GEOLOGICAL AND MATERIAL APPLICATION

Measurement of mercury isotopic ratio in stone meteorites by neutron activation analysis

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196Hg and 202Hg isotopes have been measured by neutron activation analysis in samples of twelve stone meteorites. Hg is extracted from an irradiated sample by stepwise heating. The mercury concentrations vary from 0.07 to 33 ppm. While most of the samples give 196Hg/202Hg ratios similar to terrestrial value within error limits, in some cases large anomalies are observed. A number of control experiments have been devised, that show the absence of experimental artifacts, during sample preparation, neutron irradiation, chemical separation and counting stages. Several anomalous and normal Hg distillate have been re-irradiated as Hg-diethyl-dithio-carbamate complex to eliminate the influence of neutron self shielding and interfering reactions from matrix elements. The isotopic ratio patterns persist in the distillates too proving that any artifacts during meteorite irradiation and measurement are essentially absent. Both positive and negative anomalies are observed; however, the negative anomalies are much more frequent and abundant. In an extreme case of fine grained magnetic particles of Ambapur Nagla the 196Hg is apparently absent in the Hg released at 100 °C. A 2σ 196Hg/202Hg value is only 6% relative to the monitor. This experiment shows the robustness of neutron activation analysis and suggest some constrains on the formation history of stone meteorites.

Introduction

The meteoritic high abundances of Hg and the variable 196Hg/202Hg ratio have remained unsolved puzzles in cosmochemistry for almost three decades. In this paper we report the existence of isotopically anomalous Hg in a large number of chondrites. In 1969 Reed and Jovanovic, using neutron activation method, found large variations in the 196Hg/202Hg ratio in several chondrites. Generally this ratio differed by about 20% from the normal value but in one case it was a factor of 20 too low. A depleted ratio was also found for some lunar samples and for three Antarctic achondrite samples. Similar results on mercury isotopic studies, in some specific mineral phases of meteorites, have been reported by Kumar and Goel.

The results of an extensive study of two Hg isotopes in several samples of stone meteorites are reported here. Hg was extracted from irradiated samples (neutron fluence = 6.8 × 1020) by stepwise heating under vacuum and the condensates collected in liquid N2 traps were converted into a complex of diethyl-dithio-carbamate (cupral). After recording the γ-ray spectra and appropriate cooling, these complexed samples of Hg were again irradiated to similar neutron fluence. This eliminates the matrix effects and other possibilities of interfering reactions. The two sets of results match very well confirming its reproducibility. This paper also presents a number of other control experiments that were deemed necessary in order to establish the reliability of these results.

Experimental

Out of seven stable isotopes of Hg, two can be conveniently studied by the neutron activation technique. The 196Hg and 202Hg isotopes, upon neutron activation produce radionuclides 197Hg and 203Hg, respectively. These can be measured by X- and γ-ray spectrometry. The details of the experimental procedure have been described by Thakur and Goel. Pieces of stone meteorites weighing 100–1000 mg are wrapped in Al foil. Powdered bulk samples, sieved fractions, magnetic and non-magnetic portions were enclosed in quartz capsules when masses were small. Alumina powder or MgO spiked with reagent Hg is used as a monitor. The irradiated samples were vacuum distilled at temperatures ranging from 100 to 600 °C to collect Hg in cold fingers at liquid N2 temperature. In our early work Hg was recovered in HCl + HNO3 solution for counting. Later, it was found more convenient to convert it into a complex with Na-diethyl-dithio-carbamate.

To ascertain the absence of any contamination, a number of blank experiments were done. Meteorite samples already heated to extract Hg prior to irradiation showed no Hg activity. Distillation blanks, without a sample subjected to all thermal extraction steps, gave no activity from vacuum line or glassware. Quartz tubes and thio carbamate reagent on irradiation showed no Hg activity. Absence of memory in the vacuum line is established from the results of the blank runs carried out after distilling a sample of high Hg activity. As seen in Fig. 1, the memory is essentially absent.
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Fig. 1. The Hg content of samples distilled sequentially at 400 °C. Note that between two anomalous samples 4A and 4, we have a normal sample (number 9) and also that after high activity sample, the blank is very low. These data demonstrate an absence of Hg memory and contamination in the system.

The control experiments

In view of the profound implications of the existence of isotopic anomalies of the kind reported here and elsewhere, 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 are not due to experimental artifacts which might have arisen either during irradiation or during the subsequent radiochemical purification and counting stages. It is plausible that the anomaly arises during irradiation due to causes such as (1) variation in the elemental composition of the sample, (2) modification of neutron energy spectra at different sample sites and (3) generation of secondary neutrons at some specific sites. These are interrelated factors and, if present would be responsible for significant self shielding effects. The high absorption cross section for $^{196}$Hg implies a low-lying resonance level for this nuclide. Its activity may therefore be affected by local fluctuations in the neutron energy spectrum. It must be clearly demonstrated that matrix effects are absent in the relative activation of $^{196}$Hg and $^{202}$Hg during neutron irradiation. Some meteorite samples were heated to 1000 °C in vacuum to extract mercury. The heated powders were mixed with boric acid or cadmium sulfate and were spiked with reagent mercury. These homogenized samples were irradiated along with other meteorite samples.

The results, presented in Table 1, show that the presence of thermal neutron absorbers such as Cd and B does not affect the Hg activity ratio. Two different monitor samples placed at different places in the irradiation can, one at the central and the other at the outer region, showed indistinguishable $^{197}$Hg/$^{203}$Hg ratios (2.9 ± 0.1 each) upon activation. Counting rates were also in good agreement, 13.76 and 13.38 cps for 0.85 and 0.83 mg Hg, respectively. Clearly, within an irradiation can the neutron energy spectrum in a normal packing does not get modified in a significant way to give any differences in the relative activation of $^{196}$Hg and $^{202}$Hg in the same packing. During sample counting, errors may arise from: (1) a variation in counting geometry, (2) a large variation in counting rate, (3) the presence of peaks near any of the Hg gamma-ray lines due to contamination and (4) a drift in instrument gain. In order to investigate the effect of geometry on the ratio, equal aliquots from high activity mercury monitor were taken and diluted to volumes ranging from 0.20 to 1.5 ml. In spite of large changes in the counting volume, the ratios remain unchanged. In practice we did not allow the counting volume to change by more than ±0.1 ml and

Table 1. Effect of neutron absorbers on Hg isotopic ratio

<table>
<thead>
<tr>
<th>Matrices*</th>
<th>Spiked Hg, mg</th>
<th>Code</th>
<th>cps</th>
<th>Measured Hg, mg</th>
<th>$^{197}$Hg/$^{203}$Hg activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Menow</td>
<td>0.84</td>
<td>M-1</td>
<td>0.64</td>
<td>0.84</td>
<td>0.57 ± 0.07</td>
</tr>
<tr>
<td>Menow + 2.5 mg H$_3$BO$_3$</td>
<td>0.15</td>
<td>M-2</td>
<td>0.08</td>
<td>0.11</td>
<td>Unmeasurable</td>
</tr>
<tr>
<td>Menow + 2.0 mg CdSO$_4$</td>
<td>1.68</td>
<td>M-3</td>
<td>1.26</td>
<td>1.65</td>
<td>0.51 ± 0.08</td>
</tr>
<tr>
<td>Amb. Nagla + 2.0 mg H$_3$BO$_3$</td>
<td>0.85</td>
<td>M-4</td>
<td>0.64</td>
<td>0.84</td>
<td>0.59 ± 0.06</td>
</tr>
<tr>
<td>Amb. Nagla + 1.9 mg CdSO$_4$</td>
<td>2.15</td>
<td>M-5</td>
<td>1.63</td>
<td>2.13</td>
<td>0.60 ± 0.06</td>
</tr>
</tbody>
</table>

*Menow & Ambapur Nagla (~35 mg each) are prior heated under vacuum at 1000 °C to extract mercury.