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Variable $^{190}Os/^{184}Os$ ratio in acid residues of iron meteorites

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Abstract. In residual materials obtained on dissolution of iron meteorites in 2M H_2SO_4, the ratio of $^{190}Os/^{184}Os$ has been measured by radiochemical neutron activation analysis. Most residues have a normal isotopic ratio (to within ± 2%). However, in some residues both positive and negative deviations in the isotopic ratio are seen. The most spectacular deviations are in the insoluble fragments (nuggets) from Sikhote Alin iron meteorite where the $^{190}Os/^{184}Os$ ratio is about 50% of the normal value. The new results confirm our earlier observations that iron meteorites contain pre-solar grains.

Keywords. Iron meteorites; osmium isotopes; isotopic anomalies; pre-solar grains; origin of iron meteorites.

1. Introduction

In two recent papers from this laboratory experimental evidence was presented that iron meteorites contain pre-solar grains which are apparently associated with the residues obtained on dissolving the metal in 1 to 2 M H_2SO_4 (Goel and Murty 1983; Murty *et al* 1983). The acid-insoluble residues are found to have isotopically anomalous osmium and xenon. In the present paper a number of experiments are described giving additional results to establish that the ratio of $^{190}Os/^{184}Os$ in some of the acid-residues of iron meteorites is indeed variable and anomalous. A number of control experiments are to show that our results are not due to experimental artifacts introduced during neutron irradiation or during radiochemical processing and counting of the osmium activities. In view of the startling nature of these results, experimental details on all aspects of the work are presented.

While neutron activation analysis technique has been extensively used for reliable measurements of trace elements in cosmic matter, its application to isotope ratio determination has been rather limited. In meteorites, isotopic ratios have been measured by RNA for Hg (Reed and Jovanovic 1969), Os (Takahashi *et al* 1976; Goel and Murty 1983) and Te (Oliver *et al* 1981). With the availability of high resolution gamma spectrometry systems, the RNA method stands to be developed into a powerful technique for isotopic ratio measurements.

The basis for the determination of isotopic ratio for the Os isotopes can be seen from the relevant nuclear data presented in table 1. In most samples we did not see the gammas from ^{193}Os because of the cooling time of more than one week. The gamma lines of 646·1 keV and 129·4 keV were spectrum-analysed. The samples, particularly those showing anomalous ratios were repeatedly counted over long period of time so that the identification of the nuclide could be confirmed from their characteristic half-lives.

2. Experiments and results

Acid-insoluble residues were obtained by dissolving pieces of iron meteorites slowly in 2M H_2SO_4 (Murty *et al* 1982, 1983; Goel and Murty 1983). The insoluble residues were often found to contain millimeter size brittle pieces and thin metallic flakes. Most of the material was black powder of sub-metallic luster. A low density fraction, (*L*) could be separated in the form of slurry with water. The high density fraction, (*H*) was more lustrous. We further separated the residues into magnetic and non-magnetic fractions with the help of a hand magnet. From Sikhote Alin, several large size (few mm) pieces (inclusions) were obtained which had a specific gravity of about 6·5. They were submetallic in luster, magnetic and brittle. Further characterization could not be done.

Samples from residues, masses varying from about 10 to 200 mg, were sealed in quartz capsules and packed for irradiation along with the monitors. Few milligrams of a standard solution of ammonium hexachlorosmate were weighed on MgO or Al_2O_3 matrices for use as monitors. Nine different irradiations, listed in table 2, were carried out for Os isotopic work. There were some variations in the detection systems for some of the runs. These are described in each case.

2.1 *The NBS-run*

Several acid residues were sealed in quartz tubes. Some of the residues were spiked with osmium salt, freeze-dried and sealed. Irradiation was carried out at the U.S.

Table 1. Nuclear parameters for Os isotopic ratio measurements.

Mass number (*A*)	Abundance (%)	$\sigma_{n,\gamma}$ (barns)	Daughter nuclide.		
			A	$t_{1/2}$	$E\gamma$(keV)
^{184}Os	0·018	3000	^{185}Os	93·6d	646·1
^{190}Os	26·38	12	^{191}Os^{g}	15·4d	129·4
^{192}Os	40·96	1·6	^{193}Os	30·5h	138·9
					460·5

Table 2. Different irradiations for ^{190}Os/^{184}Os measurements.

Experiment number	Date	Reactor	Flux (cm^{-2} sec^{-1})	Duration of irradiation	Target material
NBS	June '82	NBS	$1{\cdot}5 \times 10^{14}$	32 hr	Residues
No 21	Oct '82	CIRUS	1×10^{13}	24 hr	Osmate on different matrices
J-1, J-2	Oct '82	CIRUS	1×10^{13}	1 week	Residues
J-4	Jan '83	CIRUS	1×10^{13}	1 week	Residues and Os salt
Q-1	Feb '83	CIRUS	1×10^{13}	4 hr	Osmium metal and salts
P-1	Feb '83	APSARA	1×10^{12}	4 hr	Osmium metal and salts
1/84	Nov '84	CIRUS	1×10^{13}	1 week	Residues (Canyon Diablo)
1/85	Jan '85	CIRUS	1×10^{13}	1 week	Residues (Bear Creek)
2/85	Feb '85	CIRUS	1×10^{13}	1 week	Residues (Sikhote Alin)

National Bureau of Standards (Washington, D.C.) reactor in position G2 where the cadmium ratio is given as 55 (Becker and La Fleur 1974). The samples were cooled for 24 hr before radiochemical processing.

After adding osmate carrier (1·4 mg Os), a sample was dissolved in conc. HNO_3. Os was distilled with additional 2 ml HNO_3 as OsO_4 by heating the solution. The Sikhote Alin sample did not dissolve completely. The distillate (OsO_4) was collected in 5% solution of thiourea in 6N HCl. The Os-thiourea complex was made alkaline with NaOH. H_2S was passed and OsS_2 was precipitated from the solution after it had been acidified with HCl. It was necessary to purify the OsS_2 thus obtained by one more cycle of distillation and sulphide precipitation steps. The most prominent and troublesome interference was from Br isotopes. Os from several samples was lost during chemical processing. Only two residues (Odessa, m-H, spiked and Sikhote Alin inclusion) could be successfully prepared for counting. Solid OsS_2 was counted in contact geometry on a high purity Gamma-X detector. Resolution at 1332 keV was 1·65 keV (FWHM). The sensitivity was 0·208 keV per channel. The data analysis programme had ^{191}Os in the memory card. For ^{185}Os, the 646 keV peak area, taken from the print-outs was corrected for decay. The counting was done over a period of one week so as to obtain 3 points on the decay curve for each nuclide. The activities decayed with the expected half-lives. The activity ratios of three nuclides ^{185}Os, ^{191}Os and ^{193}Os were measured. The results, presented in figure 1, which show that (i) the $^{191}Os/^{193}Os$ ratios in the residues and standard are identical and (ii) spiked Odessa is about 7% enriched in ^{184}Os similar to the results of Goel and Murty (1983).

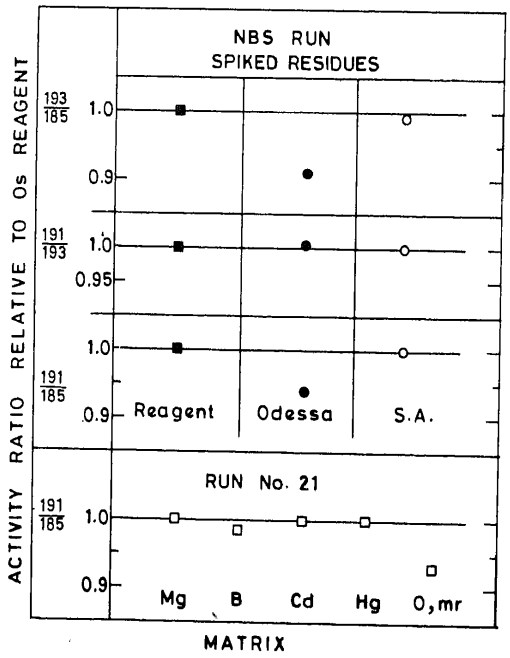

Figure 1. Osmium isotopic ratios from the NBS run and vial no. 21. The $^{190}Os/^{184}Os$ ratio in residues from Odessa is lower than the value for reagent Os in both runs.

Table 3. Contents of irradiation vial no. 21.

Matrix compound	Al_2O_3	H_3BO_3	$CdCl_2$	HgO	Odessa, m-H
Weight (mg)	5·0	11·0	14·0	12·0	160
Os added (μg)	14·5	16·8	13·1	13·1	0·5

2.2 *BARC bombardment: run no. 21*

A solution of ammonium hexachlorosmate was loaded on matrices of different reagents in quartz capsules which were dried and sealed. The Odessa magnetic residue was an aliquot from the high density fraction of the residue used earlier. It was spiked with 0·5 μg Os. The details are given in table 3.

The vial was irradiated in CIRUS reactor at Bombay for 24 hr to a thermal neutron flux of 1×10^{13} n cm^{-2} sec^{-1}. In the CIRUS reactor, in the position in which our samples are normally irradiated, the fast ($E > 1$ MeV) to the thermal neutron ratio is $< 0{\cdot}01$ and the epithermal ($E > 100$ keV) to the thermal ratio is $< 0{\cdot}1$. Radiochemical processing was done after 4 weeks of bombardment. Os carrier was added and OsO_4 from each sample was distilled. The Os-thiourea complex was made to 5 ml volume in each case and counted in liquid form. It was necessary to purify the Odessa sample by adding 5 ml conc. HNO_3 to the thiourea complex and distilling OsO_4 again in fresh thiourea solution. The detector used was a coaxial high purity germanium crystal (ORTEC; Gamma-X). At 1332 keV, the resolution (FWHM) was 2 keV. Since, only a 1024 channel MCA was available, the gain was kept low (1·5 keV/channel). No other gamma lines were seen. Area of the peaks under three channels was taken after proper background substraction. No shoulders were noted in the gamma-ray-peaks of the samples. The results are shown in figure 1. Only one sample, Odessa residue (m-H), is anomalous.

2.3 *Vial nos J-1 and J-2*

Acid-insoluble residues from different iron meteorites were sealed in quartz capsules as listed in table 4. The sample capsules were placed in an aluminium irradiation can to its full capacity, along with the monitors. The two cans were irradiated in the self-service tray of the reactor concurrently. Osmium from the samples was distilled and, when needed, was purified by redistillation as described for vial no. 21. Gamma ray intensities were measured using the Gamma-X (ORTEC) detector and the Canberra MCA (1024 channels).

The decay-corrected $^{191}Os/^{185}Os$ ratios for reagent osmium samples in J-1 and J-2, on November 25, 1982 were $15{\cdot}21 \pm 0{\cdot}15$ and $15{\cdot}53 \pm 0{\cdot}15$. Since the reproducibility of the replicate measurements on aliquots was within statistical errors, the difference of 2% in the two numbers might as well be a reflection of the variation in neutron energy spectrum over a distance of about 10 cm (a likely separation between capsules of the two different vials). Within one vial such an effect should be negligible since the capsules were all stacked within a lateral distance of about 2 cm.

The decay-corrected $^{191}Os/^{185}Os$ activity ratios for vials J-1 and J-2 are given in table 4. The results, given for three different days, show good reproducibility. We

Table 4. Results from vial numbers J-1 and J-2.

Acid residue	Mass (mg)	Os (ppm)	$(^{191}Os/^{185}Os)_s/(^{191}Os/^{185}Os)^*_{std}$ Nov. 9	Nov. 13	Nov. 25
Sikhote Alin, nm	10	9	0·98	1·00	1·00
Sikhote Alin, m	100	0·8	0·98	1·00	0·99
Sikhote Alin, flakes	40	0·03	1·04±0·04	1·00±0·04	0·97±0·05
Sikhote Alin, inclusion	100	0·004	0·9 ±0·1	0·8 ±0·2	0·8 ±0·2
Henbury, nm(1)	4·0	17	1·00	1·00	1·00
Henbury, nm(2)	4·5	500	1·01	1·02	1·00
Henbury, m	119	45	1·00	1·01	1·00
Henbury, flakes	47	9	0·98	0·99	0·98
Toluca, nm	4·5	430	0·99	1·01	1·00
Toluca, m	58	56	0·99	1·00	1·00
Toluca, flakes	31	40	1·01	1·01	1·00
Canyon Diablo, nm(1)	10	160	1·02	1·00	0·99
Canyon Diablo, nm(2)	10	234	1·04	1·02	1·01
Canyon Diablo, nm(3)	6	314	1·01	1·01	1·00
Canyon Diablo, m(H)	175	5	1·03	1·00	0·99
Canyon Diablo, M(L)	42	155	1·00	0·99	0·98
Canyon Diablo, flakes	16	13	1·04	0·98	1·00
Odessa, m(H)	104	1·4	1·01	0·98	0·98
Odessa, m(L)	38	5	1·02	1·00	0·99
Campo del Cielo, nm	17	1000	0·98	0·96	1·00
Campo del Cielo, m(H)	118	520	1·00	1·00	1·00
Campo del Cielo, m(L)	50	120	0·98	0·99	1·00

* Statistical errors are ± 1% unless specified.

find that the Os isotopic ratio in all the samples of J-1 and J-2 is remarkably constant to within 2%. This is clearly seen from the plot of data for November 25 in figure 2. The possibility that the Sikhote Alin inclusion has a 20% lower value of the isotopic ratio, is not ruled out. Unfortunately, due to low counting rates in these samples, the measurement error could not be reduced. The osmium contents of the iron meteorite residues were calculated assuming that the distillation step is quantitative. If the recovery is $< 100\%$, the Os contents may be higher than the values given in table 4.

These results may appear to negate the large variations that we found earlier (Goel and Murty 1983) and also in the subsequent runs that are reported in this work. A significant heterogeneity in the $^{190}Os/^{184}Os$ isotopic ratio must be present in some minor phase which shows up only when the normal osmium is low and the presolar component is not overshadowed by the homogenized component which is present in widely variable concentrations in all fractions of the acid insoluble residue. It is intriguing to note that Os varies from 4×10^{-3} to 1×10^{3} ppm in residues of iron meteorites. The negative results of these vials may be taken to provide further support to the reliability of our measurements.

2.4 *Run no. J-4*

This vial contained acid-insoluble residue (magnetic, heavy) from Odessa iron meteorite and osmate salt on different matrices as listed in table 5. The matrix

elements were chosen keeping in view their high resonance capture cross-sections for thermal neutrons so that the perturbation in the neutron spectrum could be enhanced. The irradiation was carried out using the CIRUS reactor. Os from the samples was distilled and its gamma activities measured as described for samples of vial no. 21. The values of the $^{191}Os/^{185}Os$ ratio are shown in figure 3. Acid residue, Odessa (m, H), is anomalous.

2.5 *Vial no. P-1*

Samples of natural osmium (table 6) in the form of osmate salt and metal powder were packed in a polythene tube and were bombarded in Apsara reactor at Trombay for 4 hr. The neutron flux was about 10^{12} cm^{-2} sec^{-1} with a fast-to-thermal ratio of $< 0{\cdot}20$ and the epithermal-to-thermal ratio of 0·40 to 0·45. The irradiated samples were subjected to gamma counting on Gamma-X detector connected to the Canberra MCA. The decay of the radio-nuclides was followed for two weeks and was found to be consistent with the respective half-life. Since the activities were quite high, no radiochemical separation was done. The results given in figure 3 show no abnormal behaviour and an absence of self-shielding effects.

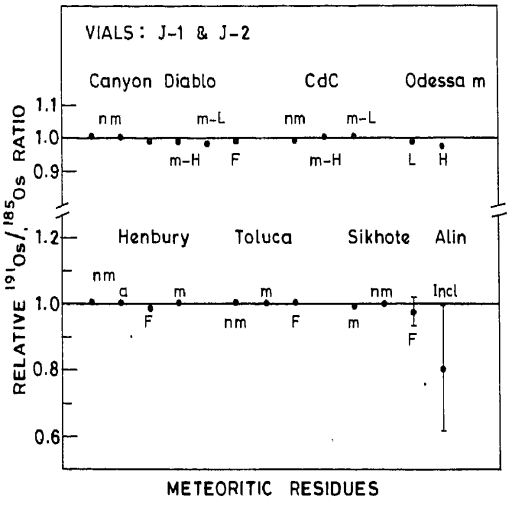

Figure 2. Results from vials J-1 and J-2.

Table 5. Contents of vial no. J-4.

Sample (matrix)	Mass (mg)	Os(μg)
Odessa m-H	96·4	0·65^{+}
Al_2O_3	10	1·44
Odessa, m+H	88	nil^{+}
$CdCO_3$	5·9(Cd)	11·6
H_3BO_4	1·7(B)	18·7
$AgNO_3$	8·6(Ag)	13·5
Al_2O_3	3 mg	16·8

$^{+}$ plus natural osmium contents (about 0·2 μg)

2.6 *Vial no. Q-1*

Table 7 describes the samples packed for this run in a quartz vial for irradiation in CIRUS reactor. Additional information is given in table 2. The quantities packed were sufficiently large and pure so that the Os activities could be easily measured without radiochemical processing. It was also possible to measure the 2-day ^{193}Os in samples from this run. No variations were seen. However the measurement errors for ^{193}Os were large (about 5%).

The samples of Os metal powder after the bombardment were found smeared over the inner walls of the sample capsules which posed a serious problem in keeping the geometry of counting the same for all samples. This was overcome by

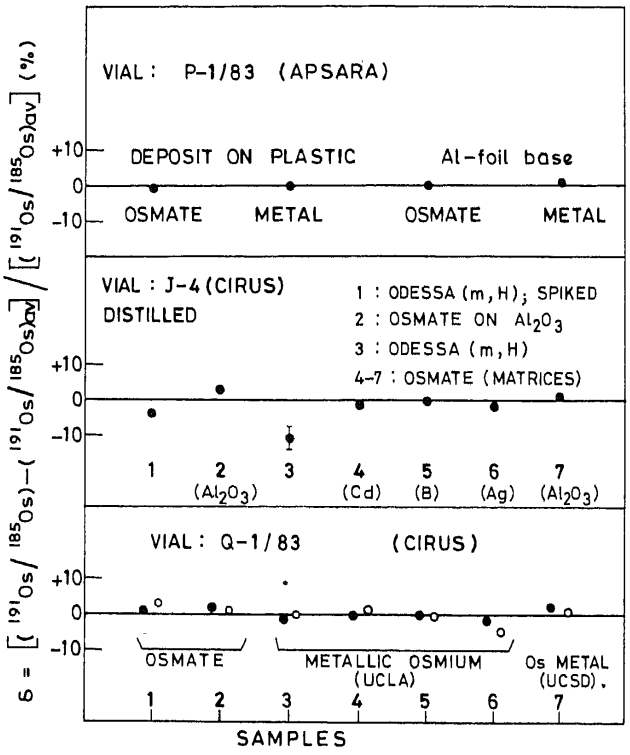

Figure 3. Osmium isotopic ratios (δ values in per cent) for samples of Os metal and Os salts on different matrices. Only Odessa, m-H is anomalous.

Table 6. Packing of vial P-1.

Number	Description
49 μg Os	Osmate on plastic
77 μg Os	Osmate on aluminium foil
460 μg Os	Osmium metal* powder on plastic
790 μg Os	Osmium metal* powder on aluminium foil

* Kindly provided by Professor J T Wasson (UCLA).

crushing each quartz sample capsule, along with osmium, into powder which was transferred to a 1 cm dia round bottom glass tube for counting. The counting was done on Gamma X detector connected to the Canberra MCA. The results are presented in figure 3. All samples gave identical values for the activity ratio of $^{191}Os/^{185}Os$, showing again an absence of self-shielding effects on isotopic ratio measurements.

2.7 *Vial no. 1/84*

Magnetic residue from Canyon Diablo iron meteorite was subjected to sieving by Sonic sifter into various size fractions with the hope that some of these would show enhanced anomalous component. The packing pattern and irradiation conditions were similar to the other vials, as listed in table 2. Aliquots of irradiated residues were dissolved in aqua regia and OsO_4 was distilled at 90°C, after adding 2 ml conc. HNO_3. The aliquots were labelled as A and B. Some samples were distilled twice. In most cases, the second distillation (labelled II) of the once-distilled (labelled I) residue gave much lower activity. Some data on repetitive distillations are given in table 8. Counting was done on the Canberra detector connected to the ND-65 multi-channel analyser. The net counts were summed up in the 10 and 4 channels (1 channel = 0·5 eV) in the two gamma-ray energy peaks of the Os isotopes. The decay-corrected gamma ray activity ratios were calculated for both the 10-channel peak areas (R_{10}) and the 4-channel peak areas (R_4). This was done to guard against

Table 7. Packing on vial Q-1

11 μg Os (osmate)
40 μg Osmate Os
680 μg osmium metal (UCLA)
60 μg osmium metal (UCLA)
330 μg osmium metal (UCLA)
810 μg osmium metal (UCLA)
550 μg osmium metal sponge (La Jolla)*

* Kindly sent by Dr S V S Murty.

Table 8. Os activity ratios for successive distillations.

Residue		^{191}Os(c/s)	R_{10}
Canyon Diablo, m-H	I	3·9	21·9 ± 0·2
No. 5	II	3·6	22·0 ± 0·2
Canyon Diablo, m-H	I	18·6	22·1 ± 0·2
No. 7	II	20	21·4 ± 0·2
Canyon Diablo, m-H	I	14	22·8 ± 0·2
Nos. 8 and 9	II	13	22·5 ± 0·2
Toluca, m	I	55	22·2 ± 0·2
No. 14	II	8	22·1 ± 0·2
Toluca, nm	I	279	22·4 ± 0·2
No. 15	II	75	22·2 ± 0·2
	III	13	21·9 ± 0·2

the influence of any spurious neighbouring gamma rays on the measured activity ratios and their intercomparisons. No inconsistencies were found. The results are given in table 9. The major aliquots of Canyon Diablo residues 8 and 9 happened to get accidentally mixed. These are given as '8 and 9' collectively. Comparisons of aliquots A and B are made in table 10. The agreement is good taking into consideration the possibility of heterogeneous distribution. In table 9 the data on aliquots A only are presented.

In vial 1/84, several samples show an enhancement of ^{190}Os over ^{184}Os. The maximum variation is + 8% (see table 9, figure 4) and is noted in both R_{10} and R_4. Since the measurement errors are within 1% (or 2%, conservative) this variation is significant. In order to ensure that the variation is not due to such factors as drift of gain and instability of the counting system, or the variations in counting geometry etc many replicate countings were made of several standard samples and also of the sample (8 and 9). These results are given in the form of histograms for R_4 and R_{10} in figures 5 and 6. The results clearly show that the two sets of samples have different gamma activity ratios. The gamma ray spectra of (8 and 9) I and 2D3 (diluted standard no. 2) are shown in figures 7 and 8. In these two samples, the counting rates are comparable and the spectra shapes are similar, yet the activity

Table 9. Results on vial no. 1/84

Meteorite residue	Code	Mass (mg)	Os (ppm)	R^* 10 ch	R^* 6 ch
Canyon Diablo m-H					
< 30 μm	5	35	23	22·0	24·4
30–45 μm	6	37	19	22·3	24·7
45–75 μm	7	34	20	21·9	24·2
75–105 μm	8	36	5	22·0	23·6
105–125 μm	9	35	6	22·0	24·2
75–125 μm	8 and 9	70	5·7	22·53	24·78
125–150 μm	10	37	7·8	21·8	23·8
> 150 μm	11	36	5	21·9	24·4
Sikhote Alin, nm	12	30	2·7	22·7	25·0
Bear Creek, m	13	31	0·1	22 ± 3	—
Toluca, m	14	20	140	22·0	24·4
Toluca, nm	15	18	210	22·0	23·8
Standards	1 and 2	—	—	21·42	23·65

* Error: less than 2% unless specified.

Table 10. Measurements on aliquots *A* and *B* of some residues (vial no. 1/84).

Sample	Code	R_{10} *A*	R_{10} *B*
Canyon Diablo, m-H			
< 30 μm	5	22·0 ± 0·2	21·7 ± 0·2
30–45 μm	6	22·3 ± 0·2	21·5 ± 0·3
45–75 μm	7	21·9 ± 0·2	21·4 ± 0·2
125–150 μm	10	21·8 ± 0·2	22·6 ± 0·4

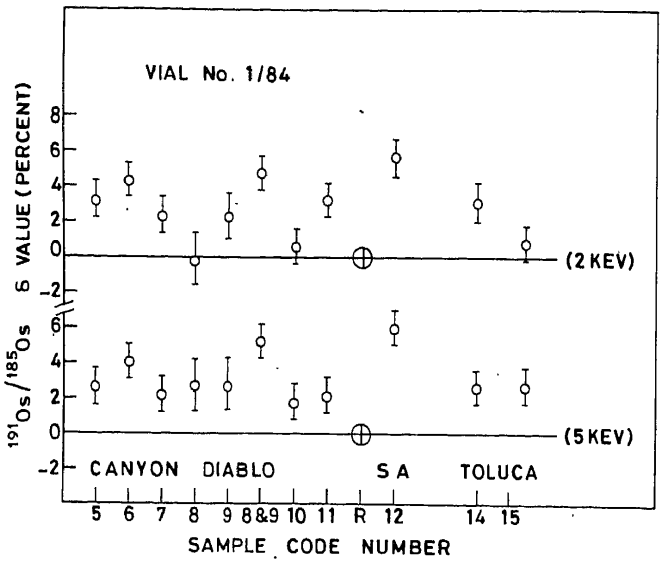

Figure 4. δ values for $^{190}Os/^{184}Os$ ratio for samples from vial no. 1/84 in 4 channels (upper line) and in 10 channels (lower line). The anomalous samples are (8 and 9) and 12.

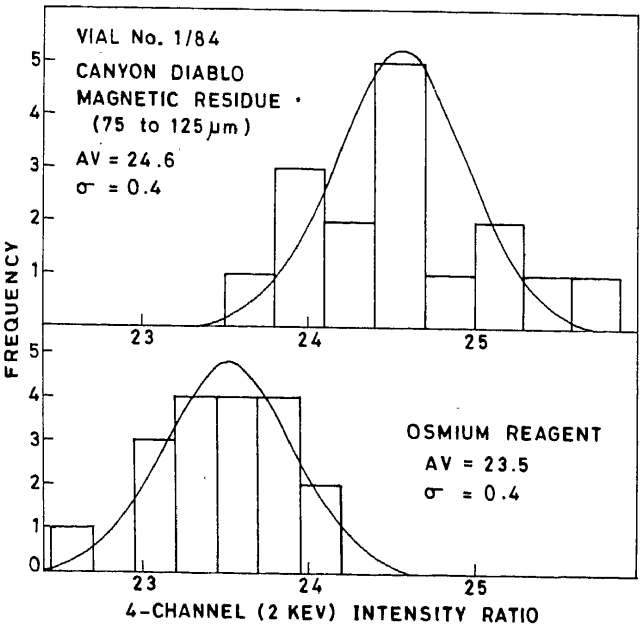

Figure 5. Frequency distributions of measured values (decay corrected) of $^{191}Os/^{185}Os$ ratios in 4 channels of the peak area for samples (8 and 9) and the reagent standard. The averages in the two cases are different.

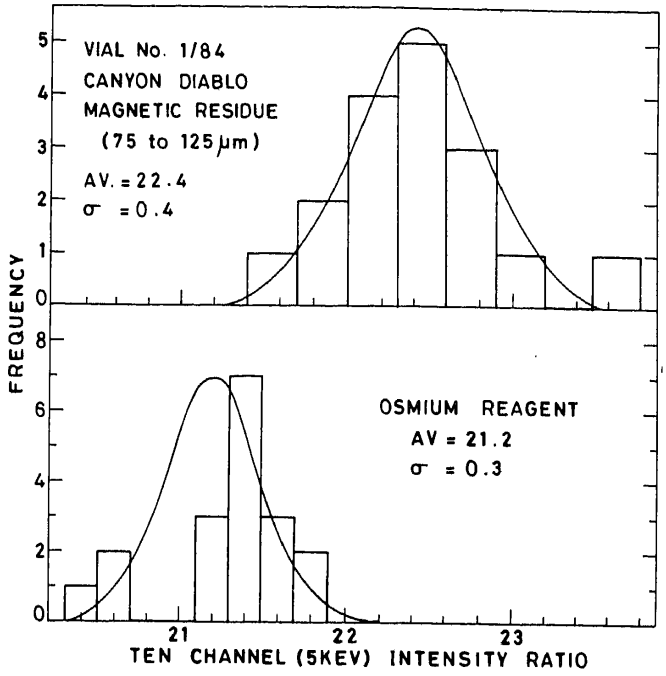

Figure 6. Frequency distribution of measured values (decay corrected) of $^{190}Os/^{185}Os$ ratios in 10 channels of the peak area for samples (8 and 9) and the reagent.

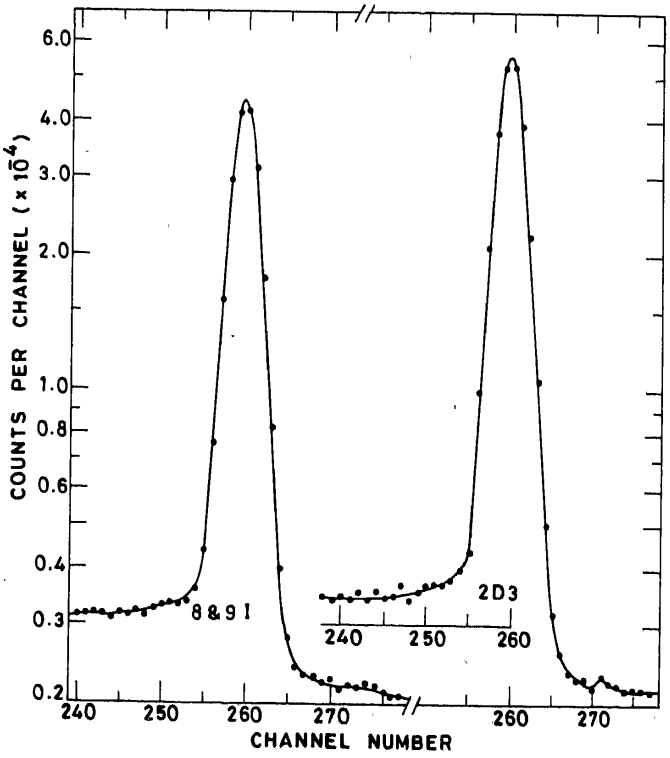

Figure 7. Comparison of the 129·4 keV gamma-ray spectra for Canyon Diablo residue (nos 8 and 9 I) and osmate standard.

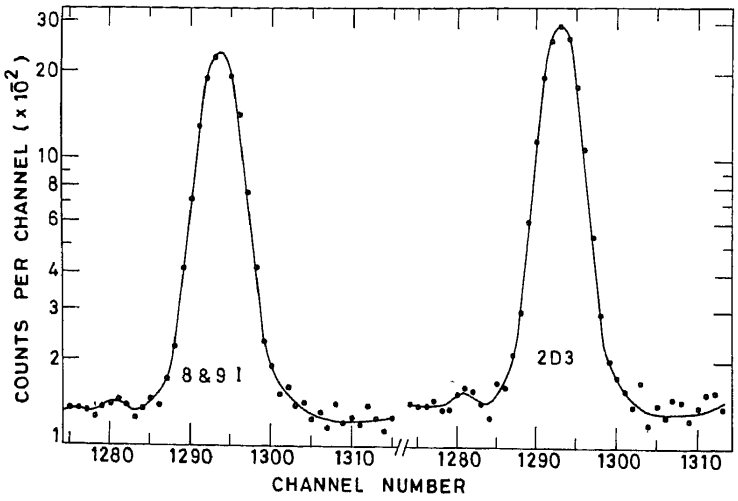

Figure 8. Comparison of the 646·1 keV gamma-ray spectra from residue of Canyon Diablo (nos 8 and 9 I) and the reagent osmium (2D3).

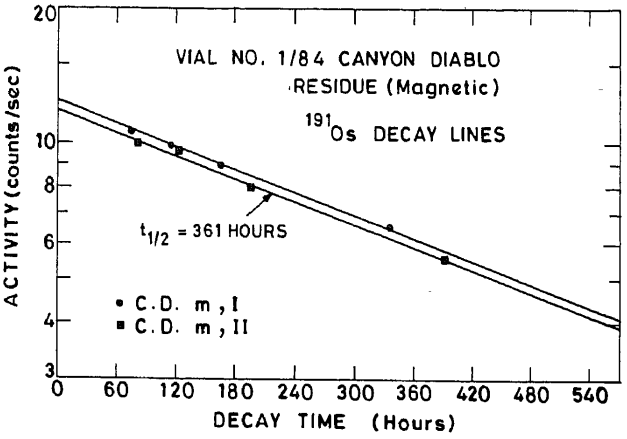

Figure 9. Decay curve for ^{191}Os gamma rays from a residue of Canyon Diablo of anomalous isotopic composition.

ratios in sample (8 and 9) are about 6 to 7% higher. A final check no reliability of our radiochemical measurement was done by following the decay of sample (8 and 9). The ^{191}Os peak decreased with the expected half-life (figure 9). Also the $^{191}Os/^{185}Os$ ratio decreased as expected and in parallel with the ratio for a standard osmium sample. This is shown in figure 10. It may be noted that all the data points on the sample (8 and 9) in figure 10 are above the line for the standard sample.

2.8 *Vial no. 1/85*

The preceding results suggested that perhaps a sieving of the residues could provide some clues to the nature of the anomalous osmium bearing phase in a sample. The magnetic residues of some iron meteorites were sieved through a 32 μm size hand sieve, to yield coarse and fine fractions. The coarse fraction was grounded in an

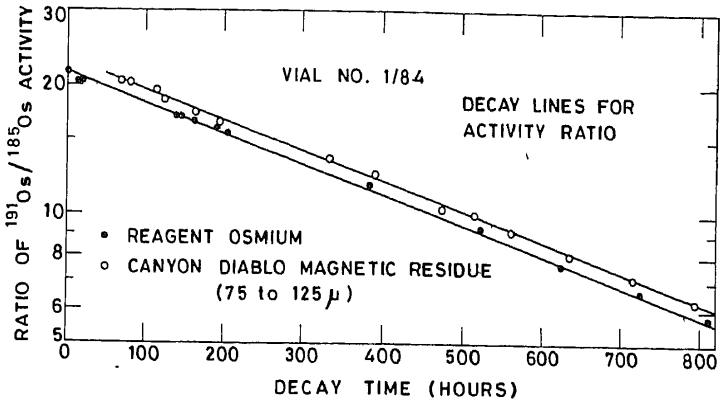

Figure 10. Decay curve for the activity ratio of $^{191}Os/^{185}Os$ for anomalous sample is identical to that for the reagent osmium. However, the data on sample (8 and 9) are always higher.

Table 11. $^{191}Os/^{185}Os$ activity ratio in vial no. 1/85.

Meteorite residue	Code	Mass (mg)	Os (ppm)	Activity ratio* 10 ch	Activity ratio* 5 ch
Bear Creek, magnetic					
< 32 μm	1	160	0·3	29·4	31·0
Crushed, < 32 μm	2	170	0·5	29·7	31·3
Crushed, > 32 μm	3	230	0·2	28·8	30·8
Campo del Cielo, magnetic					
H, < 32 μm	4	143	84	30·5	31·5
H, crushed, < 32 μm	5	76	145	31·4	33·2
H, crushed, > 32 μm	6	16	690	29·4	31·0
L, < 32 μm	7	84	261	30·5	32·5
L, > 32 μm	8	22	267	30·2	31·9
Bulk < 32 μm	9	21	308	30·0	31·9
Osmate salt on Fe_2O_3				29·22	30·85
Osmate salt on Al_2O_3				29·05	30·61

* Error is ± 0·3

agate mortar to further yield, after sieving, two crushed fractions of < 32 μm and > 32 μm sizes. These were packed and processed for measurement of $^{191}Os/^{185}Os$ activity ratios. The details, along with the results on this vial, are given in table 11. Only one sample in this vial (sample number 5) showed an anomalous osmium isotopic ratio. The activity ratio of $^{191}Os/^{185}Os$ was about 8% greater than the standard value. To ensure that this small but significant difference is not due to any shortcomings of the analysis and detection technique the following measures were undertaken: (i) Aliquots of the anomalous sample were counted repeatedly over a period of several weeks along with samples of the aliquots of the two standards. The values of R for sample no. 5 were always higher than those for the standards. Both sets of the activity ratios decreased exponentially with the expected slope as shown in figure 11. (ii) The distribution pattern of decay-corrected R_5 and R_{10}

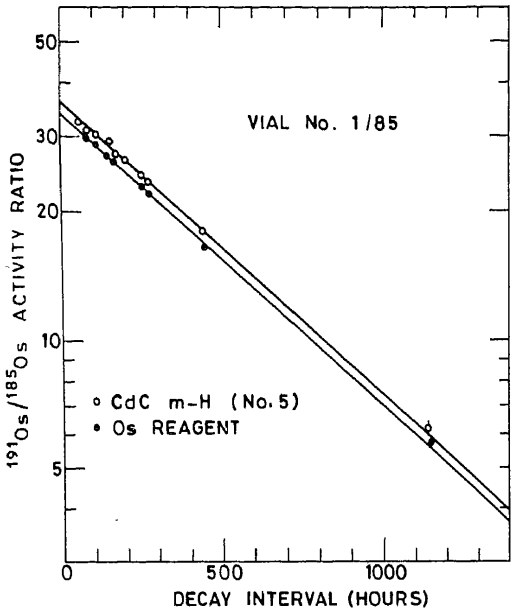

Figure 11. Decay lines for the activity ratios for reagent and CdC-m-H from vial no. 1/85. The slopes are the same but the value of the ratio for the meteoritic residue is consistently higher than the reagent value.

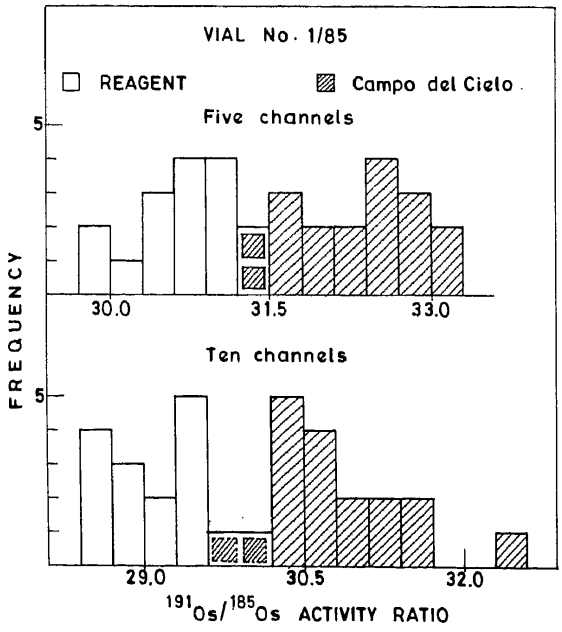

Figure 12. Frequency distribution of measured values of $^{191}Os/^{185}Os$ ratios (decay-corrected) for osmate reagent and CdC, m-H (no. 5) from vial no. 1/85.

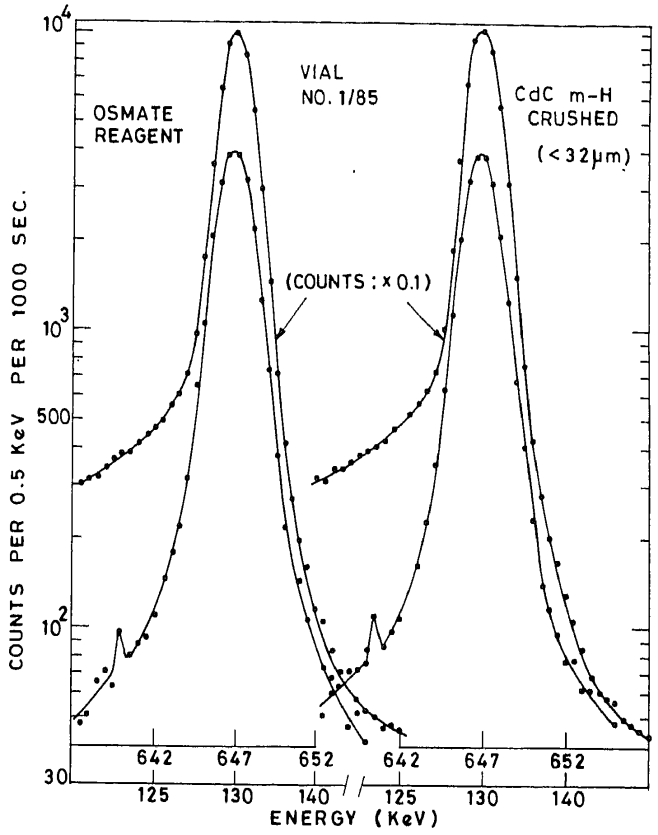

Figure 13. Comparison of the gamma-ray spectra from osmium samples of reagent osmate and CdC-m-H. In both cases the upper curves refer to the lower energy peak. Its relative area is greater for CdC-m-H.

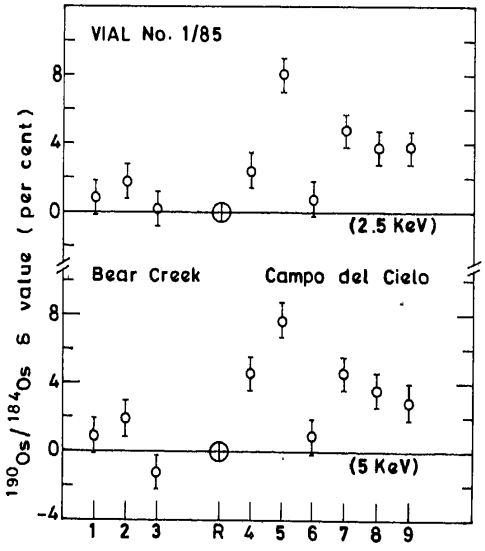

Figure 14. Results on $^{190}Os/^{184}Os$ δ values for samples from vial no. 1/85. Sample no. 5 is clearly anomalous.

values for no. 5 and standards showed distinctly different average values for the two sets (figure 12). (iii) The gamma ray spectra of no. 5 and standard (both aliquots of comparable activity) are quite similar and show no abnormal shape (figure 13). The δ values are shown in figure 14.

2.9 *Vial no. 2/85*

Since the Os anomaly was most pronounced in the inclusions of Sikhote Alin meteorite, this run was planned to investigate these residues more carefully and with larger sample sizes. During the dissolution of Sikhote Alin iron meteorite many large size (few mm) inclusions were obtained with a density of about 6·5 g cm^{-3}. These could be easily crushed into a powder. During this process, two fragments of magnetic material were found that did not crush, and these malleable pieces were examined for Os isotopic anomaly. For lack of any proper identification and better name, these are called "nuggets". The nuggets were irradiated in capsules containing powdered masses of the inclusions to optimize space in the vial. Thus the no. 9 nugget was sealed in the capsule containing powder of the inclusion no. 9 and the no. 4 nugget was irradiated with 160 mg of the inclusion powder in capsule no. 4. The three sets of powders 9, 4 and 5 were from different inclusions. The densities of the samples were estimated from the length that each weighed sample occupied in the capsules and are only crude estimates.

Realizing that the Os contents of Sikhote Alin inclusions are very low, the decomposition sequence of the samples was adopted in the order listed in table 12. This avoided the possibility of memory effects. The results are also given in table 12. The δ values are shown in figure 15. These measurements confirm the large

Table 12. Results from vial no. 2/85.

Sample	Code	Mass (mg)	Density* (g/cc)	Os (ppm)	$^{191}Os/^{185}Os$	δ (%)
Sikhote Alin residues						
nugget	9N	8·2	8·0	0·22	14·0 ± 2	−53 ± 7
nugget	4N	7·2	8·0	0·22	13·0 ± 2	−56 ± 7
inclusion	4	160	6·5	0·07	25·2 ± 1·2	−16 ± 4
inclusion	5	240	6·5	0·04	26·5 ± 0·5	−11 ± 2
inclusion	9	61	6·5	0·13	24·4 ± 1·0	−18 ± 3
m, 32 μm	1	55	2·0	1·8	29·8 ± 0·4	*n*
m, crushed, 32 μm	2	18	2·0	5·6	29·8 ± 0·3	*n*
m, crushed, 32 μm	3	55	2·5	6·5	30·0 ± 0·3	*n*
nm, crushed, 32 μm	6	29	2·0	4·0		*n*
nm, crushed, 32 μm	7	11	1·5	10·7	28·8 ± 0·3	−3·4 ± 1
nm, 32 μm	8	6·8	1·5	6·5	30·0 ± 0·5	*n*
Toluca, residues						
m, 32 μm	11	27	1·5	504	30·0 ± 0·2	*n*
m, crushed, 32 μm	12	51	2·0	12	30·0 ± 0·2	*n*
m, crushed, 32 μm	13	83	4·0	35	29·2 ± 0·2	*n*
Osmate on Fe_2O_3	14	—	—	25 μg	29·7 ± 0·2	—
Osmate on Al_2O_3	15	—	—	20 μg	29·9 ± 0·2	—

* Approximate values only. Normal δ values are indicated by *n*.

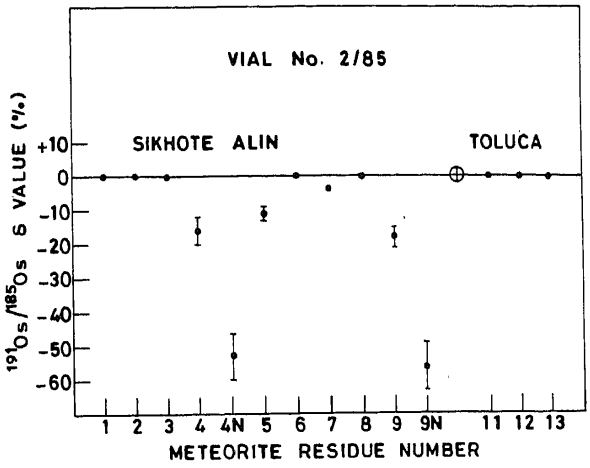

Figure 15. Results on $^{190}Os/^{184}Os$ values for samples from vial no. 2/85. Several Sikhote Alin residues are abnormally low.

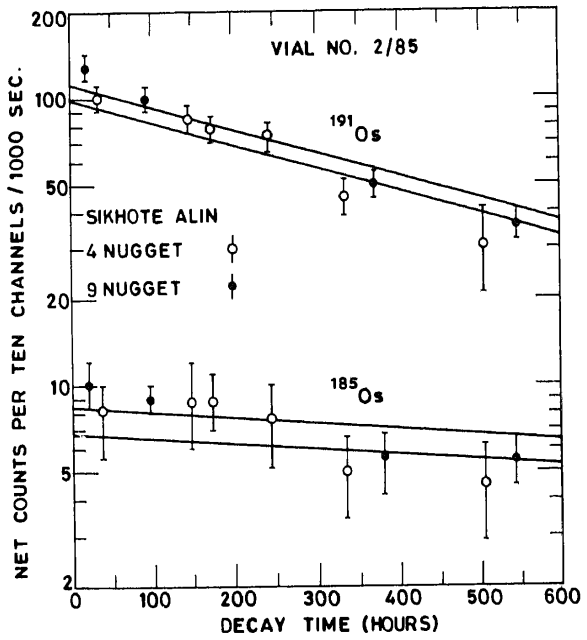

Figure 16. Spectrum of the 129·4 keV gamma rays from ^{191}Os (upper scale) and the 646-1 keV gamma rays from ^{185}Os (lower scale) from a sample of Sikhote Alin nugget having highly anomalous isotopic ratio.

anomaly reported by Goel and Murty (1983). A gamma ray spectrum of S.A. nugget no. 4 is shown in figure 16. The decay curves for Os isotopes for the two nuggets are shown in figure 17. Even though the scatter in the points is large, the decay curves are consistent with the half-lives of ^{191}Os and ^{185}Os, keeping in view the large statistical error of counting for these samples.

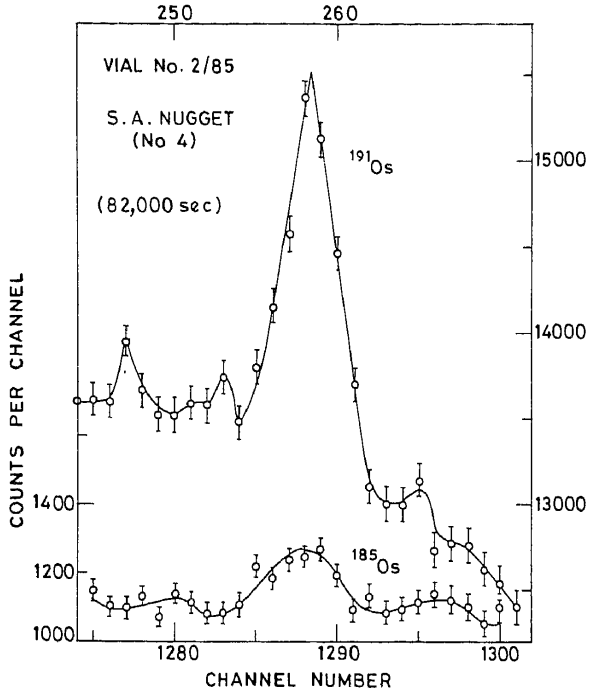

Figure 17. Decay lines for ^{191}Os and ^{185}Os from nuggets of Sikhote Alin. Due to low counting rates the scatter is rather large.

3. Discussions

In view of the profound implications of the existence of isotopic anomalies of the kind found by Goel and Murty (1983) in iron meteorites, it is necessary that a thorough scrutiny of various steps involved in the experiments is carried out to ensure that the observed abnormal activity ratios that we have sporadically found are not due to experimental artifacts which might have arisen either during the irradiation step or during the subsequent radio-chemical purification and counting steps.

It may be plausible that the anomaly is caused during neutron irradiation due to such causes as (i) variations in the composition of the residues, (ii) modification of neutron energy spectra at different sample sites and (iii) generation of secondary neutrons at some specific positions. These are inter-related factors and, if present, would be responsible for significant self-shielding effects. The high absorption cross-section for ^{184}Os (table 1) implies a low-lying resonance level for this nuclide. Its activation may therefore be prone to local fluctuations in neutron energy spectrum. It is conceivable that the Os-bearing phase in some samples has an element which has a neutron capture resonance at the same energy as ^{184}Os. This would, however, give only a higher value for the activity ratio of ^{191}Os/^{185}Os and would not be able to explain the larger number of cases where we have found lower ratios.

The residue, Odessa-m-H, that had a δ value of $-$ 10% (Goel and Murty 1983)

gave similar anomaly when studied at the NBS reactor. A 160 mg sample of this with natural Os as 0·23 μg (or so), spiked with 0·5 μg Os, showed − 7% anomaly (figure 1). Another residue of Odessa (m-H, spiked and unspiked) also showed a −ve anomaly (figure 3, run no. J-4). Since the anomaly persists in three different irradiations and in two different reactors it cannot be explained due to perturbation in the energy spectrum of the neutrons. In two control runs (P-1 and Q-1) we kept Os contents variable from 50 to 800 μg, yet the activity ratios remained invariant. In these two runs the reactors were different and the bombarding neutrons had different energy spectra. Results of run no. 21 show that the presence of neutron absorbers like Cd and B, also does not affect the osmium activity ratio. Normal ratio in the Sikhote Alin inclusion in the NBS run may be either due to memory from preceding high Os sample or it may be that the inclusion had normal Os.

Mass fractionation of Os isotopes during distillation is insignificant as supported from the data on Os activity ratios recovered from successive distillation of some samples (table 8). During sample counting, errors may arise from (i) variations in counting geometry, (ii) variations in counting rates, (iii) presence of contamination near any of the gamma lines and (iv) drift in the instrument gain. We have made enough checks as given below to ensure that none of these is responsible for the observed osmium isotopic anomaly.

In order to investigate the effect of geometry on R we took equal aliquots of distilled osmate from a high activity sample and diluted these to volumes ranging from 4 to 7 ml. Two sets of such experiments were done. The measured activity ratios are shown in figure 18. In spite of large changes in the volume, the R values remain unchanged. In practice we did not allow the counting volume to change by more than ± 0·1 ml and kept it generally as 5 ml.

Since the osmium contents of samples in some vials varied by several orders of magnitude, the counting rates were also widely different. Even though the resolution of the detector became poor at high counting rates, it was experimentally demonstrated (figure 19) that the value of R did not change. However the samples of very high counting rates were diluted to maintain good resolution. Diluted aliquots are labelled as D1, D2, D3, etc.

Evidence that the two gamma lines do not have any contaminant in their vicinity has been presented for measurements on vial nos. 1/84 and 1/85 where it was seen that (i) the values of R_{10} and R_4 (or R_5) were consistent with each other and

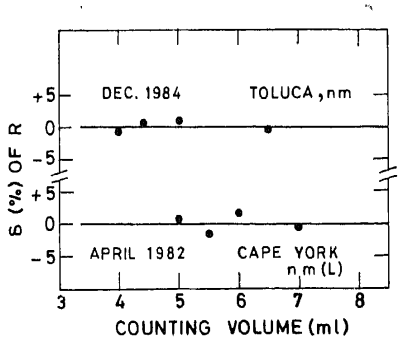

Figure 18. δ values of R for a sample of Cape York nm (L) show no variations when the volume is changed from 4 ml to 7 ml.

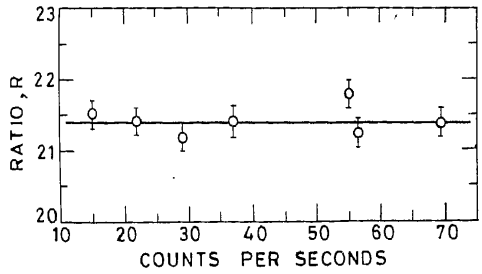

Figure 19. Activity ratio (decay-corrected) of $^{191}Os/^{185}Os$ for residue of Henbury meteorite (with normal ratio) shows no variation in R with counting rate.

Table 13. Summary of all anomalous residues with δ values $\geq \pm 5\%$.

Insoluble residue	Vial no. and code no.	δ (%)
Negative values		
Sikhote Alin, nugget	2/85 9N	53 ± 7
nugget	2/85 4N	56 ± 7
incl.	Goel and Murty, 1983	44 ± 6
m, I	Goel and Murty, 1983	36 ± 7
m, II	Goel and Murty, 1983	24 ± 9
incl.	2/85 9	18 ± 3
incl.	J-1 and J-2	20 ± 20
incl.	2/85 4	16 ± 4
incl.	2/85 5	11 ± 2
Odessa, m-H	NBS Run	> 6
m-H	J-4	10 ± 2
m	Goel and Murty, 1983	10 ± 2
Sikhote Alin, nm	Goel and Murty, 1983	6 ± 2
Cape York, mag	Goel and Murty, 1983	5 ± 2
Canyon Diablo, nm	Goel and Murty, 1983	6 ± 2
Positive values		
Campo del Cielo, nm	Goel and Murty, 1983	13 ± 2
Campo del Cielo, m-H	1/85 5	8 ± 2
Sikhote Alin, nm	1/84 12	6 ± 2
Canyon Diablo m-H	1/84 8 and 9	5 ± 2

(ii) the activity of ^{191}Os and the activity ratio $^{191}Os/^{185}Os$ decayed as expected for pure pairs. That line drift and gain shift etc. are not responsible for the abnormal ratios is clear from the patterns of frequency distributions for R values presented in figures 5, 6 and 12.

4. Cosmochemical implications

In table 13 the results on $^{190}Os/^{184}Os$ ratio are summarized for samples whose δ values are 5% or greater in magnitude. Not included in this table are a large number of residues which give normal ratio. Positive anomalies of upto 10% and negative anomalies of upto 50% are noted. It seems that the component with anomalous osmium is found to be present in iron meteorites of different classes. It

is not possible from our studies to identify the phase which contains the anomalous Os. The anomaly in osmium isotopic composition is well outside the range for known or plausible solar system processes and must be attributed to the presence of some presolar matter in iron meteorites. Apparently Os in iron meteorites has been derived from several source materials of widely different isotopic composition. The terrestrial and most meteoritical samples represent Os from a well-mixed reservoir, while iron meteorites contain some matter which has escaped homogenization. This would place iron meteorites as the most primitive objects available to mankind.

Results of other experimental works supporting the idea that iron meteorites contain presolar grains have been discussed in our earlier papers (Goel and Murty 1983; Murty *et al* 1983). Since then it has been reported by Becker and Pepin (1984) that Washington County iron meteorite contains trapped noble gases of unfractionated solar composition strengthening the idea that iron meteorites have been produced by an accretion process, entrapping some presolar grains which have been preserved essentially unaltered to retain isotopic anomalies of Os and Xe, and retain the solar flare rare gases implanted on the surface of the grains. It may also be pointed out that Prombo and Clayton (1985) have recently found large isotopic anomalies in nitrogen in the metal phase of Bencubbin mesosiderite. More recent work in our laboratory has shown that the acid-residues of Sikhote Alin iron meteorite often contain anomalously low ratio of $^{196}Hg/^{202}Hg$ (Thakur and Goel 1985; Goel and Thakur 1987).

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References

Becker D A and La Fleur P D 1974 Characterization of a nuclear reactor for neutron activation analysis; *J. Radioanal. Chem.* **19** 149–157

Becker R H and Pepin R O 1984 Solar composition noble gases in the Washington County iron meteorite; *Earth Planet. Sci. Lett.* **70** 1–10

Goel P S and Murty S V S 1983 Presolar grains in microinclusions of iron meteorites; *Adv. Space Res.* **2** 13–18

Goel P S and Thakur A N 1987 Isotopically anomalous Hg in meteorites; Presented at the 50th Annual Meeting of the Meteoritical Society at Newcastle Upon Tyne

Murty S V S, Shukla P N and Goel P S 1982 Non-cosmogenic lithium-6 in iron meteorites; *Earth Planet. Sci. Lett.* **60** 1–7

Murty S V S, Goel P S, Minh D Vu and Shukolyukov Yu A 1983 Nitrogen and xenon in acid residues of iron meteorites; *Geochim. Cosmochim. Acta* **47** 1061–1068

Oliver L L, Ballad R V, Richardson J F and Manuel O K 1981 Isotopically anomalous tellurium in Allende: another relic of local element synthesis; *J. Inorg. Nucl. Chem.* **43** 2207–2216

Prombo C A and Clayton R N 1985 A striking nitrogen isotope anomaly in the Bencubbin and Weatherford Meteorites; *Science* **230** 935–937

Reed G W and Jovanovic S 1969 ^{196}Hg and ^{202}Hg isotopic ratios in chondrites; *J. Inorg. Nucl. Chem.* **31** 3783–3788

Takahashi H, Higuchi H, Gros J, Morgan J W and Anders E 1976 Allende meteorite: Isotopically anomalous xenon is accompanied by normal osmium; *Proc. Natl. Acad. Sci. USA* **73** 4253–4256

Thakur A N and Goel P S 1985 ^{203}Hg/^{197}Hg ratio measurement in meteorites by neutron activation analysis; *Proc. Radiochem. Radiation Chem.* Symposium, Dept. of Atomic Energy, IIT, Kanpur, pp 542–554