REGULAR PAPERS

**Isotopic Abundances of Germanium Determined
by Secondary Ion Mass Spectrometry**

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Isotopic abundances of germanium were determined by secondary ion mass spectrometry. A pellet of 99.999% pure germanium was used as a sample. It was bombarded by 12 keV oxygen primary ion beam whose diameter and current were 70-100 μm and $1-5 \times 10^{-7}\text{A}$ on the sample surface. The isotopic ratios obtained are $^{70}\text{Ge}/^{74}\text{Ge} = 0.58303 \pm 0.00033$, $^{72}\text{Ge}/^{74}\text{Ge} = 0.76341 \pm 0.00028$, $^{73}\text{Ge}/^{74}\text{Ge} = 0.21458 \pm 0.00013$ and $^{76}\text{Ge}/^{74}\text{Ge} = 0.20771 \pm 0.00011$. The isotopic abundances determined are ^{70}Ge : 21.058 ± 0.012 , ^{72}Ge : 27.573 ± 0.011 , ^{73}Ge : 7.750 ± 0.005 , ^{74}Ge : 36.118 ± 0.006 , and ^{76}Ge : 7.502 ± 0.004 in percent.

1. Introduction

The isotopic abundances of germanium have been compiled in a publication by P. De Bievre et al.¹⁾. The abundances distribute in the following range, ^{70}Ge : 20.38–21.106, ^{72}Ge : 27.37–27.670, ^{73}Ge : 7.615–7.86, ^{74}Ge : 36.091–36.74 and ^{76}Ge : 7.449–7.82 in percent.

J.H. Reynolds²⁾ reported in 1953 the isotopic abundances of germanium as ^{70}Ge : 20.52 ± 0.17 , ^{72}Ge : 27.43 ± 0.21 , ^{73}Ge : 7.76 ± 0.08 , ^{74}Ge : 36.54 ± 0.23 and ^{76}Ge : 7.76 ± 0.08 in percent by an electron bombardment ion

source mass spectrometry. He concluded that the abundances had not changed from those published previously by the other investigators.

M. Shima³⁾ also reported in 1963 the isotopic abundances of germanium in 8 meteorites and compared with those in shelf reagent GeO_2 using thermal ionization mass spectrometry. The range of abundances obtained for the meteoritic samples were as follows: ^{70}Ge : 20.76–21.07, ^{72}Ge : 27.60–27.71, ^{73}Ge : 7.53–7.71, ^{74}Ge : 36.14–36.65 and ^{76}Ge : 7.35–7.52 in percent. She concluded that no

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difference was observed between the isotopic abundances of germanium in meteoritic and terrestrial samples outside of the error.

Most recently, in 1986, M. D. Green et al.⁴⁾ reported to be ^{70}Ge : 21.234 ± 0.015 , ^{72}Ge : 27.66 ± 0.015 , ^{73}Ge : 7.72 ± 0.002 , ^{74}Ge : 35.94 ± 0.012 and ^{76}Ge : 7.44 ± 0.006 in percent for a laboratory reference of germanium oxide. and ^{70}Ge : $21.121 - 21.343$, ^{72}Ge : $27.612 - 27.695$, ^{73}Ge : $7.717 - 7.726$, ^{74}Ge : $35.835 - 36.030$ and ^{76}Ge : $7.401 - 7.493$ in percent for 11 terrestrial samples. They used solid-source mass spectrometer with ion enhancing gel-loading technique.

We attempted to determine the isotopic abundances of germanium by secondary ion mass spectrometry (SIMS) and to compare the SIMS data with the above mentioned ones.

2. Experimental

A modified Hitachi IMA-2A ion microprobe mass analyzer with a 12 keV oxygen primary ion beam was used. The current and the diameter of the beam were $2-5 \times 10^{-7}\text{A}$ and $70-100\mu\text{m}$, respectively.

A pellet of pure germanium (99.999%) with a polished surface from Furuuchi

Chemicals Co. of Japan was used as a sample. The sample was cleaned ultrasonically in acetone and mounted in a sample holder. The top surface of the holder was covered with a sheet of tantalum foil with an aperture of about 3mm in diameter at the position of the sample to avoid a mass discrimination due to the uneven geometry of the sample and its surroundings. A cold finger of liquid N_2 temperature was set near the sample holder, which could lower the contributions of interfering molecular ionic species, especially hydride ions, originated from the residual gases of hydrocarbons and water vapor.

Since the mass resolution of the apparatus used in the present work is about 300, most of the ionic species which may interfere with the peaks of germanium isotopes cannot be separated. Therefore, the contributions of possible interfering atomic and molecular ionic species which may overlap with germanium, mass numbers of 70, 72, 73, 74 and 76, were carefully checked. These kinds of ionic species are tabulated in Table I.

Among the elements shown in Table I, Zn, Se, Ce, Nd, Sm and Gd have other isotopes than those in Table I with the abun-

Table I Possible Interfering Atomic and Molecular Ionic Species at Mass Numbers 70, 72, 73, 74 and 76.

mass number	interfering ionic species					
	atomic			molecular		
70	$^{70}\text{Zn}^+$	$^{140}\text{Ce}^{++}$		$^{54}\text{FeO}^+$	$^{59}\text{GaH}^-$	
72		$^{144}\text{Nd}^{++}$	$^{144}\text{Sm}^{++}$	$^{56}\text{FeO}^+$	$^{71}\text{GaH}^-$	$^{40}\text{CaO}_2^-$
73		$^{146}\text{Nd}^{++}$		$^{57}\text{FeO}^-$	$^{72}\text{GeH}^-$	
74	$^{74}\text{Se}^+$	$^{148}\text{Nd}^{++}$	$^{148}\text{Sm}^{++}$	$^{58}\text{FeO}^+$	$^{73}\text{GeH}^-$	$^{42}\text{CaO}_2^-$
76	$^{76}\text{Se}^+$	$^{152}\text{Gd}^{++}$	$^{152}\text{Sm}^{++}$	$^{60}\text{NiO}^-$	$^{75}\text{AsH}^-$	$^{43}\text{CaO}_2^-$

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dances of more than 10%. Since mass peaks originated from such abundant isotopes have never exceeded to be 1.1×10^{-4} to the peak height of $^{74}\text{Ge}^+$ for all of these elements, the contributions of the singly- and doubly-charged atomic ions were concluded to be negligibly small.

As for the molecular ionic species, a peak at mass 56 can be a measure for contributions of FeO^+ and CaO_2^+ . An observed peak height at mass 56 was about 3.1×10^{-4} relative to the peak height of $^{74}\text{Ge}^+$. The production ratio of FeO^+/Fe^+ was measured to be about 0.05 for a pure iron sample. The ratio of $\text{CaO}_2^+/\text{CaO}^+$ was also estimated to be less than 0.05. Therefore, the contributions of FeO^+ and CaO_2^+ are less than 3×10^{-5} of Ge^+ . Nickel oxide ionic species could be neglected since no peak of $^{60}\text{Ni}^+$ was

observed in the same sensitivity as that to detect germanium ions. Not only GaH^+ and AsH^+ but also GeH^+ were concluded to be negligibly small because any peaks at mass numbers 69, 71 and 75 were not observed throughout the present isotopic analysis of germanium.

Accordingly, the contributions of overlapping atomic and molecular ionic species were less than the detection limit under the conditions for germanium isotopic measurement.

A microcomputer-based controlling system which has been devised by Nishimura⁵⁾ was used for the present isotopic analysis. The system has the following capabilities. Those are (1) to switch the scanning speed of electromagnet. (2) to read out peak heights of mass spectra as digital numerals, (3) to

Fig. 1 An example of a mass spectrum obtained for a pure (99.999%) germanium sample from Furuuchi Chemicals Co. of Japan. The current corresponding to the peak height of $^{74}\text{Ge}^+$ is about 9.5×10^{-10} A after amplifying with SEM and 5.9×10^{-11} A at the first dynode of SEM.

calculate intensity ratios, and (4) to make statistical procedures.

Fifteen scans were done in each run. Runs were repeated 3 times. An example of the mass spectrum of germanium over the mass range of 69.5–76.5 is shown in Fig. 1. The detection of the ion current was carried out by using a secondary electron multiplier (SEM) followed by an OP-amplifier feed-backed with a $10^9\Omega$ resistor.

Raw intensity ratios of ${}^m\text{Ge}^+ / {}^{74}\text{Ge}^+$ ($m = 70, 72, 73, 76$) and weighted means (R_{mean}) of three data are listed in Table II. Each value in parenthesis represents the standard deviation of the mean (σ_{mean}) at the last digit. The ratios which were corrected to the ion-to-electron conversion efficiency of SEM were also shown as R_{corr} in the last line of Table II. In the correction, we assumed that the efficiency of SEM for an atomic ion of mass m is inversely proportional to the square root of m , and we used an equation; $R_{\text{corr}} = R_{\text{mean}} (m/74)^{1/2}$ ($m = 70, 72, 73, 76$).

3. Results and Discussion

The isotopic abundances of germanium obtained with SIMS are as follows;

$${}^{70}\text{Ge}/{}^{74}\text{Ge} = 0.58303 \pm 0.00033$$

$${}^{72}\text{Ge}/{}^{74}\text{Ge} = 0.76341 \pm 0.00028$$

$${}^{73}\text{Ge}/{}^{74}\text{Ge} = 0.21458 \pm 0.00013$$

$${}^{76}\text{Ge}/{}^{74}\text{Ge} = 0.20771 \pm 0.00011.$$

From these isotopic ratios, the isotopic abundances (%) of germanium have been evaluated to be

$${}^{70}\text{Ge}: 21.058 \pm 0.012$$

$${}^{72}\text{Ge}: 27.573 \pm 0.011$$

$${}^{73}\text{Ge}: 7.750 \pm 0.005$$

$${}^{74}\text{Ge}: 36.118 \pm 0.006$$

$${}^{76}\text{Ge}: 7.502 \pm 0.004.$$

A comparison of the isotopic abundances of germanium obtained in the present work with those reported by other investigators²⁻⁴⁾ is given in Table III. In the table, the values cited as Shima are the weighted means of 8 data for meteoritic samples.³⁾ The errors given in the second line were calculated for each mean value. The abundances of Green et al. are their raw data for the laboratory reference standard⁴⁾ not to be corrected to the efficiency of SEM.

Permil deviations of the isotopic ratios reported by other investigators from those in the present measurement (R_{corr}) are shown in Fig.2 as a function of mass number. The data of Reynolds fit well to our data except that there exists a positive linear mass

Table II Raw Intensity Ratios for Pure Germanium Sample and Ratios Corrected to Ion-to-Electron Conversion Sensitivity of SEM.

run	70/74	72/74	73/74	76/74
1	0.60150 (54)	0.77581 (37)	0.21586 (17)	0.20484 (24)
2	0.59828 (71)	0.77378 (11)	0.21534 (31)	0.20477 (14)
3	0.59834 (49)	0.77347 (73)	0.21648 (18)	0.20525 (16)
R_{mean}	0.59946 (34)	0.77394 (28)	0.21604 (13)	0.20496 (11)
R_{corr}	0.58303 (33)	0.76341 (28)	0.21458 (13)	0.20771 (11)

$m/74$: raw intensity ratio of ${}^m\text{Ge}^+ / {}^{74}\text{Ge}^+$.

Value in ( ): σ_{mean} error at the last digit.

R_{mean} : weighted mean of 3 data.

R_{corr} : ratio corrected to ion-to-electron conversion sensitivity of SEM.

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Table III Comparison of Isotopic Abundances of Germanium

mass number	70	72	73	74	76
Reynolds ²⁾	20.52 0.17	27.43 0.21	7.76 0.08	36.54 0.23	7.76 0.08
Shima ^{3)**}	20.96 0.02	27.63 0.03	7.67 0.008	36.25 0.01	7.49 0.008
Green et al. ^{4)**}	21.234 0.015	27.662 0.015	7.716 0.002	35.943 0.012	7.444 0.006
present	21.058 0.012	27.573 0.011	7.750 0.005	36.118 0.006	7.502 0.004

* Weighted means for 8 data of meteoritic samples.

** Data reported for laboratory reference standard.

The value given in the second line of each data is an error to the weighted mean.

Fig. 2 Permils deviations of isotopic ratios, ${}^m\text{Ge}^-/{}^{76}\text{Ge}^+$ ($m=70, 72, 73, 76$), which were reported by three other investigators, from our data (R_{corr}) as a function of mass number. Errors were omitted in this figure.

fractionation by about 10 permil per mass unit. This fractionation difference is the residual one after correcting for the ion-to-electron conversion efficiency of SEM. It may be due to a mass dependent fractionation which is related to the secondary ion formation in the sputtering phenomena of a solid sample.

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Keywords

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