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Isotopic Anomalies in High Z Elements: Uranium?

by S. Jovanovic, G. W. Reed, Jr.,
A. M. Essling, E. G. Rauh,
and D. G. Graczyk



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ISOTOPIC ANOMALIES IN HIGH Z ELEMENTS: URANIUM?

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ABSTRACT

Uranium in terrestrial volcanic ejecta from mantle-related sources has been analyzed mass spectrometrically. The objective was to seek supporting evidence for or refutation of isotopic variations reported by Fried et al. (1985) for some such samples. The possibility that terrestrial U is not of constant isotopic composition is extraordinary. If true, mechanisms for creating the variation must be sought and the lack of homogenization within the earth addressed.

Samples of 100 grams or more were processed in order to minimize reagent and environmental (laboratory) blank interference and to permit isolation of large amounts (several to tens of μg) of U for the mass spectrometer (MS) measurements, which utilize aliquots of $\sim 1 \mu\text{g}$. Aliquants from four volcanic samples gave data which indicate enrichments of ^{235}U ranging from 0.2% to 5.9% in the 235/238 ratio relative normal uranium ratios. These relative enrichments are consistent with, and in some cases, higher than the 0.18% enrichment reported by Fried et al. (1985) for two volcanic lava samples. However, we were not able to reproduce their results on the Kilauea lava for which they report 0.18% ^{235}U enrichment. The relative error in our MS ratios is 0.05%-0.07%. A reagent and environmental blank gave U concentrations, based on isotopic dilution, of less than 0.2% of the amount of U recovered in the parallel sample run. A reagent blank, run in parallel with another sample, was below the detection limits of the fluorescence method used and less than 3% of the U recovered from the sample. Substantially enriched anomalous U in the reagent blanks would be required to account for the $>0.2\%$ ^{235}U enrichment in the volcanic samples.

The ^{235}U enrichments were measured in experiments conducted at two different laboratories, Argonne National Laboratory (ANL) and the University of Chicago (UC). The normal U in a Kilauea sample extracted at the UC suggests that environmentally derived enriched U was not present, hence it is probable that other samples run at UC were not environmentally contaminated. The procedural blank results and the frequent similar ^{235}U enrichments (0.19%-0.43%) for samples prepared at the two laboratories is evidence (but not proof) that isotopically anomalous U is present in some terrestrial volcanic samples. Until observed variations in measured enrichments among different portions of a given sample material are resolved, however, this evidence remains suggestive. Additional measurements are needed to ultimately determine whether uranium isotopic variations occur in the earth's mantle.

1.0 BACKGROUND: STATUS OF HIGH Z ELEMENT ISOTOPIC ANOMALIES

The purpose of this report is to summarize the result of our investigations on the possible presence of isotopically anomalous U in terrestrial lavas of mantle origins. The presence of isotopically anomalous low and middle Z elements is well established (see review by Begemann, 1980). In all cases the matter in which the anomalies were discovered is extraterrestrial. The anomalies of interest are not necessarily radiogenically produced in-situ either by decay of a parent or by nuclear reactions.

The most significant isotopic variation in high Z elements is in Pb. The variation is not an anomaly, it is the natural occurrence of primordial Pb which has not been isotopically altered by the decay of U and Th, e.g., Reed et al. (1960) and included references. Only ^{204}Pb is not affected by this decay and hence may be used along with the primordial Pb to determine the radiogenic Pb present in solar system material.

Three instances of isotopically anomalous high Z elements (Os, Hg, and U) have been reported. None have gained general acceptance. Conflicting results are reported for Hg. ^{196}Hg and ^{202}Hg have been measured by thermal neutron activation analysis. Anomalous isotope ratios have been reported for some unequilibrated chondrites (Reed and Jovanovic, 1969; Jovanovic and Reed, 1976) and for three Antarctic achondrites (Jovanovic and Reed, 1987, 1988 (submitted)). Chondrites and residues from dilute acid dissolution of iron meteorites were also found to contain isotopically anomalous ^{196}Hg vs ^{202}Hg by Goel and Thakur (1987). In all cases the anomalous Hg was in specific temperature fractions isolated in stepwise heating experiments; usually the anomalous Hg represented only a fraction of the Hg in the sample. The ^{196}Hg was depleted relative to ^{202}Hg from ~25% to almost total absence. Lunar breccias 14305 and 14312 were also found to contain a Hg fraction that was relatively depleted in ^{196}Hg by ~25% (Jovanovic and Reed, 1977 and 1988 (submitted)).

An early mass spectrometric measurement by C. M. Stevens, ANL (private communication), using the 100-inch mass spectrometer, detected isotopically anomalous Hg. Three other efforts to detect isotopically anomalous Hg mass spectrometrically failed (von Helden and Begemann, 1976; Begemann, 1980; Lugmair et al., 1978; and Nier and Schluter, 1987). Since the anomalous fractions contain a few percent of the total Hg in the sample, usually only $\sim 10^{-9}$ - 10^{-11} g Hg/g is isolated and measured. At this level, there may be serious problems with mass spectrometer systems which have Cu and Au gaskets, efficient getters of Hg. The system will have been exposed to the bulk of the Hg, which is isotopically normal, released from the sample. A serious memory effect could result. The low Hg isotope abundance at mass 196 may also present problems, some of which are related to hydrocarbon background interference.

Goel (1987) has reported variable $^{190}\text{Os}/^{184}\text{Os}$ ratios (up to 50%) in acid residues of iron meteorites. Jovanovic and Reed (1977) presented some

preliminary data on these Os isotopes in one of the samples of Apollo 14 breccia 14305 measured for Hg. An ~16% deviation from normal was found. A very much smaller $1.023 \pm 0.008\%$ Os variation was found in an Allende meteorite sample. In neither case have experiments been carried out to confirm the results. Takahashi et al. (1976) report normal Os (an average of $0.2 \pm 0.7\%$ relative ^{184}Os depletion) in two Allende samples.

Anomalies in the U isotopes in extraterrestrial matter have been reported by Arden (1977), Chen and Tilton (1979), and Tatsumoto and Shimamura (1979, 1980), but these effects were not confirmed by Chen and Wasserburg (1981). Isotopically anomalous U has been reported in two types of terrestrial material. In one case the evidence is irrefutable; the variation in isotopic U being due to the Oklo, Gabon natural reactor. Uranium ore was analyzed. The other published anomalous U results, which have not yet been confirmed, are those from a sample of a Kilauea lava and a sample from a Katmai eruption (Fried et al., 1985). These authors reported an ~0.18% ^{235}U relative enrichment.

G. Cowan and H. Adler (1976) conducted an extensive survey of the literature on U isotopic ratios in terrestrial U ore samples. Two modal values of the isotopic ratio exhibited a relative difference of 0.03%. In comparison, the 0.18% ^{235}U relative enrichment in two basaltic lavas reported by Fried et al. (1985) is very large. Uranium isotopic ratios have been measured in hydrothermal fluids related to midocean ridge volcanism. The most recent results (Chen, 1987) based on analysis of nanogram amounts of U give $^{235}/^{238}\text{U}$ ratios equal, within error, to those of average sea water and normal U. The range of deviations from normal ($-0.52\% \rightarrow +0.34\%$) in the measurements reflects the measurement uncertainty reported. Deviations of the magnitude reported in ores and in volcanic rock samples (i.e., $0.03\% \rightarrow 0.18\%$) would not be resolved.

2.0 U ISOTOPIC MEASUREMENTS IN VOLCANIC SAMPLES

2.1 Samples

The possibility that isotopically anomalous U is present and has persisted in the earth over geologic time raises many questions about the genesis of such U and its isolation in the earth. Volcanic ejecta have the advantage for study in that they may not have been subjected to mixing with isotopically normal crustal material or to isotopic contamination from nuclear fallout. Samples studied represent many volcanically erupted lavas but of special interest are those derived from undisputed mantle sources. Possibly the best candidates for study are ocean ridge and ocean island tholeiitic basaltic glasses. These are quenched lavas and have the least probability of having been permeated by hydrothermal waters. They may best represent their upper and lower mantle sources. We have measured U in five types of volcanic ejecta:

Hat Creek basalt (California) - Early erupted high Al, olivine-rich tholeiite from A. T. Anderson, University of Chicago (Anderson and Gottfried, 1972). No macroscopically visible oxidation or segregation veins.

Auvergne (France) - Olivine basalt volcanic bomb from E. Olsen, Field Museum #G355. Material analyzed was core left after spalling off exterior "onion skin".

Mt. St. Helens (Oregon) - Volcanic ash from D. Swanson, USGS. Vesicular pumice separated by flotation from "wall rock" material was analyzed.

Mauna Loa spatter - Tholeiitic glass from D. Finnegan, LASL; March 1984 collection.

Kilauea basaltic rock - Sample 2565 from E. Olsen, Field Museum. From the batch of material erupted in 1926 and used by Fried et al. (1985).

Two basaltic glass samples were candidates for measurement. Since quantities were limited we first measured the U contents by neutron activation analysis. Mauna Loa spatter contains 0.18 μg U/g. An East Pacific Rise (EPR 4HC) glass supplied by H. Craig contained 0.04 μg U/g and was not analyzed since a typical processing yield of 20-40% may not have provided enough U for mass spectrometry.

2.2 Chemical Procedure

The analysis for U entails protracted dissolution, evaporation, and ion exchange steps. The dissolution of the samples and the chemical separations of U (and Pu) were conducted either at the Enrico Fermi Institute at the University of Chicago (UC) or at ANL. Only Auvergne was determined at both laboratories. Any possible contamination by enriched or depleted U isotopes that may be present in the environment, equipment, or reagents could contribute to a difference between the results from these Auvergne samples.

Procedures were developed for working with up to 300 g of volcanic rock with the option of combining three to four batches to process 1 kg of rock. Up to tens of μg of U can be recovered; thus, contamination related to environmental factors is reduced. In some experiments procedural blanks were run in parallel with the rock samples in order to further set limits on potential environmental and reagent contamination of the samples.

Rock fragments (> 1 cm size) were first ultrasonically cleaned with distilled H_2O followed by alcohol and ether washes and air or oven drying. Samples were then pulverized in a shatter box with a hardened-steel grinding container which was initially cleaned and rinsed by crushing and discarding aliquants of the rock fragments. The chemical procedure for dissolution of the rock was similar to that used by Fried et al. (6). The powdered rock was dissolved in two stages. An initial HCl treatment dissolved primarily olivine and some minor minerals such as phosphates. The residue from the HCl treatment was digested with HNO_3 and HF. The HCl soluble fraction was evaporated and then

also digested in HNO_3 -HF. All the samples, particularly the HCl insoluble fractions, had residues of AlF_3 which were treated further (following the initial destruction of the silicates) by fuming several times with additional HNO_3 and HF acids. AlF_3 is soluble in excess HF. Sufficient HF could not be added to dissolve all the AlF_x , but we assume that digestion with HF caused release of any U and that the hot HNO_3 oxidized it to the fluoride-soluble UO_2^{++} state. Both fractions were evaporated to fumes of HNO_3 to drive off SiF_4 and excess HF. These HNO_3 solutions were sometimes combined for U, Th, and Pu chemistry; at other times, they were run separately. The latter procedure provided information on where U is present in the rock and also made possible an additional assessment of possible environmental U contamination.

The succeeding chemical separation steps involved anion exchange columns, first with 8 M HNO_3 (nitrate column) to separate Th and Pu from U and Fe, and then with 9 M HCl (chloride column) to adsorb U (and Fe). Th and Pu were eluted from the nitrate column with conc. HCl and 0.1 M HCl, respectively. U and Fe were eluted from the chloride column with 0.1 M HCl. U was subsequently ether extracted from an NH_4NO_3 -saturated, 1 M HNO_3 solution. After scrubbing with 1 M HNO_3 - NH_4NO_3 solution, the ether was allowed to evaporate over ~5 ml 0.1 M HCl. Uranium recovered in the sample processing was determined from analysis of this HCl solution by laser fluorimetry with a SCINTREX Model UA3 Uranium Analyzer.

No tracers were used in the chemical separation procedures in order to avoid introducing this source of isotopic uncertainty. Furthermore, since it was impractical to monitor chemical yields during the chemistry, addition of tracers had no merit.

2.3 Mass Spectrometry

Uranium isotope ratios were measured with an automated, triple-filament-source, thermal-ionization mass spectrometer (VG Isotopes, Model 54R). Corrections for isotopic fractionation during the mass spectrometric analysis were determined from multiple analyses of NBS uranium standard reference materials (SRM) from the series U-050 through U-900. $^{235}\text{U}/^{238}\text{U}$ ratios measured for standard materials with this system are accurate to within $\pm 0.05\%$ (one-sigma), relative, as demonstrated by calibration-verification data accumulated over several years.

For some of the measurements reported here, a portion of the solution containing the uranium sample prepared as described above was mixed with an isotope-dilution spike consisting of an accurately known quantity (nominally 10 μg) of NBS SRM 995, which is a ^{233}U spike-assay and isotopic standard with a ^{233}U enrichment greater than 99.9%. Each spike/sample mixture was evaporated to dryness several times from concentrated, NBS-distilled nitric acid to ensure complete isotopic equilibration, and the resultant residue was dissolved in 5%

NBS nitric acid for loading on the mass spectrometer filament. From isotope ratios measured for the spiked sample and the known isotopic composition of the spike material, both the concentration and isotopy of the uranium in the sample aliquot were calculated.

In analyzing the first few samples in this series, we found that the sample solutions contained substantial amounts of extraneous salts (i.e., not uranyl nitrate), which adversely affected sample behavior during the mass spectrometric analysis, particularly for samples having a low uranium concentration and consequently requiring that a relatively large volume of solution be loaded on the filament. Under the hypothesis that these salts arose from aluminum or ammonium species that followed the uranium through earlier separations, an additional ion-exchange purification was performed on the spiked samples in the mass spectrometry laboratory. The uranium was absorbed on pre-washed Dowex AG-1 anion exchange resin from 12 M Ultrex HCl and eluted with 0.1 M Ultrex HCl. This treatment succeeded in eliminating the extraneous salts and dramatically improved the stability of ion beams obtained during the isotope ratio measurements.

A second portion of one sample solution (ANL-3, see Table) was analyzed with a different mass spectrometer (NBS Design, Teledyne Isotopes) and analysis procedure to verify the high enrichment of ^{235}U that was observed during analysis of the spiked aliquot prepared in the above manner. For this second aliquot, a portion of the unspiked sample solution was mixed on the mass spectrometer filament with a $^{233}\text{U}/^{236}\text{U}$ internal standard spike that had previously been calibrated with NBS U-500 isotopic standard. The analysis procedure, described by Callis (1982), uses the measured $^{233}\text{U}/^{236}\text{U}$ ratio to determine a fractionation correction in real time during the run, and applies this correction to the $^{235}\text{U}/^{238}\text{U}$ ratio measured for the unknown sample. In this way, the technique permits intercomparison of $^{235}\text{U}/^{238}\text{U}$ isotope ratios at the natural abundance level with very high precision. The result obtained in this way agreed well with the alternative measurement on the sample, demonstrating that the uranium in the sample solution was indeed enriched at the level indicated by the first analysis.

For two sets of samples (ANL-7 and UC-5), uranium in the HCL sample solution was purified by taking the HCL solution to dryness, redissolving the residue in 3N Ultrex HNO_3 , and adsorbing the U on an extraction-chromatography column containing 40 at. % diamylamylphosphonate on XAO-7 ion-exchange resin (Essling et al., 1988). The purified U was eluted with 0.01 N HNO_3 and taken to dryness prior to redissolution for mass spectrometric analysis. These sample sets were analyzed by the $^{234}\text{U}/^{236}\text{U}$ internal standard procedure without addition to the ^{233}U assay spike.

$^{235}\text{U}/^{238}\text{U}$ in Volcanic Samples

<u>Sample*</u>	<u>$^{235}/^{238}$ (atom ratio)</u>	<u>δ $^{235}/^{238}\%$ (sample/std - 1) $\sigma = \pm 0.07\%$</u>	<u>U recovered μg</u>
Hat Creek basalt			
UC-1S	0.007371	+1.62	5.78
UC-1R	0.007272	+0.26	10.14
UC-2 (S+R)	0.007283	+0.41	3.90
Auvergne volcanic bomb			
ANL-3 (S+R)	0.007684	+5.94	32.32
UC-3 (S+R)	0.007301	+0.66	5.21
Mt. St. Helens pumice			
ANL-4 (S+R)	0.007267	+0.19	4.52
Mauna Loa spatter			
ANL-7S	0.007284	+0.43	0.41
ANL-7R	0.007268	+0.21	2.8
Kilauea 2565			
UC-5S	0.007249	-0.06	0.34
UC-5R	0.007257	+0.06	5.7
Reagent blanks			
UC-3	(mass spect.)		<0.0075
ANL-3	(fluorescence)		<1
Uranium			
"Normal"	0.007253		

*Chemical separation at Fermi Institute, University of Chicago = UC; at Argonne National Laboratory = ANL. S = HCl soluble fraction; R = HCl insoluble residue.

3.0 RESULTS

The Table lists the results. The data we have acquired are not in conflict with the original observations (Fried et al., 1985) indicating a possible excess of ^{235}U but cannot be accepted as proof as will be discussed. The U isotopic ratios in all but one of the samples show an apparent enrichment of ^{235}U relative to normal uranium, with the enrichments ranging from 0.19% for the Mt. St. Helens pumice to 5.9% for one sample of the Auvergne volcanic bomb material. In cases where the HCl acid soluble (S) and insoluble (R) fractions were measured separately (UC-1, UC-5, and ANL-7), the pattern appears to be higher excess ^{235}U in the (S) samples. In interpreting the significance of these apparent enrichments, two important aspects must be considered. These are (1) potential contamination of the sample uranium with extraneous uranium containing a disproportionate abundance of ^{235}U and (2) potential errors in the mass spectrometric analysis.

A normal $^{235}\text{U}/^{238}\text{U}$ isotopic ratio was observed in only one case. Ironically, the sample Kilauea 2565, is the one in which Fried et al. (1985) found enriched ^{235}U . The relatively small enrichments observed with samples ANL-4 (0.19%) and UC-1R (0.26%) are on the order of 3σ uncertainties (0.2%) in the mass spectrometric measurements when allowance is made for the difference between the analytical behavior of real-world samples and the ultra-pure standard materials used for calibrating the mass spectrometer, and might not be significant relative to potential mass spectrometric errors in these early measurements. However, ANL-7R (0.21%) was measured later under more rigorous conditions and this number is significant. An internal standard procedure (Callis, 1982) that was used by Fried et al. (1985) was used for the ANL-7 and UC-5 samples.

We note that Fried et al. (1985) reported that their sample of Mt. St. Helens ash (cf. ANL-4) was not enriched relative to normal uranium. However, we do not know whether the Fried et al. sample was pumice separated from other volcanic ejecta. We find a ^{235}U enrichment of 0.19% for Mt. St. Helens vesicular pumice separated from dark "wall rock". However, this could be suspect. Sakuragi et al. (1983) reported that ^{235}U enriched U was found in rain samples falling about the time of the Mt. St. Helens eruption in May 1980. The anomalous U was probably associated with the reentry of the Soviet satellite Cosmos 954 into the atmosphere in January 1978. Sakuragi et al. (1983) estimate a 20 month descent time of radioactive debris from the stratosphere to the tropopause.

The ^{235}U enrichments, 0.41% → 5.9%, measured for the other samples in this series are well outside the range of probable mass spectrometric errors, and clearly show an enhancement of the ^{235}U abundance in the uranium samples that were analyzed. It remains, however, to determine whether these enrichments are indigenous to the volcanic materials or resulted from ^{235}U contamination during

the sample processing and preparation. As noted, dissolutions and chemical separations of the volcanic samples to isolate U were conducted in parallel in two separate laboratories to help differentiate between indigenous enrichments and enrichments caused by contamination. If the $^{235}\text{U}/^{238}\text{U}$ ratio is a "constant of nature" then samples run at the two laboratories need not be the same rock to test for contaminant ^{235}U .

Procedural blanks, run alongside the samples in each location, provide additional information which helps set limits to the potential for contamination from reagents, etc. used in processing the samples. Uranium in the reagent blank run with sample UC-3 was so low as not to be measurable with the (sensitive) isotope-dilution method we used to determine it; the blank corresponded to less than 0.2% of the uranium recovered from this sample. The blank run with sample ANL-3 was not examined as closely, but was shown to contain less than 1 g U, which corresponds to a blank smaller than 3% of the uranium obtained from the sample. Contamination of the samples by an amount of uranium corresponding to these upper limits in the blanks could, in principle, account for the enrichments that we found. However, the uranium in the blanks would have to be significantly enriched (at a level of at least 2% ^{235}U compared to 0.7% for normal U). Although these arguments make contamination during preparation of the samples seem an unlikely source of the observed enrichments, we do see a difference between the Auvergne samples processed at UC and ANL. This difference could arise from differences in ^{235}U contamination as well as non-uniformity of the sample material.

We conclude with comments on specific samples listed in the Table. The $^{235}/^{238}\text{U}$ isotopic ratios are not dependent on the amount of U recovered. The differences between samples of the same lava, ANL-3 and UC-3, for example, could be related to our failure to completely mix the material after it was pulverized. This process was carried out in a batch-wise fashion on "well mixed" sub-centimeter to centimeter-sized fragments. The UC-1S and UC-1R samples are soluble and residual fractions from HCl treatment of a 100 g sample in an initial UC experiment. In contrast to other Hat Creek samples, the amount of U recovered from the residue (UC-1R) is large and has a nearer normal isotopic composition. Either isotopically different U exists in the acid soluble and insoluble phases or the UC-1R sample reflects the effect of the extra chemical processing undertaken. In an effort to determine whether any U remained in the residue after HF-HNO₃ treatment to dissolve silicates.

4.0 CONCLUSIONS

The results obtained thus far appear to support the earlier work of Fried et al. (1985). However, our Kilauea 2565 sample has isotopically normal U. The Mauna Loa spatter enrichments of 0.21% for the HCl insoluble residue (R) and 0.43% for the soluble fraction may be particularly important since spatters may have had the least exposure to environmental U present in meteoric and hydrothermal waters and crustal rocks. As is the case for all samples, laboratory environmental effects cannot be completely ruled out.

The relative ^{235}U enrichments of 0.2% are not inconsistent with the 0.18% relative enrichment reported by Fried et al. However, confirmation of the results must await acquisition of still more data and clarification of the source(s), if not intrinsic, of the isotopic variations observed. Other trace element isotopic measurements have raised questions regarding the mixing, hence homogeneity, of the mantle of the earth over geologic time. These U data, if confirmed, will be pertinent.

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6.0 BIBLIOGRAPHY

- Anderson, Jr., A. T. and Gottfried P. (1972) Hat Creek Basalt, California: similarity to continental and oceanic-type basalts. EOS 53, 547.
- Arden J. W. (1977) Isotopic composition of uranium in chondritic meteorites. Nature 269, 788-9.
- Begemann F. (1980) Isotopic anomalies in meteorites. Reports on Progress in Physics 43, 1309-1356.
- Callis E. L. (1982) Analytical Chemistry in Nuclear Technology, Proceedings of the 25th Conference on Analytical Chemistry in Energy Technology, W. S. Lyon, ed., Ann Arbor Science, Ann Arbor, MI, pp. 115-123.
- Chen J. H. and Tilton G. R. (1979) Preliminary studies of uranium isotopic composition in chondritic meteorites. Lunar Planet. Sci. X, 192-4.
- Chen J. H. and Wasserburg G. J. (1981) Isotopic composition of uranium and lead in Allende inclusions and meteorite phosphates. Earth Planet. Sci. Lett. 52, 1-15.
- Chen J. H. (1987) U, Th, and Pb isotopes in hot springs on the Juan de Fuca ridge. J. Geophys. Res. 92, B11, 11411-15.
- Cowan G. W. and Adler H. H. (1976) The variability of the natural abundance of ^{235}U . Geochim. Cosmochim. Acta 40, 1487-90.
- Essling A. M., Graczyk D. G., and Horwitz E. P. (1988) Isolation and purification of uranium from environmental materials for mass spectrometric analysis. 34th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry, Las Vegas, NV, October 17-21.
- Fried S., Friedman A. M., Callis E., Schreiner F., Hines J., Orlandini K., Nelson D., and Olsen E. (1985) Enrichment of ^{235}U and the concentration of ^{239}Pu in volcanic samples. Nature 313, 301-303.
- Goel P. S. and Thakur A. N. (1987) Isotopically anomalous Hg in meteorites. Meteoritics (50th Annual Meeting, July 1987) 22, (4), 389-390.
- Goel P. S. (1987) Variable $^{190}\text{Os}/^{184}\text{Os}$ ratio in acid residues of iron meteorites. Proc. Indian Acad. Sci. (Earth Planet. Sci.) 96, 81-102.
- Grimanis A. P. and Pertessis-Keis M. (1987) Simultaneous determination of mercury and selenium in biological materials by radiochemical neutron activation analysis. J. Radioanal. Nucl. Chem. 113, 445-451.
- Jovanovic S. and Reed, Jr. G. W. (1976) ^{196}Hg and ^{202}Hg isotopic ratios in chondrites: revisited. Earth Planet. Sci. Lett. 31, 95-100.
- Jovanovic S. and Reed, Jr. G. W. (1976) Interrelations among isotopically anomalous mercury fractions from meteorites and possible cosmological inferences. Science 193, 888-891.
- Jovanovic S. and Reed, Jr. G. W. (1977) Preliminary results on isotopic measurements on trace elements in lunar breccias. Lunar Science VIII, pp. 519-521. Lunar Science Inst., Houston, TX.

- Jovanovic S. and Reed, Jr. G. W. (1977) Hg and Os isotopic variations in lunar breccias. *Trans. Am. Geophys. Union* 58 (6), 431.
- Jovanovic S. and Reed, Jr. G. W. (1987) Isotopically anomalous Hg in Antarctic meteorites. *Meteoritics* (50th Annual Meeting, July 1987) 22, (4), 424-425.
- Jovanovic S. and Reed, Jr. G. W. (1987) Isotopically anomalous ^{196}Hg and ^{202}Hg in Antarctic achondrites. *Geophys. Res. Lett.* 14, (11), 1127-1130.
- Lugmair G. W., Marti K., and Scheinin N. B. (1978) Incomplete mixing of products from K-, P-, and S-process nucleosynthesis: Sm-Nd systematics in Allende inclusion EK 1-04-1. *Lunar and Planet. Sci.* IX, 672-674.
- Nier A. O. and Schlutter D. J. (1987) Mass spectrometric study of the mercury isotopes in the Allende meteorite: A preliminary report. *Proc. 17th Lunar and Planet. Sci. Conf., J. Geophys. Res.* 92, B4, E124-
- Reed G. W., Kigoshi K., and Turkevich A. (1960) Determinations of concentrations of heavy elements in meteorites by activation analysis. *Geochim. Cosmochim. Acta* 20, 122-140.
- Reed G. W. and Jovanovic S. (1969) ^{196}Hg and ^{202}Hg isotopic ratios in chondrites. *J. Inorg. Nucl. Chem.* 31, 3783-3788.
- Sakuragi Y., Meason J. L., and Kuroda P. K. (1983) Uranium and plutonium isotopes in the atmosphere. *J. Geophys. Res.* 88, 3718-3724.
- 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, 4253-4255.
- Tatsumoto M. and Shimamura T. (1979) Evidence for live ^{247}Cm in the early solar system. *Meteoritics* 14, 543-4.
- Tatsumoto M. and Shimamura T. (1980) Evidence for live ^{247}Cm in the early solar system. *Nature* 286, 108-122.
- von Helden J. and Begemann F. (1976) On anomalous Hg in meteorites. *Meteoritics* 11, 297.

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