The Isotopic Constitution of Silicon, Germanium, and Hafnium

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The isotopic constitutions of silicon, germanium, and hafnium have been measured with a mass spectrometer by techniques which are described. Results for silicon are in good agreement with certain of the earlier determinations but are in poor agreement with the values adopted in the recent compilation by Bainbridge and Nier. Results for germanium do not differ significantly from earlier determinations. Results for hafnium differ only slightly from the one previous determination in which electrical detection was used, but in such a way as to suggest that determinations on hafnium which has been fractionally purified with respect to zirconium may not be faithfully representative of the true abundances. An upper limit of 0.003 percent has been placed on the abundance in nature of Hf^{182}.

THE isotopic constitution of the elements silicon, germanium, and hafnium has been measured with a 9-in. radius, 60-degree deflection, single-focusing mass spectrometer recently constructed at Berkeley. In each case the trifluoride ion from electron bombardment of the tetrafluoride was examined. The tetrafluorides were prepared by thermal decomposition of the barium or ammonium complex fluorides, a technique[1] which ensures no isotopic fractionation in the chemistry since the yield of all reactions involved is 100 percent. Prior to all runs, the spectrometer envelope was baked overnight at 350°C so as to reduce the residual hydrocarbon background to a negligible fraction of the peaks measured at any mass position. The ion source was of conventional design, but no source magnet was employed. Magnetic sweep was employed throughout, the ion accelerating voltage being held fixed at 4200 volts. Secondary electrons were repelled to the final collector by application of -45 volt to a repelling electrode. Ion currents were measured by recording the voltage across a 5×10^{10} ohm resistor in the input to a Model 30 Applied Physics vibrating reed electrometer which drove a Brown recording potentiometer. The entire detection system, including input resistor, was checked and found to be perfectly voltage linear within the sensitivity of the procedure which was 0.2 percent. Scale changing multipliers were calibrated with a type K-2 potentiometer.

For analyses of silicon and germanium, the gaseous tetrafluoride was admitted to the ion source through a leak consisting of a 0.001-in. hole in a 0.001-in. aluminum foil from a reservoir wherein the pressure was always such as to ensure pure molecular flow through the leak. The collector slit was adjusted for flat-topped, fully resolved ion peaks and the rate of sweep was kept sufficiently slow that a constant ion current was recorded on the peak top for at least 8 seconds, a precaution which effectively eliminates any errors due to variable sweep speed. A single determination consisted in ten successive sweeps of the spectrum under completely stable conditions. The mean deviation within the sets of 10 ratios so obtained was always less than 0.1 percent.

The data for silicon are presented in Table I and reflect measurements of the ratios of peak intensities to that for Si^{28}. The silicon used was from olivine from dunite (Jackson County, North Carolina). Subsequent research[2] on the variations in isotopic constitution of silicon from various geological sources has detected maximum deviations in the Si^{30}/Si^{28} ratio of only 0.2 percent from that for olivine. It is worthy of mention that in the latter research the mean deviation in the Si^{30}/Si^{28} ratio for olivine, for 39 determinations of this quantity, was 0.05 percent, the determinations extending over a period of several months within which the machine was baked several times and the ion source disassembled and reassembled twice. It is the result of this extreme constancy that the low probable error of about 0.5 percent for the silicon abundance ratios is quoted. Most of this error resides in undetermined, inherent mass discrimination of the spectrometer. Nier[3]

TABLE I. Silicon isotope abundances.

Observer	Ion used	Abundance, atomic percent		
		Si^{28}	Si^{29}	Si^{30}
Present work	SiF_3^+ from SiF_4	92.18±0.03	4.71±0.02	3.12±0.02
Hibbs,[a] 1949	SiF_3^+ from SiF_4	92.19±0.06	4.70±0.03	3.12±0.04
White and Cameron,[a] 1946	SiF_3^+ from SiF_4	92.16±0.06	4.71±0.03	3.13±0.04
Adopted average:[a] Ney and McQueen, Williams, and Yuster, Inghram, 1946	SiF_3^+ from SiF_4	92.27±0.09	4.68±0.05	3.05±0.03

[a] As reported in reference 4.

[1] J. H. Reynolds and T. J. Ypsilantis, Phys. Rev. **90**, 378A (1953).
[2] J. Reynolds and J. Verhoogen, Geochim. Cosmochim. Acta (to be published).
[3] A. O. Nier, Phys. Rev. **79**, 450 (1950).

TABLE II. Germanium isotope abundances.

Observer	Ion used	Abundance, atomic percent				
		Ge^{70}	Ge^{72}	Ge^{73}	Ge^{74}	Ge^{76}
Present work	GeF_3^+ from GeF_4	20.52±0.17	27.43±0.21	7.76±0.08	36.54±0.23	7.76±0.08
Hibbs, Redmond, Gwinn, and Harman,[a] 1949	GeF_3^+ from GeF_4	20.60±0.06[b]	27.38±0.08	7.83±0.06	36.40±0.10	7.78±0.05
Hibbs, Redmond, Gwinn, and Harman,[a] 1949	GeI^+ from GeI_4	20.65±0.04[b]	27.43±0.02	7.86±0.04	36.34±0.05	7.72±0.01
Inghram, Hayden, and Hess,[a] 1947	Ge^+ from Ge	20.55	27.37	7.67[c]	36.74	7.67

[a] As reported in reference 4.
[b] Statistical errors only.
[c] The value 7.61 appearing in reference 4 is the result of a misprint in the original publication of this assay.

reports this to be of the order of 0.4 percent per mass unit in the region of mass 85 for a similar instrument, but using a capillary leak and voltage sweep; it is felt that in the present investigation, using a molecular flow leak and magnetic sweep, the inherent discrimination should be lower. It will be noted that the present results on silicon are in good agreement with determinations made at Oak Ridge by Hibbs and by White and Cameron, but are in rather poor agreement with the values adopted by Bainbridge and Nier[4] in a recent compilation, although the last represent the average of three distinct investigations which were in good agreement with each other.

The data for germanium are presented in Table II and reflect measurements of the ratios of peak intensities to that for Ge^{74}. Shelf germanium dioxide* was the source material. Somewhat higher probable errors in the abundance ratios are quoted because of the fact that fewer determinations were made with this element. Reference to Table II shows that the present results are in slightly better agreement with the GeF_3^+ results of Hibbs than with the other determinations listed there. Discrepancies appear to be random, i.e., not systematic with mass.

For the analysis of hafnium, HfF_4 was sublimed into the electron beam from a stainless steel crucible which was initially loaded with a solid $(NH_4)_2HfF_6$. This compound, when preheated in vacuum, dissociates to form the tetrafluoride. Techniques were those described above except that with the small solid samples used, ion currents were considerably less stable than with the gas samples. This required a faster rate of sweep in order that the time between successive observations of the Hf^{178} reference peak would not be overlong and thus preclude making meaningful corrections, when reading the charts, for drift in ion intensity. Source material was hafnium oxide, 99 percent pure obtained from Research Chemicals, Inc. The data are presented in Table III and reflect measurements of the ratios of peak intensities to that for Hf^{178}. A correction proportional to $(M)^{\frac{1}{2}}$ has been applied to compensate for nonselective evaporation from the solid HfF_4. In addition to the abundance measurements, an upper limit of 0.003 percent, was placed on the abundance in nature of Hf^{182}. Reference to Table III shows random disagreement with the abundances reported by Mattauch and Ewald but systematic disagreement with those reported by Hibbs. The differences with the latter can be improved partially by application of an $(M)^{\frac{1}{2}}$ correction to Hibbs' values (which may be appropriate since he sublimed solid $HfCl_4$ into the ion source) but considerable systematic differences remain. These are possibly attributable to differences in the chemical procedure by which the source hafnium was separated from zirconium. Fractional crystallizations, precipitations, or distillations are the rule in such separations and, depending upon the method used, there would be opportunity for enrichment of either the heavy or the light isotopes in the final hafnium fractions. An unambiguous hafnium assay should probably be made from hafnium which

TABLE III. Hafnium isotope abundances.

Observer	Ion used	Abundance, atomic percent					
		Hf^{174}	Hf^{176}	Hf^{177}	Hf^{178}	Hf^{179}	Hf^{180}
Present work	HfF_3^+ from HfF_4	$0.199\pm^{0.003}_{0.010}$	5.23±0.05	18.55±0.17	27.23±0.22	13.73±0.13	35.07±0.24
Hibbs,[a] 1949	Hf^+ from $HfCl_4$	0.18±0.01[b]	5.15±0.02	18.39±0.01	27.08±0.04	13.78±0.02	35.44±0.06
Mattauch and Ewald,[a] 1944	Hf^+ and Hf^{++} from HfO_2 and Hf (spark)	0.18±0.01	5.30±0.11	18.47±0.06	27.10±0.08	13.84±0.07	35.11±0.14

[a] As reported in reference 4.
[b] Statistical errors only.

[4] K. T. Bainbridge and A. O. Nier, Prelim. Report No. 9, Nuc. Science Ser., National Research Council, 1950 (unpublished).
* Fairmount Chemical Company, "As-free, purest."

has not been highly purified with respect to zirconium.

Note Added in Proof.—Since this article was prepared, there has come to my attention the careful work of Graham[5] and co-workers on the isotopic constitution of germanium. These workers found that, with the exception of one sample, germanium from various ores was isotopically indistinguishable. Their averaged results for the isotopic constitution of six germanium ores, excluding the anomalous sample, can be brought into total agreement with results given here (except at mass 73 where the residual discrepancy is 0.25 percent of the abundance quoted) by application of a factor which reduces their abundances for heavier isotopes relative to the lighter, which is linear with mass, and which amounts to 0.24 percent per mass unit. This factor in all probability represents the relative discrimination of the two mass spectrometers involved. An attempt has been made to detect mass discrimination in this mass region in the Berkeley instrument by comparing measurements on atmospheric xenon with those of Nier,[3] which latter have been corrected for spectrometer discrimination. Agreement was such as to indicate that the mass discrimination of the Berkeley instrument is less than 0.025 percent per mass unit at mass 130.

[5] Graham, Macnamara, Crocker, and MacFarlane, Can. J. Chem. **29**, 89 (1951).

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The Angular Distribution of $Li^6(n,\alpha)H^3$ for Neutrons of 200, 270, 400, and 600 kev*

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The angular distribution of $Li^6(n,\alpha)H^3$ has been measured for neutron energies of 200, 270, 400, and 600 kev by determining the distribution of triton tracks from this reaction in Ilford *C*2 plates loaded with enriched Li^6. The results fit a series of the type $A+B\cos\phi_0+C\cos^2\phi_0$, where ϕ_0 is the neutron-triton angle in the center-of-mass system. This indicates that the *s* and *p* components of the incident neutron wave predominate in the interaction.

(1) INTRODUCTION

THERE are two reasons why an investigation of $Li^6(n,\alpha)H^3$ was undertaken. (1) The use of this reaction to study neutron spectra[1] requires that the differential cross section be known as a function of neutron energy. (2) Basic data of theoretical importance can be obtained.[2] Preliminary results have been reported.[3]

The technique used is to expose Ilford *C*2 plates loaded with enriched Li^6 to unidirectional monoergic neutrons from an electrostatic generator and to measure the distribution of tracks as a function of the neutron-triton angle. Further measurements are now in progress to determine the absolute differential cross section of the reaction for neutron energies from 100 to 2000 kev. These results will be published at a later date.

(2) PLATE EXPOSURE AND PROCESSING

The 100-micron Ilford *C*2 plates loaded with enriched Li^6 were exposed to neutrons from $Li^7(p,n)$ at the electrostatic generator of the Argonne National Laboratory. The exposure geometry is shown in Fig. 1. Each plate was inside a cadmium box during exposure to shield it from the thermal neutron background. Integrated neutron fluxes of approximately 10^9 neutrons/cm^2 were used except for the exposure at 270 kev at the peak of the resonance where approximately 10^8 neutrons/cm^2 were used. All lithium targets were about 30 kev thick. The proton energy was selected so that the neutron groups would peak at 200, 270 kev, etc.

The plates were stored for at least two weeks and then given additional latent-image fading for 24 hours in an atmosphere saturated with water vapor at 22°C. The plates were processed by the technique outlined by Keepin in University of California Radiation Laboratory Report UCRL 790 (unpublished). Some of the plates were also treated with glycerine so as to be

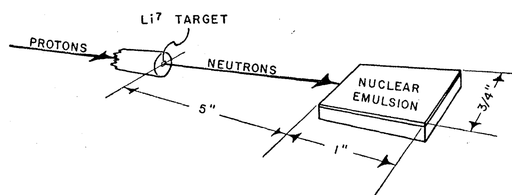

FIG. 1. Exposure geometry for Li^6 loaded plates. Each plate was inside a Cd box to shield it from the thermal neutron background due to room scattering.

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[1] G. R. Keepin, Jr., and J. H. Roberts, Phys. Rev. **76**, 154 (1949); Rev. Sci. Instr. **21**, 163 (1950).

[2] M. Peshkin and A. Siegert, Phys. Rev. **87**, 735 (1952); W. Solano and J. Roberts, Phys. Rev. **89**, 892 (1953).

[3] Roberts, Darlington, and Haugsnes, Phys. Rev. **82**, 299 (1951); J. Roberts and H. Mann, Phys. Rev. **83**, 202 (1951).