VARIATIONS OF THE HAFNIUM-ZIRCONIUM RATIO OF GRANITIC ROCKS FROM EASTERN ONTARIO

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ABSTRACT

Thirty-eight determinations of the Hf/Zr ratio fall on a normal distribution curve with mean value 0.018 and standard deviation 0.0055. Altered varieties of zircon show standard deviations increasing with degree of alteration. The Hf/Zr ratio is characteristic of petrographic provinces. The data may be explained by assuming that alteration took place by diffusion in supercritical water.

INTRODUCTION

There are few recent determinations of the hafnium-zirconium ratio of rocks, and practically none performed on rocks of well known geologic setting (Fleischer, 1955, pp. 1–2). As a result it is difficult to determine the Hf/Zr ratio of different types of rocks. This study attempts to show the variations of the Hf/Zr ratio in the granitic rocks of the Precambrian Grenville province of southeastern Ontario.

Massive and gneissic granitoid rocks compose approximately 70 per cent of the exposed Precambrian rocks in this area. They range in composition from granodiorite to nepheline syenite and in petrologic style from granitized paragneisses to intrusive igneous plugs. Variations of the Hf/Zr ratio with composition or petrologic style should therefore be plainly evident.

EXPERIMENTAL METHOD

A total of 38 specimens were examined, representing approximately one specimen per 100 square miles of granite. Twenty-two specimens were prepared by J. A. Grant, each consisting of about five pounds of rock. The specimen was ground to -100 mesh, separated with tetrabromethane (specific gravity 2.98) and the heavy fraction passed through a Frantz isodynamic separator. This latter not only removed magnetite, ilmenite, pyroxene, and amphibole, but quantitatively removed micas also. The non-magnetic fraction was leached successively with nitric and hydro-

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chloric acid. The residues were almost entirely composed of zircon and further purification was unnecessary. Spectroscopic analysis of the various discarded fractions and of the leach acid showed no detectable zirconium. It is assumed that the hafnium and zirconium are quantitatively concentrated in zircon.

Sixteen specimens were supplied through the courtesy of D. F. Hewitt of the Ontario Department of Mines. These specimens consisted of hand picked zircon concentrates. They were treated by the method described above.

A description of the location and nature of the samples is given in Table 1.

TABLE 1. LOCATION OF SPECIMENS

Number	Rock type	Location
G-4	Granite gneiss	Boulter mass, Cardiff Twp.
5	Syenite	Deer Lake syenite, Cardiff Twp.
6	Granite gneiss	Centre Lake mass, Cardiff Twp.
10	Massive granite	Mayo twp.
12	Granite gneiss	Casey Hill mass, Lyndoch Twp.
15	Granite gneiss	Essonville mass, Monmouth Twp.
17	Nepheline syenite	Harcourt Twp.
21	Massive granite	Kingston Mills
24	Hybrid granite	13 Island Lake, Bedford Twp.
27	Granitized gneisses	Elbow Lake, Hinchinbrooke Twp.
32	Hybrid granite	Perth Road, Loughborough Twp.
41	Massive granite	Silver Lake, Oso Twp.
53	Massive granite	Lyndhurst, Rear of Leeds Twp.
60	Hybrid granite	Enterprise, Camden Twp.
61	Granite gneiss	Kennebec Lake, Kennebec Twp.
62	Granitized gneisses	Elzevir Twp.
64	Hybrid granite	Westport, North Crosby Twp.
90	Hybrid granite	White Lake, Oso Twp.
95	Massive granite	Sand Hill, Front of Leeds Twp.
97	Hybrid granite	Loon Lake, Chandos Twp.
100	Nepheline syenite	Faraday Twp.
Z-1	Nepheline pegmatite	Lot 14/IV Monmouth Twp.
2	Syenite pegmatite	Lot 4/XXI Cardiff Twp.
3	Syenite pegmatite	Lot 33/III Glamorgan Twp.
4	Syenite pegmatite	Lot 2/XVIII Cardiff Twp.
5	Syenite pegmatite	Lot 30/IV Glamorgan Twp.
6	Nepheline pegmatite	Lot 11/IV Monmouth Twp.
7	Nepheline pegmatite	Lot 34/IV Glamorgan Twp.
10	Feldspar mine	Lot 12/II Dungannon Twp.
11	Feldspar mine	Lot 18/VII Monteagle Twp.
12	Granite pegmatite	Lot 30/XV Lyndoch Twp.
13	Nepheline pegmatite	Lot 12/XI Dungannon Twp.
14	Nepheline pegmatite	Lot 9/XIV Dungannon Twp.
15	Granite pegmatite	Lot 14/IV Murchison Twp.
16	Syenite	Rockingham Lake, Brudenell Twp.
17	Granite pegmatite	Lot 25/XV Lyndoch Twp.
18	Granite pegmatite	Lot 17/VI Murchison Twp.
20	Syenite pegmatite (skarn)	Cardiff Uranium Mines

The determination of the Hf/Zr ratios of the zircon concentrates was made on a Philips x-ray fluorescence spectrograph, using a flat LiF crystal. A crude ratio was determined by comparison of the peak heights of the second order $K\beta$ reflection for zirconium and the $L\beta$ reflection for hafnium. These crude ratios were converted into absolute Hf/Zr ratios by means of a calibration curve, constructed using 6 samples of known Hf/Zr ratio. The calibration curve is a straight line in the region of interest (Fig. 1). The calibration results were checked by spectrographic
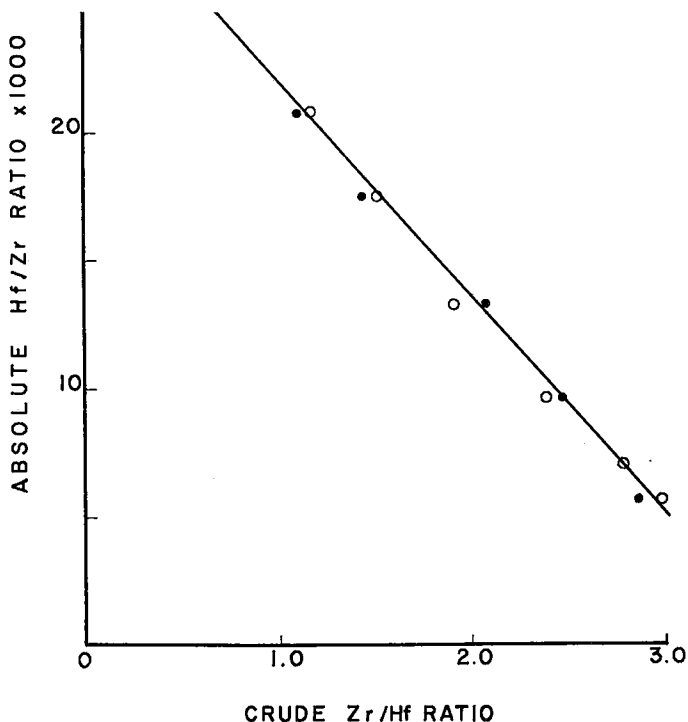

FIG. 1. Calibration curve for the conversion of crude Zr/Hf ratios to absolute Hf/Zr ratios: *Open circles*, x-ray fluorescence analysis, F. Dunphy analyst. *Solid circles*, spectrographic analysis, J. G. McDonald analyst.

analysis. Spectrographic analyses and x-ray fluorescence analyses agree within 10 per cent in all cases, and this is assumed to be the maximum experimental error in the Hf/Zr ratio. The reproducibility of the ratio is distinctly greater for the x-ray fluorescence method than for the spectrographic method. A number of specimens were analysed on the spectro-

graph using strontium carbonate as a flux to determine the content of rare earths, uranium, thorium, and lead.

RESULTS

The results of the x-ray fluorescence analyses are given in Table 2 and presented graphically in Figure 2. The results can be fitted by a normal distribution curve

$$f = (Nk/s \sqrt{2\pi} \, exp(-\tfrac{1}{2}(x - m/s)^2) \tag{1}$$

where f is the frequency of occurrence of a value x, m is the mean value of x, and s the standard deviation of x. The class interval k has been assigned the value 0.004. Analysis of the data by standard methods give $m = 0.018$ and $s = 0.0055$. This curve is compared with a histogram of the data in Figure 2.
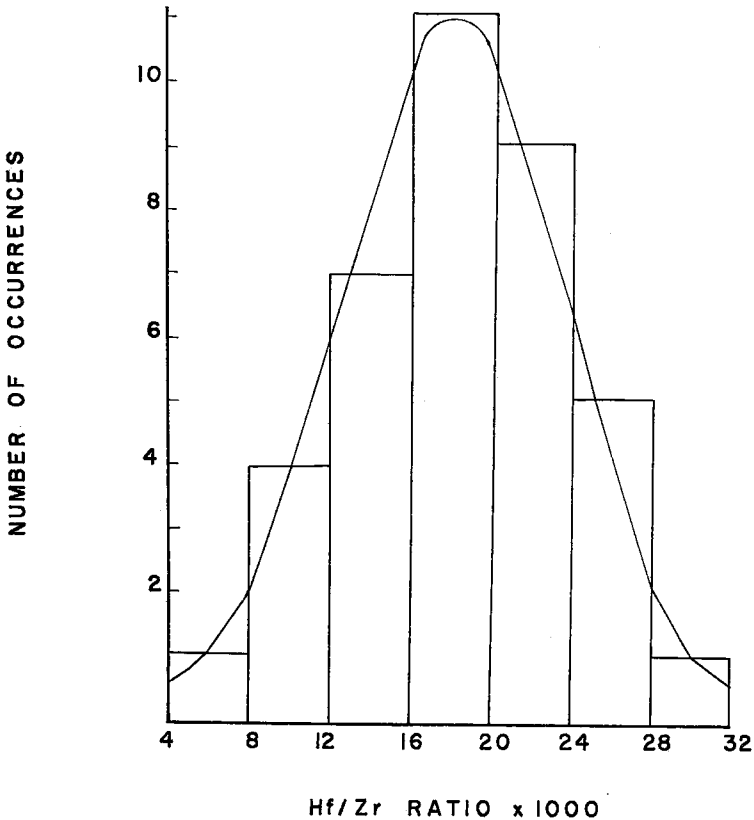

FIG. 2. Histogram of the occurrence of Hf/Zr ratios compared with a fitted normal distribution curve.

TABLE 2. Hf/Zr RATIO OF SPECIMENS

Sample No.	Type of zircon	Petrologic type	Hf/Zr (×100)
G-4	H	L	22
5	H	B	17
6	H	H	21
10	N	F	19
12	M	L	24
15	H	L	17
17	M	L	12
21	N	F	18
24	N	L	22
27	N	L	18
32	H	H	12
41	N	F	21
53	N	F	19
60	H	H	21
61	H	L	9
62	M	L	20
64	M	H	14
90	H	H	16
95	N	L	20
97	N	F	18
100	—	B	9
Z-1	—	B	22
2	—	—	18
3	C	—	6
4	C	—	19
5	C	—	11
6	—	B	13
7	—	B	16
10	—	—	25
11	—	—	25
12	C	—	28
13	—	B	9
14	—	B	14
15	—	—	26
16	—	—	14
17	—	—	21
18	—	—	26
20	—	—	12

ABBREVIATIONS: N—normal zircon, H—hyacinth, M—malacon, C—cyrtolite; B—Bancroft sub-group, nepheline bearing rocks; L—Lennox sub-group, granitized paragneisses; H—Hastings, hybrid granitic rocks; F—Frontenac, massive igneous granite.

The goodness of fit of this curve may be tested by analysing the deviations from it. The chi squared test is applied to the data in Table 3. The extreme class interval have been amalgamated to make the data more homogeneous. There are five class intervals, and therefore $(5-3)$ or two degrees of freedom. Comparing the value of chi squared (0.45) with tables (*Handbook of Chemistry and Physics*, 39th Edition 1957, p. 219) we find that the probability of random errors exceeding observed

TABLE 3. PROBABILITY OF RANDOM ERRORS EXCEEDING OBSERVED ERROR

Class interval	Observed frequency (n)	Theoretical frequency (f)	$\chi^2 = (n - f)^2/f$
0.003–0.011	5	5[a]	0.00
0.012–0.015	7	8	0.13
0.016–0.019	11	11	0.00
0.020–0.023	9	8	0.13
0.024–0.031	6	5	0.20
			$\Sigma\chi^2$ 0.45

[a]Theoretical frequencies have been rounded off to the next whole number. Using fractional values improves the fit slightly.

errors is 80 per cent. The correctness of equation (1) is strongly indicated. Of the 38 specimens, 25 have been classified on the basis of refringence and birefringence into normal, hyacinth, and malacon zircons. Four specimens are classified as cyrtolite on the basis of broadened and weakened x-ray diffraction peaks. The criteria of Winchell (1951 p. 494) were used for the division. The mean value and standard deviation of zircons falling into these groups are shown in Table 4.

TABLE 4. Hf/Zr RATIO OF VARIOUS TYPES OF ZIRCON

Type	No. of specimens	Mean Hf/Zr ratio	Standard deviation
Normal	8	0.019	0.0022
Hyacinth	8	0.018	0.0032
Malacon	4	0.018	0.0044
Cyrtolite	4	0.017	0.0075
Totals	24	0.018	0.0038

On the basis of chemical differences, Grant (1959) divided the granites of southeastern Ontario into four sub-groups; the Frontenac sub-group massive granites, apparently igneous in origin; Hastings sub-group, hybrid rocks with varying amounts of intrusive material; Lennox sub-group, granitized paragneisses; Bancroft subgroup, nepheline syenites and related alkalic rocks. The specimens of Hewitt are mostly from pegmatites and thus do not fit into this grouping. Table 5 shows the Hf/Zr ratio of 27 specimens related to their petrochemical character.

TABLE 5. Hf/Zr RATIOS OF VARIOUS PETROLOGIC PROVINCES

Sub-group	No. of specimens	Mean Hf/Zr ratio	Standard deviation
Frontenac	5	0.019	0.0011
Hastings	5	0.017	0.0032
Lennox	9	0.016	0.0042
Bancroft	8	0.014	0.0046

INTERPRETATION

The mean value of the Hf/Zr ratio of 0.018 is in good agreement with the most recent estimates of 0.020, quoted in Fleischer (1955). The generalization that nepheline syenites have lower Hf/Zr ratios than granites, and that granitic pegmatites have the highest Hf/Zr ratios is also borne out. The average value for 6 nepheline bearing rocks (G-100, Z-1-6-7-13-14) is 0.014, while that for four granite pegmatites (Z-10-12-17-18) is 0.026.

The alteration of normal zircon to hyacinth, malacon, and cyrtolite may be due to radiation damage (Winchell 1951) or to hydrothermal alteration (Poldervaart, 1956). To test the alternatives, spectrographic analyses were run on 29 zircons. These showed that the uranium and thorium content of the four cyrtolites was about equal to that of normal zircon, and that Z-1, a normal zircon, had the highest uranium thorium content. The amount of lead was very small in all specimens, but was highest in G-32, a hyacinth suite. The lack of radioactive material, or radiogenic products in the most highly altered zircons makes the hypothesis of alteration by radiation damage very unlikely for this suite of zircons.

Information on the nature of the alteration process may be deduced from Tables 4 and 5. Table 4 shows that the Hf/Zr ratio changes very slightly under the influence of alteration in the sequence normal zircon to cyrtolite, but that the size of deviations from this mean value increases rapidly with alteration. If the alteration were due to ordinary solution in aqueous liquid, a characteristic progressive change in the Hf/Zr ratio with degree of alteration would be expected, due to the slightly different solubilities of Hf and Zr. From Table 5 we find that a characteristic change in the Hf/Zr ratio is connected with the degree of metasomatism. In igneous granites the Hf/Zr ratio is practically invariant, in agreement with the statement of Mason (1952 p. 116) that this ratio is unchanged by fractional crystallization. As the degree of metasomatism increases, so does the percentage of the lighter element zirconium. The mean deviation and the occurrence of hyacinth and malacon also increase with increasing metasomatism. In fact hyacinth and malacon do not appear in the rocks of most igneous aspect, suggesting that their formation is directly related to matasomatism.

The apparently divergent data of Tables 1, 4, and 5 may reasonably be explained by assuming that alteration took place in supercritical water. This preserves Poldervaart's (1956) hypothesis of the hydrothermal alteration of zircon and introduces no further assumptions, except that the temperature and water pressure during alteration were greater than

374° C and 220 bars respectively. These conditions seem reasonable in a terrain of high metamorphic grade. Diffusion in such a system would lead to mass discrimination because the rate of diffusion in gaseous media is inversely proportional to the mass. Therefore the lighter element, zirconium, should be concentrated in the products of diffusion. If granitized paragneisses (Lennox group rocks) are accepted as such products, this conclusion holds very well, as is seen from Table 5. If an area which is large with respect to any areas of active diffusion within its borders be considered, the mean value of the Hf/Zr would be unchanged by diffusion. The standard deviation, however, will increase rapidly as diffusion produces more and more deviant values. Table 4 illustrates this kind of behaviour, and shows that the large deviations occur in the altered zircons, assumed to be the result of hydrothermal alteration and transport.

CONCLUSIONS

The Hf/Zr ratios of southeastern Ontario granites fall on a normal distribution curve with a mean value of 0.018 and a standard deviation of 0.0055. The latter figure may be slightly too large because of the inclusion of several unusual zircons from the Bancroft area. The type of zircon and the Hf/Zr ratio varies in a characteristic way with the petrologic style of the containing rock. The experimental data may be plausibly explained by assuming that alteration of zircons occurred through the action of supercritical water, and that Hf and Zr were transported by diffusion in supercritical water.

ACKNOWLEDGMENTS

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