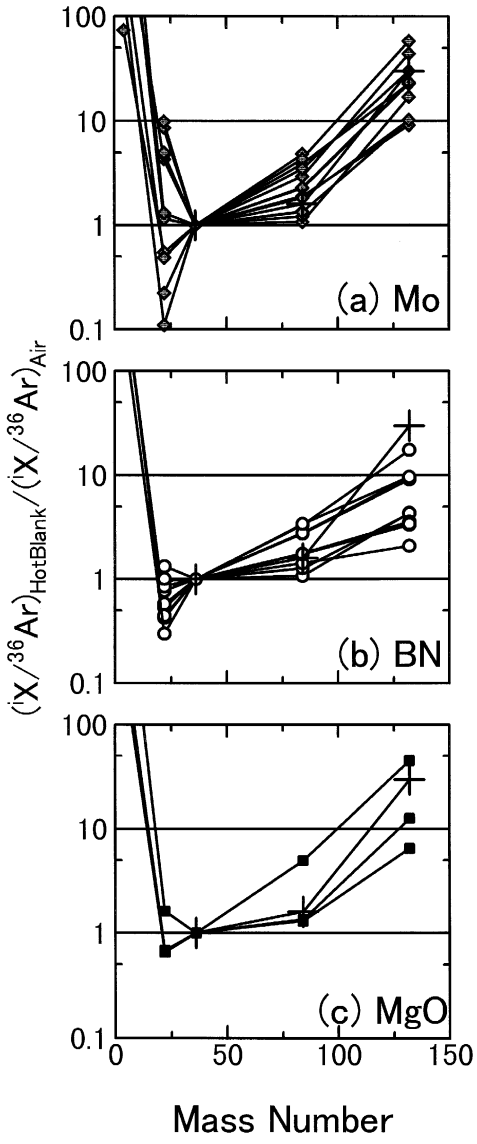

Fig. 3. Elemental abundance ratios of noble gases in hot blanks derived from (a) Mo crucible, (b) BN crucible, and (c) MgO crucible. Cross symbols represent data of cold blank. Atmospheric ratios are from the compilation of Ozima and Podosek (1983).

though the maximum temperature, i.e., 1700°C, is above the melting points of Fe–Ni metals, there may be a fraction of noble gases left in the Fe–Ni melts after heating to 1700°C (e.g., Matsuda et al., 1995). Therefore, the MgO crucible is not suitable for materials with high melting points.

4. BN crucible

A crucible composed of hot-pressed boron nitride (Grade AX05 boron nitride, Carborundum) was also examined. The Grade AX05 is free from a binder such as boric oxide or calcium borate, which enables the crucible to be heated up to 3000°C in vacuum and to release less amount of background gases. Grade AX05 is extremely inert and does not wet with molten materials such as metals, glasses, and halide salts (Technical Information, Carborundum, 1992). The BN crucible also achieved a low background even at high temperatures above 1600°C (Fig. 2).

5. Elemental abundance patterns of noble gases in hot blank

Noble gases in the "cold blank" may be composed of two components originating from air: an adsorptive component, which is derived from gases adsorbed on the surface of the crucible and the vacuum line (stainless steel), and a component, which has diffused through the glass part of the extraction system (Fig. 1). The former component is enriched in heavy noble gases, especially Xe, while the latter component should essentially be restricted to the light noble gases, He and Ne. Noble gases in the "hot blank" may include a dissolved component in the crucible in addition.

Elemental patterns of noble gases in hot blank and cold blank are shown in Fig. 3. The patterns of heavy noble gases in hot blanks derived from Mo crucibles resemble that of the cold blank (cross symbols), indicating that the gases derived from Mo crucibles may be dominated by an adsorptive component. This component may be trapped in the oxidized layer of the crucible surface. Our Mo crucibles were produced by boring a hole in a Mo rod using a lathe. Since the rough surface of the hole produces abundant oxidized materials, adsorptive noble gases weakly bound to the Mo surface might be trapped tightly during the oxidation. Hence, chemical etching may be effective in removing the oxidized surface and thus reducing the amount of hot-blank gases.

The patterns of heavy noble gases from the BN crucibles are distinguished from that of the cold blank and the hot blanks from Mo crucibles with regard to the $^{132}Xe/^{36}Ar$ ratio. It appears that the patterns from BN crucibles are dominated by the dissolved component rather than the adsorptive component, which should be enriched in Xe. Surrounding noble gases might have dissolved in BN grains

Table 2
Contents and isotopic compositions of noble gases extracted using BN crucible from the Mundrabilla meteorite

Temperature	^{4}He[a]	$^{3}He/^{4}He$	^{22}Ne[a]	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	^{36}Ar[a]	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$
600	0.8	0.192	0.002	0.7648	0.9513	0.004	1.5273	7.36
		±0.016		±0.2430	±0.0308		±0.0652	±13.05
800	6.6	0.283	0.030	0.8362	0.9088	0.040	1.5608	0.28
		±0.010		±0.0625	±0.0152		±0.0204	±4.05
1200	324.6	0.284	1.170	0.8677	0.9359	2.402	1.5637	0.41
		±0.007		±0.0137	±0.0144		±0.0040	±0.54
1600	180.7	0.285	0.904	0.9124	0.9306	2.033	1.5293	7.37
		±0.007		±0.0143	±0.0142		±0.0039	±0.57
1600			0.011	1.1557	0.8896	0.196	1.5123	11.02
				±0.0994	±0.0175		±0.0094	±1.77
Total	512.6	0.284	2.118	0.8878	0.9330	4.674	1.5466	3.89
		±0.007		±0.0164	±0.0145		±0.0050	±0.78

[a] Gas concentrations are in units of 10^{-8} cm^3 STP/g.

during their production. Production of BN grains in a noble gas-free atmosphere may be able to reduce the amount of hot-blank gases for this crucible type.

6. Inertness to metallic materials

What remains to be discussed is inertness of a BN crucible to metallic samples. As a test, we analyzed the isotopic compositions of iron meteorites using a BN crucible (Table 2). The data of our study are located on the $^{36}Ar/^{38}Ar$–$^{4}He/^{21}Ne$ correlation obtained by Voshage and Feldmann (1979) from many iron meteorites (Fig. 4). On the other hand, the data of the same iron meteorite using the traditional crucible (Schlotz, 1977) deviated from the correlation. As there seems to be the trend line toward atmospheric Ar on the $^{40}Ar/^{36}Ar$–$^{38}Ar/^{36}Ar$ diagram (Fig. 5), it should be reasonable that argon in those samples should contain atmospheric Ar as well as spallogenic Ar. The atmospheric component in iron meteorites may originate from weathering on the Earth and/or dissolved air in the crucible, which may be extracted due to alloying the sample with the crucible. The data point obtained using the BN crucible (gray circle) is furthest from the atmospheric point, meanwhile other data are more or less affected by air. It is very likely that the reaction with the conventional crucible is responsible for the air component in these cases. Thus, we conclude that the BN crucible should be inert to the metallic samples.

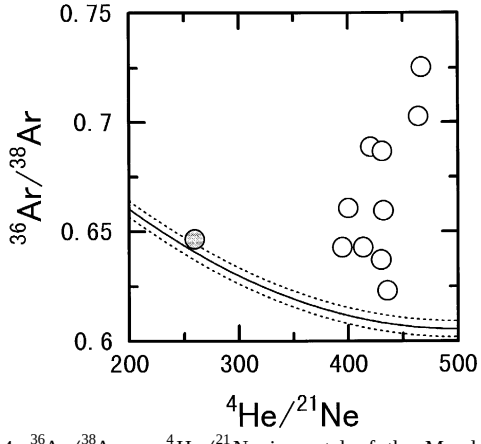

Fig. 4. $^{36}Ar/^{38}Ar$ vs. $^{4}He/^{21}Ne$ in metal of the Mundrabilla meteorite. Gray circle represents data obtained in this study using BN crucible. Open circles represent data of Schlotz (1977) obtained using the traditional crucible. Solid curve represents the correlation observed in many iron meteorites (Voshage and Felmann, 1979). The correlation can be expressed by the equation as follows: $(^{36}Ar/^{38}Ar) = 0.758–6.1\times10^{-4}\cdot(^{4}He/^{21}Ne) + 6.1\times10^{-7}\cdot(^{4}He/^{21}Ne)^2$. The standard deviation for $^{36}Ar/^{38}Ar$ of the correlation was 0.0037. The dotted curves indicate the range of uncertainty of the correlation.

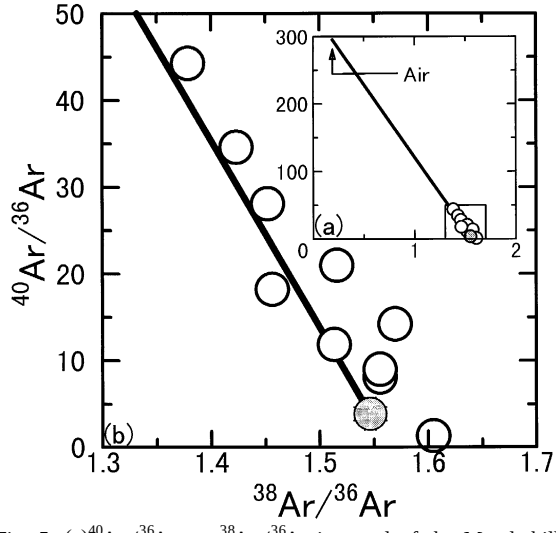

Fig. 5. (a)$^{40}Ar/^{36}Ar$ vs. $^{38}Ar/^{36}Ar$ in metal of the Mundrabilla meteorite and (b) its enlarged diagram of rectangular portion in (a). Sources and symbols are the same as those in Fig. 4. Air Ar is from Ozima and Podosek (1983). Solid line represents the direction to atmospheric Ar from our data.

7. Complete degassing from metallic materials

The maximum temperature (1600°C) used for gas extraction from Mundrabilla is above the melting points of Fe–Ni metals, and we observed that the sample melted after the first heating step at this temperature. However, some fractions of Ne and Ar remained in the Fe–Ni melt after the first 1600°C step, and were released during the second 1600°C step (Table 2). Similar phenomena were reported in previous work (Matsuda et al., 1995). Traditional crucibles composed of refractory metals are not suitable for repeat heating steps at this temperature because they are alloyed with Fe–Ni melt during the first maximum step. Some data of Schlotz (1977) deviated from the $^{3}He/^{4}He$–$^{4}He/^{21}Ne$ correlation curve obtained by Voshage et al. (1983) because of

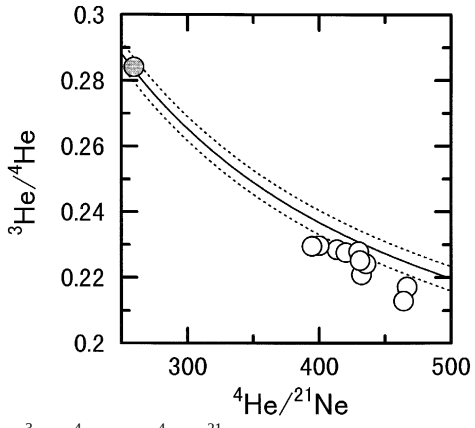

Fig. 6. $^3He/^4He$ vs. $^4He/^{21}Ne$ in metal of the Mundrabilla meteorite. Sources and symbols are the same as those in Fig. 4. Solid curve represents the correlation observed in many iron meteorites (Voshage et al., 1983). The correlation can be expressed by the equation as follows: $(^3He/^4He) = 0.151 + 34.3 \cdot (^4He/^{21}Ne)^{-1}$. The standard deviation for $^3He/^4He$ of the correlation was 0.0037. The dotted curves indicate the range of uncertainty of the correlation.

the incomplete degassing of He (Fig. 6) although the data in our study located exactly on the correlation curve. For our study, He was extracted by a single 1600°C heating, meanwhile Ne was not extracted completely only by the single 1600°C heating (Table 2). The fractionation between He and Ne at one heating step should cause the deviation for some data of Schlotz (1977). Therefore, the well-preserved $^4He/^{21}Ne$ ratio in the sample of our study indicate that the gases were completely extracted by using the newly introduced hot-pressed BN crucible.

As the recovered mass of the Mundrabilla iron meteorite were about 21 ton (Buchwald, 1975), the pre-atmospheric mass must be more than 21 ton. The production rate of ^{21}Ne corresponding to the $^4He/^{21}Ne$ ratio obtained in this study (259) and the range of the pre-atmospheric mass (from 21 000 kg to infinite) can be calculated as $(0.47–0.78) \times 10^{-10}$ cm^3 STP/g Ma from the model equations obtained by Voshage (1984). Based on this production rate, the cosmic ray exposure age of the Mundrabilla iron meteorite can be estimated as 260–440 Ma (i.e., 350 ± 90 Ma).

8. Conclusions

The crucibles composed of a single crystal MgO and hot-pressed BN described here should be suitable for noble gas extraction of metallic samples such as iron meteorites.

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