$^{196}\text{Hg}/^{202}\text{Hg}$ ratio and Hg content in meteorites and terrestrial standard rocks: A RNAA study

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(Received May 13, 1999; Accepted January 25, 2001)

Radiochemical neutron activation was applied for the determination of mercury isotopic ratios ($^{196}\text{Hg}/^{202}\text{Hg}$) for standard rock samples and meteorite samples. After neutron activation, Hg was released upon heating from 100°C to 500°C at 100°C steps and the activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ was measured for each released fraction. After the correction for the interfering γ -rays of ^{75}Se to ^{203}Hg , the ratios obtained from the Dhajala meteorite (bulk and magnetically separated samples) were identical to those of the Hg monitor as well as standard rock samples (JB-1, basalt, and JG-1, granodiorite). An apparently low ratio of $^{196}\text{Hg}/^{202}\text{Hg}$ was observed at high temperature (500°C) for the Allende meteorite reference sample. As such a low value was not reproduced in another run, the presence of isotopically anomalous Hg in the Allende reference sample can not be concluded. Hg/Se ratio was observed to be very high in the non-magnetic fraction of Dhajala compared with that in the magnetic fraction, suggesting that Hg is less chalcophile than Se. Yamato 82050 (CO3) has an anomalously high content of Hg with a normal $^{196}\text{Hg}/^{202}\text{Hg}$ ratio, being at least an order of magnitude higher than the expected value. This meteorite must have been contaminated with Hg, presumably on Antarctica.

INTRODUCTION

The presence of isotopically anomalous mercury (Hg) in meteorites has been controversial in cosmochemistry. Mercury consists of 7 stable isotopes (^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg and ^{204}Hg), which were synthesized by three processes (p-, s- and r-processes) according to a nuclear synthesis model (e.g., Burbidge *et al.*, 1957). Of these 7 nuclides, three nuclides (^{196}Hg , ^{202}Hg and ^{204}Hg) can be potentially determined by using neutron activation analysis and their relative abundance ratios can be calculated. Practically, however, a relative abundance of only two nuclides (^{196}Hg and ^{202}Hg) can be reliably determined for meteorite samples. Applying radiochemical neutron activation analysis (RNAA), Reed and coworkers (Reed and Jovanovic, 1969, 1990; Jovanovic and Reed,

1976, 1987, 1990) and Goel and coworkers (Goel and Thakur, 1987, 1989; Thakur and Goel, 1989; Kumar and Goel, 1992a, b) found a large variation in $^{196}\text{Hg}/^{202}\text{Hg}$ ratio, in various classes of meteorites. Both positive and negative anomalies of $^{196}\text{Hg}/^{202}\text{Hg}$ ratio were found in several meteorite samples and were ascribed to enrichment and depletion of the p-process nuclide ^{196}Hg . Isotopic anomalies of p-process nuclides have been reported for several elements including Hg. Except Hg and Os, whose anomalies have been detected by RNAA, only Xe shows an apparent anomaly of a p-process nuclide exceeding 1%.

In some RNAA studies for Hg, attempts were made to identify the host phases of isotopically anomalous Hg by analyzing various mineral separates obtained by physical and chemical methods such as sieving into different grain sizes, separat-

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ing magnetic and non-magnetic fractions, preparing acid-resistant residues, etc. In addition, various Hg fractions from individual samples released by heating at different temperatures under vacuum were also investigated. Anomalous Hg fractions have been mostly obtained from the acid-resistant residues of iron meteorites (treated with 2M H₂SO₄ solution) and stony meteorites (after HF-HCl demineralization). However, the nature of the host phases and the release profile of anomalous components could not be firmly established.

Some meteoriticists suspect that the observed variations of Hg isotope ratios may actually be due to experimental artifacts occurring at some stage(s) from irradiation to measurements and that the technique is not reliable enough for the precise determination of isotopic ratios. On the other hand, potentially more accurate mass spectrometric analyses of Hg are very few; von Helden and Begemann (1976) analyzed Allegan (matrix and chondrules) and Tieschitz (bulk sample), and Nier and Schlutter (1987) analyzed Allende (chondrules and bulk sample). Both studies reported normal isotopic ratios, but the uncertainties for ¹⁹⁶Hg abundance are rather high due to its low abundance (0.15%) and excessive mass spectrometric interference by hydrocarbons.

The study of isotopic anomalies helps to unravel the formation history of the early solar system and to search for presolar grains whose presence puts constraints on the evolution of solar materials. Considering that isotopic anomalies of noble gases and volatile light elements (e.g., H and N) in meteorites have greatly contributed to our understanding of these aspects, a detailed study of Hg abundance and its isotopic ratio would be equally valuable. We undertook the present work with three major objectives. The first objective is to develop and document a rigorous procedure for the determination of Hg isotopic ratios (¹⁹⁶Hg/²⁰²Hg) by RNAA. In the earlier literature analytical procedures have not been described very clearly. To accomplish this, we have examined every step which can possibly lead to erroneous values of ¹⁹⁶Hg/²⁰²Hg. The second objective is to apply this procedure to terrestrial standard rock

to confirm how reliably our procedure works and further to meteorite samples to see if any isotopically anomalous Hg can be detected. The third objective is to determine the Hg abundances in some meteorite samples. It is widely believed that Hg is distributed heterogeneously in meteorites, yielding a large variation of Hg abundances in individual meteorite groups and even in different portions of the same meteorite. This question is also addressed here to some extent.

EXPERIMENTAL

Preparation of meteorite and Hg monitor samples

We have carried out two separate radiochemical analysis series, hereafter called runs A and B. In run A, we analyzed powdered samples of two meteorites, Allende (CV3) and Y 82050 (CO3; an Antarctic meteorite), and of two Japanese standard rocks, JG-1 and JB-1 (granodiorite and basalt, respectively, prepared by the Geological Survey of Japan). The powdered sample of Y 82050 was prepared at the National Institute of Polar Research (NIPR) by pulverizing a chunk (about 10 g). For Allende, the powdered reference sample prepared by the Smithsonian Institution, USA (split 11/position 11) was used. In run B, an ordinary chondrite, Dhajala (H3), was analyzed in three different forms as described below, along with aliquots of the Smithsonian Allende reference sample and JB-1 to check consistency with run A.

A piece of Dhajala weighing ~14 g was washed with acetone and dried in an oven at ~40°C. The piece was broken in an agate mortar and small pieces along with small particles (~6 g in total) were further ground to powder. A portion (~4 g) was kept for bulk analysis. The remaining portion was separated into magnetic and non-magnetic phases using a hand magnet. A major part (~0.75 g) of the magnetic separate was treated with 1:1 HF solution in a Teflon beaker and was placed in a hot water bath (~90°C) for 2 min. The sample was washed with water and the above treatment was repeated. Finally the residue was rinsed with ethanol and was dried in an oven at 60°C for 15

min. The resulting sample appeared to be mostly metallic under a microscope. Some silicate grains were also seen and separated from the metallic fraction by using a hand magnet.

Samples of bulk, non-magnetic and magnetic (metal) separates (ranging from 70 to 160 mg) were sealed in quartz tubes which had been boiled in nitric acid, rinsed in distilled water and heated under vacuum. During sealing, the tube bottom was wrapped with asbestos cloth soaked in ice water to prevent Hg from evaporating from the samples due to heating. The Hg monitor samples were prepared by pipetting an appropriate amount of Hg standard solution (monohydrate Hg (I) nitrate in dilute HNO_3) into a quartz tube containing 3–4 mg MgO powder (specpure grade, Johnson Mathey Co. Ltd.). For drying, the tubes were first heated under a heat lamp at $\sim 50^\circ\text{C}$ for three days and finally placed in a desiccator at room temperature until the weight became constant. The tubes were sealed near the opening in the same manner as for the meteorite and terrestrial samples. The exterior surfaces of all tubes were cleaned with 2M nitric acid. The tubes were individually wrapped with high purity aluminum foil and stacked together side by side in a single pack to minimize variation in neutron flux among the samples.

Neutron irradiation and post-irradiation chemical procedure

The neutron irradiation was performed in the JRR-3 reactor of the Japan Atomic Energy Research Institute (JAERI) at a thermal neutron flux of $\sim 1 \times 10^{14} \text{ cm}^{-2}\text{sec}^{-1}$ for 7 days. After cooling for 5 days, radiochemical separation of Hg and its analysis were done as outlined below.

Mercury was volatilized from meteorite and rock samples under vacuum (0.01–0.06 torr) at various temperature steps ranging from 100°C up to 500°C and was trapped in a bulb cooled at liquid nitrogen temperature. Mercury was then taken up with 0.5 ml of sodium diethyldithiocarbamate solution prepared in chloroform. The extract and chloroform used for washing (2 times 0.5 ml) were combined and measured for radioactivity. Blank

heating was often performed between two samples to ensure the absence of memory effect. Radiochemical purification of monitor samples was done after that of all rock samples. A carrier-free radiochemical procedure was employed for purification of Hg monitors. In this procedure the tube was opened and immersed in dilute HNO_3 . Mercury was scavenged with AgCl by adding in a sequence few drops of AgNO_3 and diluted HCl solutions. At pH ranging from 9 to 10, Hg was extracted into an organic phase (sodium diethyldithiocarbamate-chloroform solution). An aqueous phase was washed with chloroform and the wash was combined with the first extract.

Activity measurement and calculation of isotopic ratios

The Hg samples were counted in solution (volume: $1.50 \pm 0.01 \text{ ml}$) with a fixed geometry. A high purity germanium co-axial detector (hereafter, HP-Ge; EG & G, ORTEC) (relative efficiency = 16%; energy resolution at 1332 keV = 1.8 keV) and a high purity germanium planar detector (hereafter, LEPS; EG & G, ORTEC) (resolution at 122 keV = 0.50 keV) were used for the measurement of high energy γ -rays and low energy γ - and X-rays, respectively. The reduction of X-ray and γ -ray spectra was done by using the software developed by the Seiko EG & G Co. Ltd., the manufacturer of the computer-assisted multichannel analyzer.

Only two stable isotopes, ^{196}Hg and ^{202}Hg , can be measured by neutron activation technique. By neutron capture reaction, these nuclides are converted to ^{197}Hg (half life, $t_{1/2} = 64.1 \text{ h}$) and ^{203}Hg ($t_{1/2} = 46.6 \text{ d}$), respectively. The relevant nuclear data are summarized in Table 1. Both ^{197}Hg and $^{197\text{m}}\text{Hg}$ are produced by neutron capture of ^{196}Hg . The latter decays with a half life of 23.8 h either to ^{197}Hg by isomeric transition (IT) (93.5%) or to ^{197}Au by electron capture (EC) (6.5%). In activity measurement of the Hg fractions, prominent photopeaks appeared at 77.4 keV and 279.2 keV, which are γ -rays emitted with EC decay of ^{197}Hg to ^{197}Au and with β -decay of ^{203}Hg to ^{203}Tl , respectively. EC decay always produces X-rays from

Table 1. Nuclear data related in this study

Target nuclide	Isotopic abundance (%)	Produced nuclide	Thermal neutron cross section (barn)	Half life	Decay-mode	γ -ray ^(a) energy (keV)	X-ray ^(b) energy (keV)
¹⁹⁶ Hg	0.15	^{197m} Hg	120	23.8 h	IT (93.5%) EC (6.5%)	133.9 279.0	(Au X-ray) 68.8 (K _{α1}), 67.0 (K _{α2}), 78.0 (K _{β1}), 80.2 (K _{β2})
		¹⁹⁷ Hg	3100	64.1 h	EC	77.4	
²⁰³ Hg	29.65	²⁰³ Hg	5	46.6 d	β ⁻	279.2	(Tl X-ray) 72.9 (K _{α1}), 70.8 (K _{α2}), 82.6 (K _{β1}), 84.9 (K _{β2})
⁷⁴ Se	0.9	⁷⁵ Se	52	119.78 d	EC	136.0, 264.66, 279.54	

^(a)Main γ -ray emitted with the preceding decay mode.^(b)X-ray emitted with the capture of neutron by the target nuclide.

a decay (daughter) nuclide. In the case of ¹⁹⁷Hg, K_{β1} X-ray of Au is emitted at 78.0 keV, which is very close to the 77.4 keV γ -ray of ¹⁹⁷Hg, yielding a combined peak. Intense X-ray peaks of Tl also were observed at 72.9 keV (K_{α1}) and 82.6 keV (K_{β1}).

The intensity of the combined peak consisting of 77.4 keV γ -ray and 78.0 keV X-ray was used for calculating the abundance of the ¹⁹⁷Hg isotope and that of the 279.2 keV γ -ray peak for the ²⁰³Hg isotope with a band width of 2.5 keV for each peak. The ¹⁹⁷Hg/²⁰³Hg activity ratio is expressed as the intensity ratio of the 77.4–78.0 keV peak to the 279.2 keV peak and was calculated from their decay-corrected total counts. The activity measurements were repeated several times over a week to a month. For the calculation of Hg abundances, the intensity of the 279.2 keV γ -ray emitted by ²⁰³Hg was used assuming its normal isotopic abundance.

RESULTS

Run A

The analytical data are given in Table 2 arranged in order of heating temperatures from 100 to 500°C in 100°C steps. Individual samples were measured at different decay intervals and replicate values of activity ratios normalized to a fixed time (the 5th day from the end of irradiation) were obtained. We detected the presence of ⁷⁵Se (*t*_{1/2} = 119.8 d) in most of the samples through its photopeak at 264.7 keV. Another γ -ray peak of ⁷⁵Se at 279.5 keV is unresolvable from the ²⁰³Hg peak at 279.2 keV and has to be properly corrected for in estimating the ²⁰³Hg activity. As no Se monitor samples were irradiated with the rock samples, we used the recommended branching ratio (0.426) of 279.2 to 264.7 γ -rays of ⁷⁵Se (Lederer and Shirley, 1978) to calculate the contribution of ⁷⁵Se to the peak at 279 keV. This contribution is probably slightly overestimated because the counting efficiency decreases with increasing energy at the energy range of 200–300 keV. However, the two energies are so close that the difference is small (~5%).

Table 2. Analytical results of Hg (run A)

Sample [weight, mg]	Release temp. (°C)	²⁰³ Hg ^(a) (cps)	Hg ^(b) (ng/g)	(R _S) ₀ ^(c) (weighted means)					(R _S) ₀ /(R _M) ₀ ^(d)	
<i>Meteorites</i>										
Allende (CV3) [89.5]	100	1.30	13.7	2.02	1.94	1.97	1.87	(1.97)		1.02
	200	3.17	33.5	2.01	1.93	1.91	1.91	1.89	(1.94)	1.00
	300	1.38	14.6	1.94	1.92	1.88	1.85	1.92	(1.91)	0.99
	400	0.80	8.5	1.92	1.86	2.01	(1.90)			0.98
	500	0.12	1.3	1.97						1.02
		(total)	71.6							
Y 82050 (CO3) [94.1]	100	0.42	4.2	1.96	1.95	1.92	1.81	(1.93)		1.00
	200	30.3	305	2.01	1.95	1.96	1.99	1.94	(1.98)	1.02
	300	34.4	346	1.97	1.92	1.94	1.92	1.95	(1.95)	1.01
	400	14.8	149	1.97	1.93	1.93	1.92	(1.94)		1.00
	500	1.07	10.8	1.86	1.85	(1.86)				0.96
		(total)	805.2							
<i>Standard rocks</i>										
JB-1 (basalt) [157.2]	100	2.79	16.8	1.95						1.01
	200	12.00	72.2	1.97	1.98	1.96	1.88	(1.95)		1.01
	300	2.85	17.2	1.92	1.83	1.87	(1.88)			0.97
	400	1.37	8.2	1.83	1.86	(1.84)				0.95
	500	0.47	2.8	1.91						0.99
		(total)	117.2							
JG-1 (grano-diorite) [100.0]	100	1.22	11.5	1.93						0.99
	200	4.66	44.1	1.96	1.95	1.85	1.87	(1.92)		0.99
	300	2.42	4.0	1.81						0.93
	400	0.17	1.6	1.79						0.92
	500	0.07	0.7	1.88						0.97
		(total)	61.9							
<i>Monitors (Hg)</i>										
Mon-1 [0.0615 μg]		65.06		1.93	1.93	1.98	1.95	1.93	1.94	1.00
		(1058 cps/μg)		1.91	1.85	(1.93)				
Mon-2 [0.0506 μg]		45.35		1.94	1.95	1.94	1.91	1.88	(1.93)	1.00
		(896 cps/μg)								

^(a)Activity at the time when chemical analysis started (~5 days after the end of irradiation).^(b)Calculated on the basis of ^{203}Hg activity (cps/µg Hg) for Mon-1.^(c)Decay-corrected activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ for samples. Error associated with values are $\leq 5\%$ (1 σ).^(d) $(R_M)_0$ means the decay-corrected activity ratio (mean value) of $^{197}\text{Hg}/^{203}\text{Hg}$ for monitors.

Run B

The results for run B are presented in Table 3. JB-1 was heated only at 500°C for 2 h, following the Allende sample. Other samples were subjected to step by step heating. The metal fraction of Dhajala gave the highest activity of ^{75}Se , especially in the 500°C fraction compared to other samples. Most of the Hg fractions yielded activity ratios of $^{197}\text{Hg}/^{203}\text{Hg}$ identical to the monitor value within 5% except three samples of Allende

at 300, 400 and 500°C. These Allende samples showed progressive depletion in activity ratios of $^{197}\text{Hg}/^{203}\text{Hg}$ with higher temperature.

Some of the experimental steps related to volatilization of Hg were tested in this run. After the heating of JB-1, a blank heating was carried out at 500°C for 2 h. The blank sample gave 0.003 count per second (cps) at 279 keV peak of ^{203}Hg , which is negligibly small to the extent that memory effects can be ruled out. Washing of ten

Table 3. Analytical results of Hg (run B)

Sample [weight, mg]	Release temp. (°C)	$^{203}\text{Hg}^{(a)}$ (cps)	$\text{Hg}^{(b)}$ (ng/g)	$(R_S)_0^{(c)}$ (weighted means)					$(R_S)_0/(R_M)_0^{(d)}$	
<i>Meteorites</i>										
Allende (CV3) [87.0]	100	2.65	34.1	4.41	4.40	4.37	4.44	4.31	(4.39)	1.04
	200	2.51	32.3	4.12	4.19	4.21	3.93	(4.14)		0.98
	300	0.37	4.8	3.61	3.92	3.67	4.31	(3.81)		0.90
	400	0.21	2.7	3.20	3.53	4.02	4.11	(3.63)		0.86
	500	0.08	1.0	3.05	3.26	3.65	2.58	(3.33)		0.80
	(total)	74.9								
Dhajala (H3) non-magnetic [158.8]	100	62.94	444.2	4.25	4.25	4.23	4.28	(4.25)	1.00	
	200	46.88	330.8	4.17	4.15	4.21	4.31	(4.20)	1.00	
	300	3.67	25.9	4.06	4.06	4.02	3.87	(4.02)	0.95	
	400	2.86	20.2	4.21	4.17	4.19	4.15	(4.18)	1.00	
	500	2.23	15.7	4.15	4.02	4.05	4.21	(4.10)	0.97	
	(total)	805.2								
Dhajala (H3) bulk (powder) [122.5]	100	50.53	460.4	4.24	4.21	4.23	4.35	(4.25)	1.01	
	200	48.37	442.4	4.18	4.16	4.13	4.11	(4.14)	0.98	
	300	4.04	37.0	4.22	4.07	4.14	4.13	(4.12)	0.98	
	400	2.63	24.0	4.05	4.05	4.00	(4.04)	0.96		
	500	2.46	22.5	4.08	4.17	4.08	4.33	(4.15)	0.98	
	(total)	117.2								
Dhajala (H3) magnetic [73.9]	100	1.28	19.4	4.29	4.28	4.17	4.28	(4.26)	1.01	
	200	1.30	19.7	4.16	4.15	4.53	4.61	(4.28)	1.01	
	300	0.52	7.9	3.99	4.31	4.04	3.89	(4.06)	0.96	
	400	0.17	2.6	4.32	4.73	4.17	4.20	(4.35)	1.03	
	500	0.05	0.8	4.09					0.97	
	(total)	50.4								
<i>Standard rocks</i>										
JB-1 (basalt) [74.8]	500	8.54	127.9	4.18	4.26	4.31	4.46	(4.27)	1.01	
<i>Monitors (Hg)</i>										
Mon-1 [0.02007 μg]		11.74 (585.0 cps/μg)		4.18	4.18	4.36	4.27	(4.24)	1.00	
Mon-2 [0.02557 μg]		22.82 (892.5 cps/μg)		4.20	4.08	4.16	4.34	(4.22)	1.00	

^(a)Activity at the time when chemical analysis started (~5 days after the end of irradiation).

^(b)Calculated on the basis of ^{203}Hg activity (cps/ μg Hg) for Mon-2.

^(c)Decay-corrected activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ for samples. Error associated with values are $\leq 5\%$ (1σ).

^(d) $(R_M)_0$ means the decay-corrected activity ratio (mean value) of $^{197}\text{Hg}/^{203}\text{Hg}$ for monitors.

distillate traps gave an activity of ~0.02 cps (0.002 cps per trap), suggesting almost complete transfer of the distillate into the counting vial.

Problem in monitor samples

Although the major concern in this study is the Hg isotopic composition ($^{196}\text{Hg}/^{202}\text{Hg}$), determination of the Hg abundances in bulk meteorites

and separates was also of interest. For this purpose, in each run two monitor samples of Hg were also irradiated along with other samples. As seen in Tables 2 and 3, there is an inconsistency in specific activity (cps $^{203}\text{Hg}/\mu\text{g}$ Hg) between two monitors in each run; in run A the difference is relatively small (~15%), whereas a larger difference (~35%) was found in run B. We suspect that

Hg was partly lost in some of the steps either during the preparation of Hg monitor samples before the irradiation or during opening of the sealed tube after the irradiation. It is probable that Hg is partly volatilized by heat generated during neutron irradiation and gets adsorbed on the inner wall of the quartz tube after irradiation. Some Hg may even exist as vapor which can be lost when the tube is cracked. The radiochemical steps involving dissolution to extraction steps were checked by using radioactivity tracer of Hg and could at most account for 10% loss. The inconsistency in the Hg monitors poses no problem in assessing the isotopic anomaly of Hg ($^{196}\text{Hg}/^{202}\text{Hg}$) but introduces unacceptable uncertainty in determining Hg abundances in samples. Since the quantitative collection of Hg was confirmed for the terrestrial and meteorite samples as discussed later, the specific activities of the geological standard rocks were used for quantitative determination of Hg.

DISCUSSION

Reliability of RNAA for the determination of $^{196}\text{Hg}/^{202}\text{Hg}$

All samples were measured once with a LEPS to see if there was any interfering peak for the ^{197}Hg activity measurement. Furthermore, replicate measurements were performed with a HP-Ge. Typical spectra of LEPS and HP-Ge are shown in Figs. 1(a) and (b). In the LEPS spectrum two Tl X-ray peaks at 70.8 keV ($K_{\alpha 2}$) and 72.9 keV ($K_{\alpha 1}$) emitted with the β^- -decay of ^{203}Hg are well resolved from each other and do not interfere with the ^{197}Hg photopeaks (Au X-rays at 67.0 keV, 68.8 keV and 78.0 keV, and γ -ray peak at 77.4 keV). As mentioned before, even with a LEPS, the photopeaks of 77.4 keV and 78.0 keV are not resolved and, hence, they need to be taken jointly for activity calculation of ^{197}Hg . ^{203}Hg emits a photopeak at 279.2 keV (relative intensity: 81.0%), for which there seem to be three possible interfering nuclides: $^{197\text{m}}\text{Hg}$ (279.0 keV; $t_{1/2} = 23.8$ h), ^{203}Pb (279.2 keV; $t_{1/2} = 2.16$ h) and ^{75}Se (279.5 keV; $t_{1/2} = 119.8$ d). Considering production rate, half life, branching ratio and relative peak inten-

sity, the contribution from $^{197\text{m}}\text{Hg}$ is negligible when a counting is performed after about 4–5 days from the end of irradiation. The contribution of ^{203}Pb must be extremely low because its production is negligibly small by thermal neutrons. Only a very small amount can be produced from ^{204}Pb via ($n, 2n$) reaction (cross section: 2×10^{-3} barn) with fast neutrons. In contrast to these two nuclides, presence of ^{75}Se in the released fractions was confirmed by its γ -ray peak at 264.7 keV and also by the half life. Besides Se, other volatile elements such as halogens, Zn, Cd, Te were also observed in some cases. Fortunately, they do not interfere with Hg in the γ -ray regions of interest.

The contribution of ^{75}Se was observed to increase with increasing temperature. In run A, the contribution of ^{75}Se to ^{203}Hg is increased from 0.2–1.5% for the 100°C–400°C fractions to 11% for the 500°C fraction. This contribution is up to 53% in the 500°C fraction in run B. The relative contributions of Se to Hg isotopic ratios in two runs A and B for the 500°C fraction from Allende are quite different. This could be due to different release pattern of Se and Hg in the two cases.

For most samples, the decay of the two Hg isotopes, i.e., ^{197}Hg (via two joint photopeaks: 77.4 keV γ -ray + 78.0 keV X-ray and 67.0 keV X-ray + 68.8 keV X-ray) and ^{203}Hg (via 279.2 keV γ -ray), was followed at least for one half-life. The purity of the isotopes was verified by fitting an exponential curve for each decay. The fitted decay curves for Allende (run A) are shown in Figs. 2(a) and (b) for ^{197}Hg and ^{203}Hg , respectively. All the curves of different temperature fractions are parallel to each other and to those of monitor sample and the calculated decay curve, suggesting that our radiochemical procedure and data processing are rigorous enough to discuss the isotopic variation of Hg in meteorite and terrestrial samples. Based on Figs. 2(a) and (b), the activity ratio $^{197}\text{Hg}/^{203}\text{Hg}$ (R) as function of time over the counting period is shown in Fig. 3, which shows that change of R with time for the monitor matches with those of the temperature fractions of Allende (run A). Minor deviations are seen towards the end when counting statistics are poor.

Fig. 1. (a) X/γ-ray spectrum obtained for the Hg monitor sample with the low energy photon spectrometer. One channel corresponds to 0.1 keV. A complex peak appearing at 77.4–78.0 keV, which is composed of the 77.4 keV γ-ray and the 78.0 $K_{\beta 1}$ Au X-ray emitted with EC-decay of ^{197}Hg , is taken for activity calculation of ^{197}Hg . Thallium X-rays emitted with β^- -decay of ^{203}Hg also are seen in this spectrum but are well separated from the complex peak denoted for ^{197}Hg abundance. (b) Gamma-ray spectrum obtained by using high purity Ge detector for Allende. One channel corresponds to 0.5 keV. A prominent peak of ^{203}Hg appears at 279.2 keV. A small peak of ^{75}Se is observed at 264.7 keV, showing an apparent contribution of the ^{75}Se γ-ray activity (279.5 keV) to the 279.2 keV ^{203}Hg γ-ray peak. Some halogen nuclide (^{82}Br and ^{131}I) were detected as impurities. Values in parentheses are X/γ-ray energy in keV. The low energy range (<100 keV) is shown in (a) with a high energy resolution.

Fig. 2. Radioactivity decay plots of ^{197}Hg (a) and ^{203}Hg (b) for Allende temperature fractions from 100°C to 400°C in run A. For comparison, plots for the Hg monitor sample are shown. All lines are parallel to each other, showing that Hg γ -ray (+X-ray) peak intensities used in this study (after the correction of interfering activity from ^{75}Se if any) are suitable for the determination of the activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ (that is, isotopic ratio of $^{196}\text{Hg}/^{202}\text{Hg}$).

Variation of $^{196}\text{Hg}/^{202}\text{Hg}$ ratio in meteorite and terrestrial rock samples

Terrestrial rock samples After appropriate corrections, isotopic ratios of $^{196}\text{Hg}/^{202}\text{Hg}$ for the meteorite and the terrestrial rock samples normalized to those of the monitors (R_S/R_M) are listed in the last columns of Tables 2 and 3 for runs A and B, respectively. These values are also plotted in Figs. 4(a) and (b) for individual temperature steps. The normalized values of terrestrial rock samples range from 0.92 to 1.01. There are several sources of uncertainties associated with these values. Uncertainties due to counting statistics are generally smaller than 3% (1σ). Thus, uncertainties for the decay-corrected activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ (R_S) and its sample to monitor ratio (R_S/R_M) are smaller than 5% (1σ) and 7% (1σ), respectively. The correction for the contribution of ^{75}Se to ^{203}Hg yields an error, but it is less than 1.5% (1σ) for all frac-

tions of up to 400°C. An error stemming from the difference in self-shielding during neutron irradiation must be equally small. These errors may be merged with the uncertainty due to counting statistics. As exact values of these errors cannot be strictly evaluated, we have estimated an overall uncertainty to be 10% (1σ) at maximum based on the analytical results of geological standard rocks, where Hg isotopic composition is assumed to be normal.

Isotopic anomalies of p-process nuclides detected by mass spectrometry are mostly small, being in the order of 0.1% or smaller. Exceptional is the case for Xe, where ^{124}Xe anomaly far exceeds 10% (e.g., Manuel *et al.*, 1972; Lewis *et al.*, 1975). Similarly large anomaly has been reported for ^{196}Hg in several meteorites and lunar samples by RNAA (e.g., Jovanovic and Reed, 1976; Thakur and Goel, 1989). Our technique is

Fig. 3. Change of activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ for Allende temperature fractions and monitor sample (from run A). This figure is entirely based on Fig. 2. Essentially, all lines are overlapped, showing that there is no deviation of $^{197}\text{Hg}/^{203}\text{Hg}$ activity ratio (decay-corrected) (or, $^{196}\text{Hg}/^{202}\text{Hg}$ isotopic ratio). Theoretical (calculated) change is also shown for comparison. Values in parentheses are decay constants (in h^{-1}). All lines shown have the same decay constant (i.e., gradient in the figure), confirming a validity for data reduction of R in this study.

fully capable of detecting such a variation in $^{196}\text{Hg}/^{202}\text{Hg}$ ratio in meteorite and geological samples, as discussed above.

Meteorite samples Meteorite samples also yielded normal $^{196}\text{Hg}/^{202}\text{Hg}$ ratios ranging from 0.95 to 1.03 times the normal ratio in various temperature fractions of both bulk and magnetic separate samples except for three Allende fractions released at 300, 400 and 500°C in run B, which show somewhat deviant ratios from 0.90 down to 0.80. These values are derived from small amounts of released Hg with relatively large correction in ^{203}Hg (due to relatively large ^{75}Se).

Isotopic ratio $^{196}\text{Hg}/^{202}\text{Hg}$ of various fractions obtained at sequentially increasing temperatures corresponding to each sample is plotted against

Fig. 4. $^{196}\text{Hg}/^{202}\text{Hg}$ ratios of the meteorite and the terrestrial rock samples normalized to those of the monitors ($R_{\text{sample}}/R_{\text{monitor}}$) for runs A (a) and B (b). Contribution of ^{75}Se to ^{203}Hg is corrected if any. The normalized values range from 0.93 to 1.04 with the exception of three Allende fractions in run B, which deviate considerably from unity (1). Nevertheless we hesitate to insist on the presence of isotopically anomalous Hg in the Allende sample because it was not produced in another run (run B). (See text for detailed discussion about these deviations.) Except for these three temperature fractions of Allende, we found no evidence of an isotopic anomaly in Hg for the meteorite samples and the standard rock samples studied in this work.

fraction of Hg left in Fig. 5 for run A. A small decrease is seen for all samples, which is consistent with isotopic fractionation due to diffusion during high temperature volatilization. The diffusional fractionation factor between isotopes ^{203}Hg and ^{197}Hg is expected to be about 1.015 (based on the simple law of square root of mass

Fig. 5. Change of activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$ against Hg fraction left in the residual sample for run A. A small decrease of the ratio is observed for all samples. This change is consistent with the isotopic fractionation due to diffusion of Hg during high temperature heating. An error bar corresponds to a standard deviation (1σ) for those fractions whose $^{197}\text{Hg}/^{203}\text{Hg}$ ratios were measured more than three times (see Table 2). For the rest, 10% is denoted as a maximum error (see text for this value).

ratio) which agrees with the general nature of the decrease in $^{197}\text{Hg}/^{203}\text{Hg}$ ratio shown in Fig. 5. This agreement also supports the reliability of the procedure of correction and calculation of isotopic ratio. It may be pointed out that the Hg fraction released at low temperature would have a higher $^{197}\text{Hg}/^{203}\text{Hg}$ ratio than that for bulk sample if the diffusional isotopic fractionation occurs. This is exactly the trend which we observed for the Hg fractions recovered at 100°C .

A similar change was observed for the samples in run B, but the degree of change varies from sample to sample; essentially no change was seen in the Dhajala magnetic fraction, whereas a large decrease in $^{197}\text{Hg}/^{203}\text{Hg}$ ratio occurred with increasing temperature for Allende. A 20% depletion (1σ) of ^{197}Hg relative to ^{203}Hg observed in the 500°C fraction is too large to be explained in terms of isotopic fractionation due to diffusion, suggesting the existence of isotopically anomalous Hg, which is depleted in the p-process nuclide ^{196}Hg . Since such an anomalous ratio was not reproduced in another run (run A), we cannot insist for the presence of isotopically anomalous Hg in the Allende reference sample used in this

study. A 20% depletion may be explained in terms of statistical deviation.

As discussed in the previous section, ^{75}Se is the only important interfering nuclide in the photopeak of ^{203}Hg and its presence lowers the apparent value of the $^{197}\text{Hg}/^{203}\text{Hg}$ ratio. Therefore, the deviation of this ratio from its real value is proportional to the relative activities of ^{75}Se to ^{203}Hg . The ^{75}Se activity is found to increase with increasing heating temperature, while the low temperature ($100\text{--}400^\circ\text{C}$) fractions do not carry large amounts of Se. Jovanovic and Reed (1987) reported that Se does not become volatile at 130°C and, therefore, the Hg isotope anomaly found by them in this temperature fraction must be real. However, a quantitative estimation of the Se correction is necessary to establish their claim. It should be pointed out that the vacuum condition in the present set up was strong and this may have enhanced the volatilization efficiency of Se even at low temperature.

This study raises serious question about the reliability of reported results where the ^{75}Se contribution had not been properly corrected for. If such a contribution had been overlooked, any apparent negative anomaly (relative depletion of ^{196}Hg isotope) needs further verification. On the other hand, any reported positive anomaly (enrichment of ^{196}Hg) may increase in magnitude due to this correction. For example, a 60% enrichment of ^{196}Hg has been reported in the Hg fraction from carbon-rich residues of Allende, heated up to 1200°C (Reed and Jovanovic, 1990). If ^{75}Se is present in those fractions, the magnitude would go up after correction. We are not in a position to make specific comments about the reliability of these observations except pointing out that there is a need to redetermine $^{196}\text{Hg}/^{202}\text{Hg}$ ratios in the meteorites in which the anomalous isotopic ratio due to the depletion of ^{196}Hg relative to ^{202}Hg has been reported.

As discussed in the following section, the Hg released from Y 82050 must be terrestrial in origin for the most part; its $^{196}\text{Hg}/^{202}\text{Hg}$ ratios for temperature fractions are all consistent with those for terrestrial standard rock samples.

Mercury abundances in some meteorite samples

As already pointed out, determination of Hg abundances from these two runs could not be done on an absolute basis due to unacceptable differences in the data of two monitor samples in the same run. However, a closer scrutiny showed that the data can still be used for relative abundances. From Tables 2 and 3, it is observed that most of the Hg in meteorite and geological standard rock samples is released before 500°C. Table 4 shows the Hg content released with heating up to 500°C for the bulk meteorites and the separated fractions analyzed in this work. In calculating these values, the monitor samples giving higher specific activities of ^{203}Hg (as expressed in cps $^{203}\text{Hg}/\mu\text{g}$ Hg and obtained from data of Mon-1 for run A and Mon-2 for run B) were adopted with no clear justification. Although Hg contents in JB-1 and Allende are consistent between the two runs, this can be regarded as fortuitous considering that two Hg monitor samples in each run gave different specific activities. The Hg amounts obtained for standard rocks, JB-1 (117 ppb) and JG-1 (62 ppb) from run A are about four times higher than re-

ported values (28 ppb and 16 ppb, respectively; Ando *et al.*, 1989). Thus, in spite of a large difference in the absolute contents, the abundance ratio of Hg in these two standard rocks is almost the same between the present data and the literature values. The difference then can be explained in terms of either Hg loss from monitor samples during their preparation and/or processing, which would yield larger values by a constant factor for the two samples, or errors in the literature values. The latter possibility seems to be less likely because this would happen only when two literature values are coincidentally higher than the real values by the same factor. Both Allende and JB-1 samples were irradiated at both runs A and B. Considering that the ratio of decay-adjusted cps of ^{203}Hg per mg for JB-1 to that for Allende is almost identical within 4% between two runs and that the irradiation conditions for two runs were essentially identical, it is concluded that Hg was recovered quantitatively from JB-1 and Allende and that the apparent higher abundances than the literature values were caused by loss in the Hg monitors. If the literature values for two standard

Table 4. Mercury contents in meteorites and standard rocks analyzed in this work

Sample	Hg content (ppb)		Literature
	This work		
	(uncorrected)	(corrected) ^(a)	
<i>Meteorites</i>			
Allende (CV3)	71.6 (run A)	17.8	35 ^(b)
	74.9 (run B)	16.4	
Y 82050 (CO3)	810 (run A)	201	—
Dhajala (H3)			
bulk	986 (run B)	216	—
non-magnetic	837 (run B)	183	
magnetic	50.4 (run B)	11.0	
<i>Standard rocks</i>			
JB-1 (basalt)	117.2 (run A)	=28	28 ^(c)
	128.0 (run B)	=28	
JG-1 (granodiorite)	62.0 (run A)	=16	16 ^(c)

^(a)Literature values of Hg for JB-1 and JG-1 were used (see text).

^(b)Becker *et al.* (1987).

^(c)Ando *et al.* (1989).

rocks are used, the Allende Hg values are recalculated to be 17.8 and 16.4 ppb, which is about half the literature value (35 ppb, Becker *et al.*, 1987). Our values for the Allende reference samples are thus reasonably consistent with each other.

Mercury in meteorite samples has been mainly determined by neutron activation method and its abundance has been acknowledged to be highly variable within a given class of meteorite and even within a given meteorite. Such a large variation was noted earlier by Reed (1971) and later emphasized by Mason (1979). Mason (1979) even gave up the calculation of mean abundance of Hg for different classes of meteorites.

In his compilation, Mason (1979) introduced the papers by Tanner (1968) and Ozerova *et al.* (1973), which suggest that Hg is chalcophile in meteorites. Our results are somewhat contrary to this suggestion. In the Dhajala mineral separates, the largest ^{75}Se activity was found for the metallic fraction (114 cps/g sample), implying that the metallic fraction contains a large amount of Se. As Se is a typical chalcophile element associated with troilite in meteorites (Kiesl and Hecht, 1969; Mason and Graham, 1970), a high activity of ^{75}Se in the magnetic fraction implies the presence of troilite in the Dhajala magnetic separate. This is understandable because Dhajala is type 3 ordinary chondrite, where metal and troilite often coexist (Kong and Ebihara, 1996). Under the conditions adopted in this study, it is likely that some troilite still remains in association with metal. In contrast with Se, Hg was observed to be enriched in the non-magnetic fraction of Dhajala relative to the magnetic fraction with a factor as high as 18 (Table 4). This implies that Hg is not enriched in the troilite phase like Se and is not so chalcophile as Se. We suspect that the considerable enrichment of Hg in troilite observed by Tanner (1968) was due to the contribution of ^{75}Se to the 279 keV peak. We further suspect that the large variation of Hg content in meteorite samples reported so far could be partly due to erroneous determination of Hg possibly by ignoring the presence of ^{75}Se in the released Hg fraction. The release pattern on heating is considerably different between Hg and Se;

Hg is more easily volatilized than Se (Reed and Jovanovic, 1967; Biswas *et al.*, 1980). This would cause a variation of Hg content derived from ^{75}Se -uncorrected ^{203}Hg activities.

The Dhajala chondrite was observed to contain a considerably high Hg content (as high as 216 ppb). Dhajala is classified to be type 3, unequilibrated ordinary chondrite (UOC). It is well known that some UOCs contain anomalously high contents of volatile elements such as In and Bi (Higuchi *et al.*, 1977). Probably, Hg is present in Dhajala, being grouped with these volatile elements. Figure 6(a) shows the release pattern of Hg at various temperature for bulk and mineral separates of Dhajala and Allende bulk sample, which were performed at run B. Both bulk and non-magnetic samples of Dhajala have an identical release pattern. The Allende bulk sample also shows a similar pattern, with an order of magnitude lower abundance. For these samples, Hg was mostly released at 100°C and 200°C. The magnetic fractions of Dhajala was separated by a hand magnet and finally purified by leaching in hot HF solution (~90°C) for few minutes. During HF leaching, Hg could be lost to some extent. Considering that the release patterns for all samples including the Dhajala magnetic fraction are essentially identical at low temperature heating, it is likely that Hg was mostly kept retained in the magnetic fraction. An overall similarity of release patterns for these meteorites suggests that Hg is present in a similar site in Dhajala and Allende. Mercury may be a constituent element of late condensate, which is simply mixed with the other mineral phases in the matrix. Alternatively, Hg was trapped on the surface of minerals and present in the grain boundary.

The Hg abundance in Antarctic CO meteorite Y 82050 is about an order of magnitude higher than that in the Allende meteorite (Table 2). If we uses the literature values of Hg for two standard rocks, JB-1 and JG-1, the abundance of Hg in Y 82050 is calculated to be 209 ppb. It is known that in CO chondrites, the volatile elements are considerably depleted and that the depletion increases sharply with increasing the degree of elemental

Fig. 6. Release patterns of Hg at various temperatures for runs B (a) and A (b). Both Dhajala (bulk, magnetic and non-magnetic samples) and Allende show a similar pattern, suggesting that Hg is present in a similar site in these samples (a). For run A, two standard rocks, JB-1 and JG-1, and Allende show a similar release pattern while the Hg release pattern of Y 82050 is considerably different, being characterized with a peak at 300°C step. The Hg released in the range from 200°C to 400°C is suspected to be due to contamination on Antarctica.

volatility (Kallemeyn and Wasson, 1981), being in contrast to CV chondrites which do not show such a pattern of decrease. Accordingly, Y 82050 classified as CO is expected to be depleted in Hg in comparison with Allende CV chondrite, which is contrary to what we observed in this work.

Figure 6(b) shows the release patterns of Hg at various temperature steps for samples conducted in run A. In this run, both JB-1 and JG-1 show a parallel pattern, having a peak at 200°C with a sharp decrease towards 500°C. Allende also shows a similar pattern. In contrast the Hg release pattern of Y 82050 is considerably different from those for Allende as well as two terrestrial rock samples; the Hg in Y 82050 is mostly released in the range from 200 to 400°C. We suspect that the most Hg released in this temperature range is due to contamination on Antarctica. The Antarctic meteorites have been reported to be enriched in halogens, especially bromine and iodine (Heumann *et al.*, 1987). Such an enrichment must have been caused by exposure and weathering processes in Antarctica (Langenauer and Kraehenbuehl, 1993; Shinonaga *et al.*, 1994). The observed enrichment of Hg in Y 82050 seems to be consistent with that for halogens and implies that Hg was transferred in the volatile form and

loaded onto the surface of meteorites in Antarctica. If this is the case, the Hg released from Y 82050 is mostly terrestrial in origin and its isotopic composition is expected to be normal, which we have observed in this study.

CONCLUSIONS

On the basis of isotopic analysis of Hg in meteorites and geological standard rocks by RNAA, the following conclusions are derived:

(1) RNAA can be successfully applied for determining the Hg isotopic ratio ($^{196}\text{Hg}/^{202}\text{Hg}$) by selecting appropriate photopeaks emitted by radioisotopes of interest and correcting the contribution of interfering photopeaks.

(2) To obtain an accurate activity ratio of $^{197}\text{Hg}/^{203}\text{Hg}$, the contribution of ^{75}Se to the apparent ^{203}Hg photopeak needs to be corrected. The ratios obtained in this way for most samples from Allende, Y 82050 and Dhajala meteorites were identical to those of the monitor as well as standard rock samples. An apparently low ratio of $^{196}\text{Hg}/^{202}\text{Hg}$ was released in the high temperature (500°C) fraction of the Allende meteorite (the powdered sample prepared by the Smithsonian Institution). As such a low value was obtained in a

small Hg fraction with relatively large correction due to ^{75}Se interference and was not reproduced in another run, we may be conservative for the presence of isotopic anomaly of Hg in the Allende meteorite.

(3) The contribution of ^{75}Se to the ^{203}Hg peak could lead to erroneously high apparent concentrations of Hg, if Hg is determined by use of ^{203}Hg without any consideration of the interference due to ^{75}Se . We do not support the earlier suggestion that Hg is chalcophile in meteorites. It is suspected that previous inferences for the chalcophile nature of Hg and the anomalously variable content of Hg even in the same meteorite are partly due to erroneous determination of Hg.

(4) An Antarctic meteorite, Y 82050, has an anomalously high Hg content, being at least an order of magnitude higher than the expected value. It is probable that the Antarctic meteorites are contaminated with Hg like halogens.

Acknowledgments—We are grateful to the meteorite group of NIPR and A. N. Garg for samples of Y 82050 and Dhajala meteorites, respectively. Helps from H. Hidaka and K. Shinotsuka are appreciated. We are indebted to the reactor committee of the University of Tokyo for the use of the reactor facility at JAERI. Constructive reviews by D. Lindstrom and P. N. Shukla are greatly appreciated. One of the authors (P.K.) deeply appreciate Monbusho (Ministry of Education, Science and Culture) and JSPS foundations for his stay in Japan. This work was completed when one of the authors (SKB) stayed at the Tokyo Metropolitan University under the international cooperative research program supported by the Tokyo Metropolitan Government. This work was partly supported by a Grant-in-Aid by the Ministry of Education, Science and Culture of Japan (No. 08454167 to M.E.).

REFERENCES

- Ando, A., Kamioka, H., Terashima, S. and Itoh, S. (1989) 1988 values for GSJ rock reference samples, "Igneous rock series". *Geochem. J.* **23**, 143–148.
- Becker, R., Koller, P., Morschl, P., Kiesel, P. and Hermann, F. (1987) Determination of trace elements by Neutron Activation Analysis in the Allende meteorite reference sample. *Smithsonian Contrib. Earth Sci.* No. 27, 16–17.
- Biswas, S., Walsh, T., Bart, G. and Lipschutz, M. E. (1980) Thermal metamorphism of primitive meteorites—XI. The enstatite meteorites: origin and evolution of a parent body. *Geochim. Cosmochim. Acta* **44**, 2097–2110.
- Burbidge, E. M., Burbidge, G. R., Fowler, W. A. and Hoyle, F. (1957) Synthesis of the element in stars. *Rev. Modern Phys.* **29**, 547–649.
- Goel, P. S. and Thakur, A. N. (1987) Isotopically anomalous Hg in meteorites. *Meteoritics* **22**, 389–390.
- Goel, P. S. and Thakur, A. N. (1989) Variable $^{196}\text{Hg}/^{202}\text{Hg}$ ratio in meteorites. *Meteoritics* **24**, 270.
- Heumann, K. G., Neubauer, J. and Weiss, H. (1987) Geochemical investigations to explain iodine-overabundances in Antarctic meteorites. *Geochim. Cosmochim. Acta* **51**, 2541–2547.
- Higuchi, H., Ganapathy, R., Morgan, J. W. and Anders, E. (1977) "Mysterite": a late condensate from the solar nebula. *Geochim. Cosmochim. Acta* **41**, 843–852.
- Jovanovic, S. and Reed, G. W. (1976) ^{196}Hg and ^{202}Hg isotopic ratios in chondrites: revisited. *Earth. Planet. Sci. Lett.* **31**, 95–100.
- Jovanovic, S. and Reed, G. W. (1987) Isotopically anomalous ^{196}Hg and ^{202}Hg in Antarctic achondrites. *Geophys. Res. Lett.* **14**, 1127–1130.
- Jovanovic, S. and Reed, G. W. (1990) Hg isotopes in the moon and in achondrites. *Chem. Geol. (Isot. Geosci. Sect.)* **80**, 181–191.
- Kallemeyn, G. W. and Wasson, J. T. (1981) The compositional classification of chondrites—I. The carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **45**, 1217–1230.
- Kiesel, W. and Hecht, F. (1969) Meteorites and the high-temperature origin of terrestrial planets. *Meteorite Research* (Millman, P. M., ed.), 67–74, D. Reidel Publish. Co., Dordrecht, Holland.
- Kong, P. and Ebihara, M. (1996) Metal phases of L chondrites: Their formation and evolution in the nebula and in the parent body. *Geochim. Cosmochim. Acta* **60**, 2667–2680.
- Kumar, P. and Goel, P. S. (1992a) Further measurements on isotopic anomalies of $^{196}\text{Hg}/^{202}\text{Hg}$ ratio in some of acid insoluble residues of Sikhote Alin and other iron meteorites. *Geochem. J.* **26**, 51–61.
- Kumar, P. and Goel, P. S. (1992b) Variable $^{196}\text{Hg}/^{202}\text{Hg}$ ratio in stone meteorites and in some of their carbon-rich residues. *Chem. Geol. (Isot. Geosci. Sect.)* **102**, 171–183.
- Langenauer, M. and Kraehenbuehl, U. (1993) Depth-profiles and surface enrichment of the halogens in four Antarctic H5 chondrites and in two non-Antarctic chondrites. *Meteoritics* **28**, 98–104.
- Lederer, C. M. and Shirley, V. S. (eds.) (1978) *Table of*

- Isotopes*. 7th ed., John-Wiley & Sons, New York.
- Lewis, R. S., Srinivasan, B. and Anders, E. (1975) Host phase of a strange xenon component in Allende. *Science* **190**, 1251–1262.
- Manuel, O. K., Hennecke, E. W. and Sabu, D. D. (1972) Xenon in carbonaceous chondrites. *Nature* **240**, 99–101.
- Mason, B. (1979) *Data of Geochemistry*. 6th ed., Chap. B. Cosmochemistry; Part 1. Meteorites, Geol. Surv. Professional Paper 440-B-1, p. B95–B97.
- Mason, M. and Graham, A. L. (1970) Minor and trace elements in meteoritic minerals. *Smithsonian Contrib. Earth Sci.*, No. 3, 17 pp.
- Nier, A. O. and Schlutter, D. J. (1987) Mass spectrometric study of the mercury isotopes in the Allende meteorite. *Proc. 17th Lunar Planet. Sci. Conf. (Part 1)*, *J. Geophys. Res.* **92**(B4), E124–E128.
- Ozerova, N. A., Kvasha, L. G., Bulkin, G. A. and Aidinian, N. K. (1973) Certain peculiarities in the distribution of mercury in meteorites. *Geochim. Cosmochim. Acta* **37**, 569–582.
- Reed, G. W. (1971) Mercury. *Handbook of Elemental Abundances in Meteorites* (Mason, B., ed.), 487–491, Gordon and Breach Science Publishers, New York.
- Reed, G. W. and Jovanovic, S. (1967) Mercury in chondrites. *J. Geophys. Res.* **72**, 2219–2228.
- Reed, G. W. and Jovanovic, S. (1969) ^{196}Hg and ^{202}Hg isotopic ratios in chondrites. *J. Inorg. Nucl. Chem.* **31**, 3783–3788.
- Reed, G. W. and Jovanovic, S. (1990) Isotopic Hg in an Allende carbon-rich residue. *Meteoritics* **25**, 345–346.
- Shinonaga, T., Endo, K., Ebihara, M., Heumann, K. G. and Nakahara, H. (1994) Weathering of Antarctic meteorites investigated from contents of Fe^{3+} , chlorine, and iodine. *Geochim. Cosmochim. Acta* **58**, 3735–3740.
- Tanner, J. T. (1968) Mercury and bismuth abundances in iron meteorites by neutron activation. U.S. Atomic Energy Comm. Rept. NYO-844-75, 37–41.
- Thakur, A. N. and Goel, P. S. (1989) Huge variations in the isotopic ratio $^{196}\text{Hg}/^{202}\text{Hg}$ in some acid-insoluble residues of Sikhote Alin and other iron meteorites. *Earth. Planet. Sci. Lett.* **96**, 235–246.
- Von Helden, J. and Begemann, F. (1976) On anomalous Hg in meteorites. *Meteoritics* **11**, 297.