

Chemical Composition and Noble Gas Isotopic Abundances of Nantan Iron Meteorite

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Abstract

The abundances of selected siderophile elements and the isotopic compositions of noble gases have been measured by instrumental neutron activation analysis and noble gas mass spectrometry, respectively, in what has been labeled as the "Nantan iron meteorite" recently purchased by the National Science Museum, Tokyo. Analytical results from these methods revealed that the "iron" is an iron meteorite. The siderophile abundances obtained in this work are in good agreement with the literature values for Nantan. Although no detailed discussion was available on the noble gas data, the relative abundances of cosmogenic components suggest that the size of the "iron" before breakup at the atmospheric entry was fairly large.

1. Introduction

In 1958, 19 individual iron blocks with a combined mass of more than 10 tons were found in the course of iron ore prospecting at Lihu town and the Lada and Baya areas, Nantan County, Guanxi province, China. It was recorded in the old Chinese literature that the meteorite shower had fallen over an area of 28 km wide to the north-westerly direction. Those irons were named as "Nantan" and the largest piece, so-called 1900 kg, was stored in the Institute of Geochemistry, Academia Sinica, Guiyang, Guishou province. The iron meteorite, Nantan, is the largest meteorite recovered in the Asia. Since that time further surveys for iron meteorites have continued. In 1990, another large piece (1.71 ton) was found at Lihu town (geographical coordinate: 107°42'E, 25°06'N) and was purchased by the National Science Museum, Tokyo, via U.S.A. for display, in 1994.

Scientific studies of the iron meteorite Nantan first started in 1964. Since then, several reports have been published. Most of the studies were performed on the largest piece in the Institute of Geochemistry. Using instrumental neutron activation analysis (INAA) and several other analytical methods, ONUMA *et al.* (1979) grouped Nantan into group IA. Later, KRATHER *et al.* (1980) reclassified as IIICD by their own data.

Iron meteorites are conventionally classified based on the abundances and interrelations of Ga, Ge, Ni and Ir (WASSON, 1967; KRATHER *et al.*, 1980). According to their classification, iron meteorites are classified into 13 groups. Among these 13 groups, ten groups are thought to be of magmatic origin (KRATHER and WASSON, 1982), but the origin of the remaining three groups, IAB, IIE and IIICD, are still under discussion (WASSON *et al.*, 1980; WASSON and WANG, 1986), though it has been suggested based on cooling rates that most of iron meteorites in each group are genetically related (GOLDSTEIN and SHORT, 1967).

In this study, Fe, Ni and trace elements (mostly siderophile elements) in a tiny piece of the "iron", so-called the iron meteorite Nantan, displayed at the National Science Museum, Tokyo, were analyzed by INAA. Isotopic abundances of noble gases were also determined using another chip of the "iron" by mass spectrometry. Here we compare these results with literature values of Nantan and other iron meteorites to show that the newly obtained "iron" is surely the iron meteorite "Nantan".

2. Experimental Procedures

2.1 INAA

2.1.1 Sample Preparation

In this work, we analyzed another iron meteorite, Odessa in addition to the "iron". Small chips of metal (about 40 mg) were cut from the original pieces of the "iron" and Odessa. After etching in dilute HCl to remove possible contaminants, they were doubly sealed in clean polyethylene bags. The Allende reference sample, prepared by the Smithsonian Institution, and a geological standard rock, JB-1, issued by the Geological Survey of Japan, were used for reference materials. About 30 mg of these materials were also sealed in polyethylene bags.

2.1.2 Chemical Standards

Chemical standards were prepared from high purity chemical reagents of Au, Pt, Mn, Ge, Rh, Cu, Ru, Re, Sb, Ga, Pd, Os, Ir, Ni, Fe, Cr, W, Mo and Co. A known amount of metal or compound of each element was dissolved in an appropriate solvent. The solution thus prepared was stored as a stock solution, from which running solutions were further prepared. 40 μ l of each running solution was pipetted on a small piece of filter paper and dried at room temperature. To minimize the volume in irradiation, several elements were mixed. Two sets of chemical standards were irradiated and mean values were used for calculation. The deviations of specific activities between duplicate samples of chemical standards are less than 2% for most elements.

Table 1. Nuclear data related to the INAA used in this work

Element	Radionuclide	Half life	γ -ray energy used (keV)	Interfering nuclide (energy, keV)
Short irradiation (100 s)				
Rh	^{104}Rh	41.8 s	555.8	$^{104\text{m}}\text{Rh}$ (555.8)
Ge	^{75}Ge	48 s	139.8	
Cu	^{66}Cu	5.1 min	1039	
Mn	^{56}Mn	2.58 h	1811	
Long irradiation (5 h)				
Pd	^{109}Pd	13.4 h	88.0	
Ga	^{72}Ga	14.1 h	630	
W	^{187}W	23.9 h	685.5	
As	^{76}As	26.5 h	559.1	
Au	^{198}Au	2.70 d	411.8	
Mo	^{99}Mo	2.75 d	140.5	^{59}Fe (142)
Sb	^{122}Sb	2.80 d	563	
Pt	^{199}Au	3.15 d	158.4	$^{199}\text{Au}^*$
Re	^{186}Re	3.78 d	137.0	^{192}Ir (136), ^{191}Os (139)
Os	^{191}Os	19.4 d	129.4	
Cr	^{51}Cr	27.7 d	320.08	^{192}Ir (316)
Ru	^{103}Ru	39.4 d	497.9	
Fe	^{59}Fe	44.6 d	1099.3	
Ni	^{58}Co	71.3 d	810.8	
Ir	^{192}Ir	74.2 d	316, 468	
Co	^{60}Co	5.26 y	1173	

* Produced by a reaction of $^{197}\text{Au}(n,\gamma)^{198}\text{Au}(n,\gamma)^{199}\text{Au}$.

2.1.3 Neutron Irradiation

The samples were irradiated in the TRIGA-II reactor at the Institute for Atomic Energy, St. Paul's University. All the samples were first irradiated for 100 sec at a neutron flux of $1.5 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ for the determination of Ge, Rh, Cu and Mn contents. In this measurement, Cu and Cd plates (1 mm thick each) were used to absorb low energy activities, mainly 58.6 keV γ -ray emitted by $^{60\text{m}}\text{Co}$ (half life: 10.48 min). The samples were then reirradiated for 5 h at the same neutron flux as that for the first irradiation for the measurement of Au, Pt, Re, As, Sb, Ga, Pd, Ru, Os, Ir, Ni, Fe, Cr, W, Mo and Co. Nuclear data for the nuclides concerned in the present INAA are listed in Table 1.

2.1.4 γ -ray Measurement

γ -ray measurements were carried out at the Institute for Atomic Energy, St. Paul's Univ. for short-lived nuclides and at the RI research laboratory, Tokyo Metropolitan Univ. for long-lived nuclides, for which γ -ray counting was repeated at different cooling intervals. All γ -ray spectrometry was performed using pure Ge detectors. For the determination of Rh, we used the activity of ^{104}Rh (half life: 41.8 s) corrected for the contribution from $^{104\text{m}}\text{Rh}$ (half life: 4.36 min). Platinum contents were determined by measuring the activities of ^{199}Au , which is produced by a reaction of $^{198}\text{Pt}(n,\gamma)^{199}\text{Pt}$

followed by β -decay. ^{199}Au can be also produced from Au by a double neutron capture reaction, $^{197}\text{Au}(n, \gamma)^{198}\text{Au}(n, \gamma)^{199}\text{Au}$. For the determination of Pt, a pure Au monitor was irradiated simultaneously with the samples and an activity ratio of ^{198}Au to ^{199}Au was monitored. As the activity of ^{199}Au was below the detection limit for the Au monitor sample, no correction was made in determining Pt. For the remaining elements which may suffer from interferences (see Table 1), contributions from interfering nuclides were estimated and were subtracted when not negligible.

2.2 Noble Gas Mass Spectrometry

The “iron” sample weighing 89.8 mg was put in a sample holder connected to the gas extraction and purification line and heated at about 180°C for 30 h in vacuum to reduce adsorbed atmospheric noble gas contamination. Noble gases were extracted by heating the sample at 1800°C for 30 min in an Al_2O_3 crucible which had been degassed at 1850°C for 7 h. To assess the efficiency of extraction, the sample was heated twice under the same conditions after the first extraction. The noble gases were purified with Ti–Zr getters and separated into four fractions, He–Ne, Ar, Kr and Xe, using a charcoal trap. Each fraction was introduced into the mass spectrometer (modified VG 5400) to measure isotopic ratios and concentrations. Both sensitivity and mass discrimination for each noble gas were determined by measuring a known amount of atmospheric noble gases. The mass discrimination of $^3\text{He}/^4\text{He}$ ratio was determined by measuring a helium gas with $^3\text{He}/^4\text{He} = 1.71 \times 10^{-4}$ prepared in our laboratory.

Blanks were 1.3×10^{-14} , 5.5×10^{-10} , 2.8×10^{-11} , 5.8×10^{-9} , 3.4×10^{-13} and $4.8 \times 10^{-14} \text{ cm}^3 \text{ STP}$ for ^3He , ^4He , ^{20}Ne , ^{40}Ar , ^{84}Kr and ^{132}Xe , respectively. They were 8, 39, 14, 9 and 1% of the amounts of ^4He , ^{20}Ne , ^{40}Ar , ^{84}Kr and ^{132}Xe , respectively, in the first extraction. At the second and third extractions, about 3.5% of the total ^{40}Ar was recovered, but for other noble gases, the recovered amounts were negligible compared to the blank levels.

3. Results

3.1 INAA Data

INAA results for the “iron”, Odessa and Allende meteorites as well as JB-1 are present in Table 2. Literature values for these four samples also are listed for comparison. No data were obtained for Pd. Since the chemical standard of As was not prepared, its contents were calculated using a literature value for JB-1 (2.48 ppm; ANDO *et al.*, 1989).

Our results are generally in good agreement with the literature values. For Odessa, literature values of HONDA *et al.* (1991) are lower for Ir, Pt and Au, and higher for Ru than those from PERNICKA and WASSON (1987). The present results for Ir, Pt and Au agree with the latter data, while the Ru values obtained in this work are systematically higher ($\sim 40\%$) than the literature values, if an abnormally high value of HONDA *et al.* (1991) for Odessa is neglected. These high values for Ru may be explained by volatile loss of Ru in the standard following partial oxidation. Although the chemical standard

Table 2. INAA results for the "iron" (Nantan), Odessa and two reference materials (Allende and JB-1) (contents in ppm, unless otherwise indicated)*

Element	The "iron" (Nantan)			Odessa			Allende		JB-1	
	This work	Lit.** (a)	Lit.** (b)	This work	Lit.** (b)	Lit.** (c)	This work	Lit.** (d)	This work	Lit.** (e)
Cr	47.8 (2.7)			41.9 (4.6)			3670 (0.5)	3626	459 (1.2)	469
Mn	37.3 (7.1)			45.9 (7.2)			1480 (1.0)	1470	1270 (1.7)	1240
Fe (%)	91.0 (0.3)		92.4	92.6 (0.5)			23.4 (0.4)	23.6	6.11 (0.8)	6.26
Co	4790 (0.5)		4800	4660 (0.2)			690 (0.4)	600	39.6 (1.4)	38.7
Ni (%)	6.73 (0.5)	6.84	7.09	7.38 (0.3)	7.22	7.3	1.43 (0.5)	1.42	0.0147 (7)	0.014
Cu	165 (5.7)		146	217 (9.2)						
Ga	84.0 (1.8)		81.9	81.2 (2.6)		70				
Ge	308 (3.0)		291	300 (4.8)		285				
As	14.2 (1.0)		13.0	11.6 (0.8)		12	1.72 (2.2)	1.55	=2.48 (4.4)***	
Mo	6.91 (3.3)			6.90 (3.6)					19.7 (4.6)	34
Ru	7.68 (9.2)	5.4	5.11	6.03 (14)	4.7	7	1.2 (13)	0.85		
Rh	1.53 (6.2)			1.43 (5.2)		1.3				
Sb	0.39 (15)		0.31	0.476 (4.9)			0.132 (9.3)	0.08	0.305 (7.2)	0.35
W	1.08 (11)		1.14	0.878 (9.6)		0.9			23.7 (1.2)	20
Re	0.150 (9.9)	0.170	0.17	0.247 (11)	0.245	0.23				
Os	1.77 (16)	1.88	1.73	2.42 (12)	2.52	2.6	0.85 (11)	0.83		
Ir	1.89 (1.5)	1.7	1.81	2.60 (0.6)	2.44	1.9	0.746 (1.5)	0.76		
Pt	6.20 (13)	6.4	6.18	5.72 (4.7)	5.5	4.9				
Au	1.49 (0.8)	1.56	1.43	1.68 (0.5)	1.51	1.1	0.152 (1.0)	0.15		

* Values in parentheses are errors (in %, 1σ) due to counting statistics involved in γ -ray spectrometry.

** Literatures: (a) PERNICKA and WASSON (1987); (b) OUYANG (1988); (c) HONDA *et al.* (1991); (d) JAROSEWICH *et al.* (1987); (e) ANDO *et al.* (1989).

*** Used as standard.

for Os was prepared in the same manner as that for Ru, the Os contents were consistent with the literature values. This suggests that the high Ru contents for the meteorites analyzed in this work were not due to loss of Ru in preparing its chemical standards. The chemical standard of Ru was prepared from $(\text{NH}_4)_2\text{RuCl}_6$. If this compound is not stoichiometrical and/or partly decomposed with humidity, high values of Ru are also expected. Assuming that Ru content in Nantan is 5.4 ppm (PERNICKA and WASSON, 1987), the Ru contents for Odessa and Allende are calculated to be 4.3 and 0.85 ppm, respectively, which are consistent with the corresponding literature values. The Mo value obtained for JB-1 is also 40% smaller than its literature value. The Mo contents were calculated using a γ -ray peak at 140.5 keV, which can be interfered by the ^{59}Fe peak of 142 keV. In reducing the data for Mo, such a contribution was monitored by comparing two sets of data taken at the different cooling intervals and was accordingly corrected. Although we are confident with our data for Mo, these values should be regarded as reference values as no credit was available for them.

Cosmochemically, all the elements listed in Table 2 are siderophiles except Mn and Cr, which are lithophiles. In iron meteorites, Mn and Cr are rather depleted in FeNi

Table 3. Elemental abundances* and isotopic compositions** of noble gases in the "iron" (Nantan iron meteorite)

³ He*	⁴ He*	³ He/ ⁴ He	²⁰ Ne*	²¹ Ne*	²² Ne*	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	²² Ne/ ²¹ Ne	
0.648	6.91	0.09372 ±0.00029	0.0485	0.0116	0.0165	2.94 ±0.67	0.700 ±0.065	1.43 ±0.13	
³⁶ Ar*	³⁸ Ar*	⁴⁰ Ar*	³⁸ Ar/ ³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar	⁸⁴ Kr*	⁸⁰ Kr	⁸² Kr	⁸³ Kr	⁸⁶ Kr
0.195	0.104	44.4	0.531 ±0.021	227.9 ±2.6	39.9	4.087 ±0.040	20.42 ±0.22	20.41 ±0.10	30.58 ±0.30
¹³² Xe*	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe	
42.8	0.457 ±0.041	0.286 ±0.124	7.18 ±0.23	97.0 ±2.1	15.20 ±0.49	76.99 ±0.71	39.01 ±0.61	32.88 ±0.34	

* Concentrations are given in unit of 10^{-8} cm³ STP/g for He, Ne and Ar, and 10^{-12} cm³ STP/g for Kr and Xe.

** Relative to ⁸⁴Kr (=100) and ¹³²Xe (=100) for Kr and Xe, respectively.

matrix, instead enriched in troilite (BUCHWALD, 1975). OUYANG (1988) reported Mn contents of 3.1 and 388.5 ppm in FeNi and troilite, respectively, in Nantan. The relatively high contents of Cr and Mn for Nantan and Odessa obtained in this work may be attributed to the small contamination of troilite in the FeNi phase.

3.2 Noble Gas Data

Isotopic ratios and concentrations of noble gases obtained in this work are shown in Table 3. The uncertainties shown for the isotopic ratios are statistical errors (1σ) while the analytical uncertainties for gas concentrations are estimated to be about 10% for He and Kr, and about 5% for Ne, Ar and Xe. ⁷⁸Kr was not measured due to an instrumental problem, so the isotopic ratio of ⁷⁸Kr/⁸⁴Kr is not shown in the table.

4. Discussion

4.1 Siderophile Abundances

IAB and IIICD irons are specific groups among iron meteorites; they have high planetary-type noble gas contents and contain silicate inclusions of chondritic compositions. These features suggest that both IAB and IIICD groups are mechanical mixtures of metal and silicate phases that were not completely melted (WASSON *et al.*, 1985).

On a log-log plot for Ir vs. Ni, IAB and IIICD show different slopes from those of the magmatic groups (WASSON, 1985). Nantan and Odessa are low-Ni IIICD and IAB irons, respectively. The low-Ni IIICD and IAB iron meteorites are similar in texture and structure, and cannot be distinguished from each other on the basis of structural observations. However, they are resolved on the basis of their metal compositions (PERNICKA and WASSON, 1987; WASSON *et al.*, 1980). The abundance of Ni, Re, Os and Ir are lower in Nantan than in those in Odessa, while contents of Pt, Ru, Rh and W are slightly higher in Nantan. According to WASSON *et al.* (1980), low-Ni contents

of IAB and III CD were caused by intense shock events that yielded higher temperature melts, which in turn effectively extracted refractory elements from the parent body. Ni contents in Nantan and Odessa are near the low-Ni extreme of these two groups (Fig. 1), but the Ni-normalized contents of Ir and Os in these two meteorites are still lower

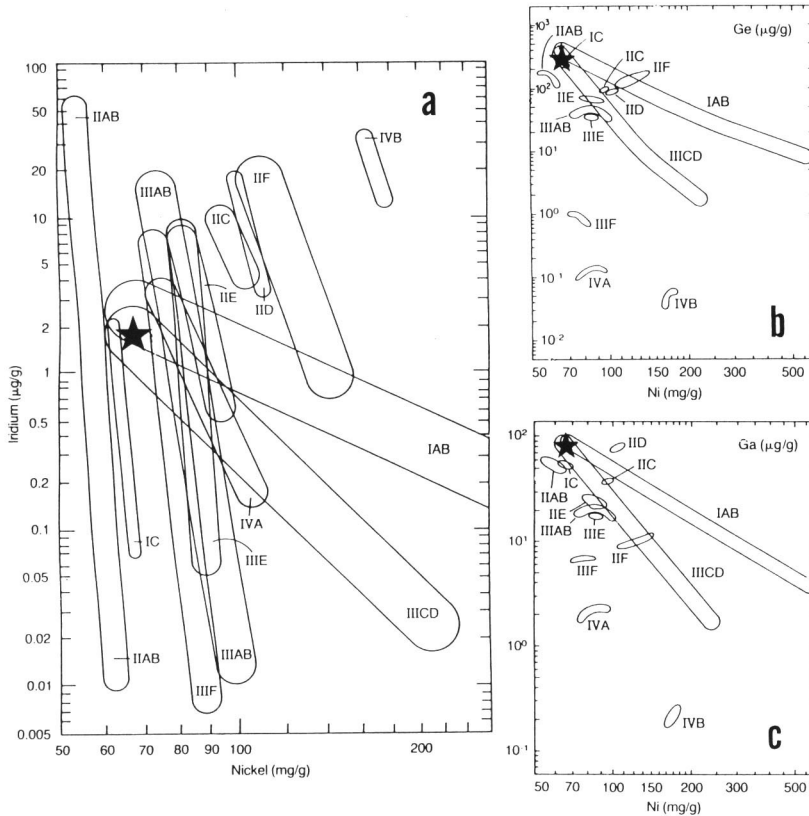


Figure 1. Relationships among siderophile contents in iron meteorites (a: Ir vs. Ni; b: Ge vs. Ni; c: Ga vs. Ni) (from WASSON, 1985). The data obtained in this work for the “iron” (Nantan iron meteorite) are marked by stars. The data for Odessa are also located almost at the same position as those for the “iron” (Nantan).

Table 4. Relative abundances of some elements in the “iron” (Nantan) and Odessa (normalized to Ni contents, $\times 10^6$)

Element	Ir	Os	Re	W	Mo	Ru	Pt	Rh	Au	Ga	Ge	As	Cu	Sb
Nantan	28	26	2.2	16	103	114	92	23	22	1200	4600	211	2500	5.8
Odessa	35	33	3.3	12	93	82	78	19	23	1100	4100	160	2900	6.4
CI*	44	44	3.3	8.4	84	65	90	12	13	910	3000	170	11000	13

* CI chondrite values from ANDERS and GREVESSE (1989).

Table 5. Cosmogenic He, Ne and Ar* in the "iron" (Nantan)

^3He	^4He	^{21}Ne	^{38}Ar	$^3\text{He}/^{21}\text{Ne}$	$^4\text{He}/^{21}\text{Ne}$	$^4\text{He}/^{38}\text{Ar}$
0.648	6.91	0.0114	0.0763	56.8	606	90.6

* Concentrations are given in unit of $10^{-8} \text{ cm}^3 \text{ STP/g}$.

than that of CI (Table 4). If Os and Ir were more likely to reside in the high temperature condensates, such as CAI-like materials on the parent body, and were not quantitatively transferred into the metal phases, then W, another highly refractory element, would have behaved similarly. However, W/Ni ratios in Nantan and Odessa are higher than the CI value. This indicates that if Nantan and Odessa are shock-melted products, their parent bodies must have had much lower Ir/Ni and Os/Ni ratios than those for CI chondrites.

4.2 Noble Gas Abundances

The high $^3\text{He}/^4\text{He}$ ratio due to a spallogenic component confirms the extraterrestrial origin for the "iron". The high $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ ratios compared to those of the trapped components also support the extraterrestrial origin. Since the Ne and Ar isotopic ratios are plotted along the mixing lines between cosmogenic and terrestrial atmospheric components on $^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{38}\text{Ar}/^{36}\text{Ar}$ diagrams, respectively, the trapped Ne and Ar should be atmospheric contaminations released from the sample or from the alumina crucible. Consequently, the isotopic compositions of Kr and Xe similar to those of atmospheric noble gases must be due to air contamination.

Cosmogenic He, Ne and Ar concentrations and relative abundances calculated on an assumption of atmospheric isotopic ratios for trapped components are summarized in Table 5. These concentrations are very low compared with the values reported for iron meteorites (SCHULTZ and KRUSE, 1989) except for Campo del Cielo (El Taco) (IA) and Gibeon (IVB), which have low He, Ne and Ar concentrations comparable with those for our sample. For iron meteorites, the $^4\text{He}/^{21}\text{Ne}$ ratio depends on the meteoroid size as well as the depth at which meteorites were located and are typically in the range of 200–450 (VOSHAGE, 1984). According to the diagrams showing the production rates of ^4He , ^{21}Ne and ^{38}Ar vs. $^4\text{He}/^{21}\text{Ne}$ ratio by VOSHAGE (1984), a high $^4\text{He}/^{21}\text{Ne}$ ratio of 606 for our sample indicates that the "iron" had a preatmospheric size of much larger than 10000 kg. The low concentrations of cosmogenic noble gases are also consistent with this size and are almost certainly due to the heavy shielding against cosmic-ray irradiation.

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