Contributions to General Geology 1955

GEOLOGICAL SURVEY BULLETIN 1021

This bulletin was printed as separate chapters A–N

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1958

UNITED STATES DEPARTMENT OF THE INTERIOR

FRED A. SEATON, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

CONTENTS

[The letters in parentheses preceding the titles designate separately published chapters]

	Page
(A) Hafnium content and hafnium-zirconium ratio in minerals and rocks, by Michael Fleischer	1
(B) Hawaiian volcanoes during 1952, by G. A. Macdonald	15
(C) Geologic and airborne radioactivity studies in the Rock Corral area, San Bernardino County, California, by R. M. Moxham, G. W. Walker, and L. H. Baumgardner	109
(D) Hawaiian volcanoes during 1953, by G. A. Macdonald and J. P. Eaton	127
(E) Geology of Comb Ridge and vicinity north of San Juan River, San Juan County, Utah, by J. D. Sears	167
(F) Ordovician and Silurian coral faunas of western United States, by Helen Duncan	209
(G) Some curves from a portable differential thermal analysis unit, by C. J. Parker, J. C. Hathaway, and P. D. Blackmon	237
(H) Annotated bibliography of Alaskan Paleozoic paleontology, by J. Thomas Dutro, Jr	253
(I) Geology of Devils Tower National Monument, Wyoming, by C. S. Robinson	289
(J) The problem of the Cochrane in late Pleistocene chronology, by T. N. V. Karlstrom	303
(K) Geology of the Atomic Energy Commission Nevada proving grounds area, Nevada, by M. S. Johnson and D. E. Hibbard	333
(L) Geology of the area east and southeast of Livingston, Park County, Montana, by P. W. Richards	385
(M) Ordovician fossils from wells in the Williston basin, eastern Montana, by R. J. Ross, Jr	439
(N) Geology of the Clarkdale quadrangle, Arizona, by R. E. Lehner	511

Hafnium Content and Hafnium-Zirconium Ratio in Minerals and Rocks

GEOLOGICAL SURVEY BULLETIN 1021-A

Hafnium Content and Hafnium-Zirconium Ratio in Minerals and Rocks

By MICHAEL FLEISCHER

A CONTRIBUTION TO GENERAL GEOLOGY

GEOLOGICAL SURVEY BULLETIN 1021-A

A compilation of all published determinations of the hafnium dioxide content and the hafnium-zirconium ratio of minerals and rocks

---

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1955

UNITED STATES DEPARTMENT OF THE INTERIOR

Douglas McKay, *Secretary*

GEOLOGICAL SURVEY

W. E. Wrather, *Director*

For sale by the Superintendent of Documents, U. S. Government Printing Office
Washington 25, D. C. - Price 15 cents (paper cover)

CONTENTS

	Page
Abstract	1
Introduction	1
Hafnium and zirconium content and the ratio Hf/Zr in the earth's crust and in rocks	2
Hafnium and zirconium content and the ratio Hf/Zr of minerals	2
Annotated bibliography	11

TABLES

TABLE 1. Estimated abundances of hafnium and zirconium in the earth's crust and the ratio Hf/Zr	3
2. Hafnium and zirconium content and Hf/Zr ratio of rocks	4
3. Composition of minerals listed in tables 4–8	4
4. The hafnium and zirconium content and the Hf/Zr ratio in zircon	5
5. The hafnium and zirconium content and the Hf/Zr ratio in varieties of zircon	7
6. The hafnium and zirconium content and the Hf/Zr ratio in zirconium oxide minerals and ores	8
7. The hafnium and zirconium content and the Hf/Zr ratio in zirconium silicates	9
8. The hafnium and zirconium content and the Hf/Zr ratio in other miscellaneous minerals	10
9. Averages of Hf/Zr ratios of minerals according to source	10

A CONTRIBUTION TO GENERAL GEOLOGY

HAFNIUM CONTENT AND HAFNIUM-ZIRCONIUM RATIO IN MINERALS AND ROCKS

By Michael Fleischer

ABSTRACT

All published data on the hafnium content and hafnium/zirconium ratio in minerals and rocks have been compiled. The Hf/Zr ratio is probably about 0.02 in the earth's crust. Minerals from alkalic rocks such as nepheline syenites have lower Hf/Zr ratios than does zircon from granitic rocks. Minerals from granitic pegmatites have the highest Hf/Zr ratios, especially some peculiar varieties of zircon such as alvite, cyrtolite, and naegite, and the rare scandium silicate, thortveitite, which is the only mineral that is reported to contain more hafnium than zirconium.

INTRODUCTION

This report is a compilation of all published determinations of the hafnium content and the hafnium/zirconium ratio of minerals and rocks. The published literature has been scanned with the aid of the notched-card file on geochemistry of the U. S. Geological Survey. In addition, the following bibliographies on zirconium were checked:

Voress, H. E. and Croxton, F. E., 1951, Zirconium, a bibliography of unclassified literature: U. S. Atomic Energy Commission, TID–3010, 138 p., and supp. no. 1, 17 p.

Williams, G. C., Baker, E. G., Jr., Holzknecht, E. W., and Moody, R. G., 1950, Zirconium and hafnium—a bibliography: U. S. Atomic Energy Commission, NYO–1008, 236 p.

Few of the data are recent. The methods of determination and the estimated error of each study are given in the annotated bibliography. It is probable that determinations of hafnium by purely chemical methods or by determination of the density of the mixed oxides of zirconium and hafnium are of low accuracy.

Most of the determinations cited are by Hevesy and coworkers. Probably some samples are given more than once in the tables, as redeterminations were made on many of their samples. The sample descriptions are inadequate, so that it is not known whether two sets of figures for material from a given locality refer to the same sample or to different samples.

Most of the samples that have been analyzed have not been well characterized as to the type of geological occurrence, so that only a few broad generalizations can be made as to the variation of the hafnium/zirconium ratio in rocks and minerals from different types of deposits. New analyses of carefully selected samples of known geologic setting are highly desirable.

HAFNIUM AND ZIRCONIUM CONTENT AND THE RATIO HF/ZR IN THE EARTH'S CRUST AND IN ROCKS

Estimates of the abundances of zirconium and hafnium are assembled in table 1. It will be noted that most of the recent estimates are the same. The estimates for zirconium are based on the analysis of many samples by Hevesy and Würstlin (1928), but the estimates for hafnium are not so well established. Very few rocks have been analyzed directly for hafnium, as shown in table 2. The estimates for hafnium are based largely on analyses of zirconium minerals, especially of zircon, as given in tables 4–8, and it is uncertain whether the different rock types have been sampled well enough to give confidence in the values given for the ratio Hf/Zr.

HAFNIUM AND ZIRCONIUM CONTENT AND THE RATIO HF/ZR OF MINERALS

The available data are given in table 4 for zircon, table 5 for alvite, cyrtolite, and other similar varieties of zircon, table 6 for baddeleyite and other zirconium oxide minerals, table 7 for zirconium silicates, and table 8 for miscellaneous minerals. A list of the mineral names used in these tables is given in table 3, with the chemical formulas. In each table, the determinations are grouped by minerals and, for each mineral, geographically in the order North America, South America, Greenland, Europe, U. S. S. R., Asia, Australia, and Africa. As the type of deposit is not stated for many of the samples, particularly for zircon in table 4, averaging by type of deposit is not here attempted. It should be noted that all or nearly all the samples of alvite, cyrtolite, and other similar varieties of zircon, listed in table 5, and of thortveitite and other minerals listed in table 8 are from granitic pegmatites, whereas baddeleyite in table 6, and the zirconium silicates, table 7, are all from nepheline syenite pegmatites or similar alkalic rocks. The minerals from granitic pegmatites show very high Hf/Zr ratios; those from alkalic rocks distinctly low Hf/Zr ratios. Hevesy (1925a) and Hevesy and Jantzen (1925) have given averages of their own determinations; these are tabulated in table 9.

Some of the samples that have high ratios of Hf/Zr have high contents of rare earths, uranium, and thorium. There is not, however, a close correlation between radioactivity and hafnium content in most zircons.

In view of the very high Hf/Zr ratios of the pegmatite minerals of tables 5 and 8, it is somewhat surprising that higher ratios are not reported for some of the zircons listed in table 4. New determinations of the hafnium content of zircon separated from analyzed pegmatite rocks, granites, granodiorites, and diorites might help to fill this gap in our knowledge. The Geological Survey, in the course of its work on the determination of geological age by analysis of zircon, has separated such zircon. This should be an excellent collection on which to determine Hf/Zr ratios.

TABLE 1.—*Estimated abundances of hafnium and zirconium in the earth's crust and the ratio Hf/Zr*

No.	Percent by weight		Ratio Hf/Zr	References
	ZrO_2	HfO_2		
1	0.030	0.00058	0.020	(1)
2	.030	.00058	.020	(1)
3	.028	.00058	.021	(1)
4	.031	.0029	.109	(1)
5	.030	.00058	.020	(1)
6	.034	.00047	.016	(1)
7	.031	.0029	.109	(1)
8	.031	.0029	.109	(1)
9	.035	.0035	.115	(1)
10	------	------	.034	Hevesy (1925a).
11	------	------	[2] .020	Hevesy and Würstlin (1928).

[1] Quoted in Fleischer (1953) from the following: 1. Mason, 1952; 2. Rankama and Sahama, 1950; 3. Polanski, 1948; 4. Anderson, 1945; 5. Goldschmidt, 1937; 6. Fersman, 1933; 7. Schneiderhöhn, 1934; 8. Berg, 1929; 9. Clarke and Washington, 1924.

[2] Ratio, $\frac{HfO_2}{ZrO_2+HfO_2}$.

TABLE 2.—*Hafnium and zirconium content and Hf/Zr ratio of rocks*

No.	Material	Percent by weight		Ratio Hf/Zr	References
		ZrO_2	HfO_2		
1	Average ultramafic rock	0.008			Hevesy and Würstlin (1928).
2	Average gabbros	.019			Do.
3	Average diorites	.038			Do.
4	Average granites	.062			Do.
5	Rapakivi granites [1]	.12	0.0028	0.027	Sahama (1945).
6	Igneous rocks [2]	.026	.00038	.017	Hevesy (1931).
7	Estimated average, eruptive rocks	.039	.001	.029	Tröger (1935).
8	Zinc sulfide ore, Saxberg, Sweden [3]	.019	.0001	.008	Landergren (1935).

[1] Spectrographic determination on a mixture of 34 granites.
[2] X-ray spectroscopic determination on a mixture of 300 igneous rocks that contained 56.3 percent SiO_2.
[3] Spectrographic determination on ore that contained 30 percent SiO_2.

TABLE 3.—*Composition of minerals listed in tables 4–8*

Mineral	Composition
Alvite [1]	$ZrSiO_4$ containing rare earths, BeO, U, and Th.
Baddeleyite	ZrO_2.
Caldasite	Zirconium oxide ore, chiefly baddeleyite.
Catapleite	$(Na_2,Ca)ZrSi_3O_9.2H_2O$.
Cyrtolite	*See* alvite.
Elpidite	$Na_2(Zr,Ti)Si_6O_{15}.3H_2O$.
Eudialyte-eucolite	$(Ca,Na)_5Zr_2Si_6(O,OH,Cl)_{20}$.
Euxenite	$(Y,Ce,U)(Nb,Ta,Ti)_2(O,OH)_6$.
Favas	Pebbles in gravel. Commonly baddeleyite, may also be zircon.
Fergusonite	$(Y,Er)(Nb,Ta)O_4$.
Hagatalite	*See* alvite.
Malacon	*See* alvite.
Naegite	*See* alvite.
Oyamalite	*See* alvite.
Pitchblende	UO_2 with UO_3, ThO_2.
Polymignite	$(Ca,Fe,Y,Zr)(Nb,Ta,Ti)O_4$.
Pyrochlore	$(Ca,Na)(Nb,Ti)_2O_6(OH,F)$.
Rosenbuschite	$(Ca,Na)_3(Zr,Ti)Si_2O_8F$.
Thalenite	$Y_2Si_2O_7$.
Thortveitite	$(Sc,Y)_2Si_2O_7$.
Wöhlerite	$NaCa_2(Zr,Nb)Si_2O_8(O,OH,F)$.
Yamagutilite	*See* alvite.
Zircon	$ZrSiO_4$.
Zirkelite	$(Ca,Fe)(Zr,Ti)_2O_5(?)$.
Zirkite	Commercial name for zirconium oxide ore.

[1] Alvite, cyrtolite, hagatalite, malacon, naegite, oyamalite, and yamagutilite are names given to varieties of zircon. Some of the names are not well defined, but in general they apply to varieties of zircon that contain appreciable water and may contain rare earths, uranium, thorium, beryllium, and P_2O_5. Some of this material may not be zircon.

TABLE 4.—*The hafnium and zirconium content and the Hf/Zr ratio in zircon*

[Methods of analysis are designated as follows: C, Chemical separation as phosphate; D, Hf content computed from density of mixed oxides $(Zr,Hf)O_2$; S, Spectrographic; XS, X-ray spectroscopic]

No. and locality	Percent by weight		Ratio Hf/Zr	Method of analysis	References
	ZrO_2	HfO_2			
1. Connecticut		1.0		XS	Hevesy and Jantzen (1925).
2. North Carolina, Henderson County.		4.0		XS	Hevesy (1925b); Hevesy and Jantzen (1925).
3. Do		1.3		XS	Hevesy and Jantzen (1923).
4. Do			0.016	S	Cooley and others (1953).
5. Do		1.0		D	Prandtl, Mayer, and Büttner (1937).
6. Florida			.027	S	Cooley and others (1953).
7. Pennsylvania, Berks County			.026	S	Do.
8. Oklahoma [1]	[2](66.5)	1.1	[2](.018)	S	Larsen, Waring, and Berman (1953).
9. Do [3]	[2](59.5)	.8	[2](.016)	S	Do.
10. Do	[2](59.7)	.6	[2](.011)	S	Do.
11. Oregon, Coos Bay			.023	S	Cooley and others (1953).
12. Ontario			[4].010	XS	Hevesy and Würstlin (1928).
13. Ontario, Renfrew		.6		XS	Hevesy and Jantzen (1925).
14. Ontario, Eganville		1.2		XS	Hevesy (1925b); Hevesy and Jantzen (1925).
15. Brazil			.008	S	Cooley and others (1953).
16. Do			.015	S	Do.
17. Do			.010	S	Do.
18. Do	63.7	1.3	.023	XS	Hevesy and Jantzen (1923).
19. Do		1.0		XS	Hevesy and Jantzen (1925).
20. Brazil, Minas Gerais		1.0		XS	Do.
21. Brazil, Minas Gerais, Poços de Caldas.		1.8		XS	Do.
22. Do		1.0		D	Prandtl, Mayer, and Büttner (1937).
23. Do			[4].014	C	Loewenstein (1952).
24. Do			[4].014	C	Do.
25. Do			[4].017	C	Do.
26. Do			[4].017	C	Do.
27. Do			[4]0	C	Do.
28. Brazil [5]	64	.4	.007	XS	Hevesy (1925b).
29. Greenland		3		XS	Hevesy and Jantzen (1923).
30. Greenland, Narsarsuk		.8		XS	Hevesy (1925b); Hevesy and Jantzen (1925).
31. Austria, Carinthia	65	4	.07	XS	Hevesy (1925b); Hevesy and Jantzen (1923).
32. France, Espailly	64.23	1.8	.032	XS	Hevesy and Jantzen (1923).
33. Do		1.1		XS	Hevesy and Jantzen (1925).
34. Do		.7		XS	Do.
35. Do	64.83	1.2	.021	XS	Hevesy (1925b).
36. Italy, Lonedo		.7		XS	Hevesy and Jantzen (1925).
37. Do		.7		XS	Do.
38. Italy, Novale		.9		XS	Do.
39. Italy, Vesuvius		.7		XS	Do.
40. Italy, Vicenza		.8		XS	Hevesy (1925b).
41. Do		1.8		XS	Hevesy and Jantzen (1923).
42. Norway	60.55	3.5	.066	XS	Do.
43. Norway, Brevik	63.05	1.0	.018	XS	Hevesy (1925b).
44. Norway, Frederiksvärn	63.96	2.8	.05	XS	Hevesy and Jantzen (1923).
45. Do	65.2	1.0	.018	XS	Hevesy (1925b).
46. Norway, Langesundfjord		1.7		XS	Hevesy and Jantzen (1923).
47. Do		2.2		D	Prandtl, Mayer, and Büttner (1937).
48. Norway, Larvik		6		XS	Hevesy and Jantzen (1923).
49. Do			[2].035	XS	Hevesy and Würstlin (1928).
50. Portusok			[2].015	XS	Do.
51. Avigait			[2].021	XS	Do.
52. Schluchtsee [6]			[2].026	XS	Do.
53. Do [7]			[2].0024	XS	Do.
54. U. S. S. R		.2		XS	Borovsky and Blochin (1937b).
55. Do		.24		XS	Do.
56. Do		.35		XS	Do.
57. Do		.35		XS	Do.
58. Do		.5		XS	Do.
59. Do		.5		XS	Do.
60. Do		.6		XS	Do.
61. Do		.6		XS	Do.
62. Do		.6		XS	Do.
63. Do		.6		XS	Do.
64. Do		.7		XS	Do.
65. Do		.7		XS	Do.
66. Do		.7		XS	Do.
67. Do		.8		XS	Do.
68. Do		.8		XS	Do.
69. Do		1.2		XS	Do.
70. Do		1.2		XS	Do.
71. Do		1.3		XS	Do.

See footnotes at end of table.

TABLE 4.—*The hafnium and zirconium content and the Hf/Zr ratio in zircon*—Continued

No. and locality	Percent by weight		Ratio Hf/Zr	Method of analysis	References
	ZrO_2	HfO_2			
72. U. S. S. R.[8]	46	1.0	0.029	XS	Borovsky and Blochin (1937a).
73. Do	44	.7	.021	XS	Do.
74. Do	59	.7	.016	XS	Do.
75. Do		1.0		XS	Do.
76. Do		.5		XS	Do.
77. Do		.8		XS	Do.
78. Do		.7		XS	Do.
79. U. S. S. R., Botogolski		.5			Kostyleva (1946).
80. U. S. S. R., Kukisvumchorr		.7-1.0			Do.
81. U. S. S. R., Mariupol		.5			Do.
82. U. S. S. R., Poachvumchorr	66	1.6	.028	XS	Borovsky and Blochin (1937a).
83. U. S. S. R., Sludyanka (with allanite).		.5			Kostyleva (1940).
84. U. S. S. R., upper Tulia River.	66	1.0	.018	XS	Borovsky and Blochin (1937a).
85. U. S. S. R., Ural Mts., Ilmen Mts.		1.0		D	Prandtl, Mayer, and Büttner (1937)
86. U. S. S. R., Ural Mts., Miask	59.92	5.4	.10	XS	Hevesy and Jantzen (1923).
87. Do	64.22	1.1	.020	XS	Hevesy (1925b); Hevesy and Jantzen (1925).
88. U. S.S. R., Rojkow Kluitsch		.5		XS	Hevesy (1925b).
89. U. S. S. R., Vishnevye Gory		.9		XS	Borovsky and Blochin (1937b).
90. India			.020	S	Cooley and others (1953).
91. Do	62.3	2.7	.05	XS	Hevesy and Jantzen (1923).
92. India [5]	64	1.2	.021	XS	Hevesy (1925b).
93. Ceylon		2.0		XS	Hevesy and Jantzen (1923).
94. Do		2.7		XS	Hevesy (1925b); Hevesy and Jantzen (1925).
95. Do		1.0		D	Prandtl, Mayer, and Büttner (1937).
96. Ceylon [9]		2.1		XS	Hevesy and Jantzen (1925).
97. Ceylon, Walawe Ganga		2.0		D	Prandtl, Mayer, and Büttner (1937).
98. Siam	60-67	3.5	.060-.067	XS	Hevesy and Jantzen (1924).
99. Do		4		XS	Hevesy (1925b).
100. Korea, Chinpyong-ni	66.0	.79	.014	XS	Kimura and Tanaka (1936).
101. Korea, Pokchin-san	63.4	1.9	.034	XS	Do.
102. Taiwan, Keelung River			.025		Do.
103. Australia			.019	S	Cooley and others (1953).
104. Do		4.5		D	Prandtl, Mayer, and Büttner (1937).
105. Australia, Queensland			.015	S	Cooley and others (1953).
106. Tasmania		1.1		XS	Hevesy (1925b).
107. Madagascar		3		XS	Hevesy and Jantzen (1923).
108. Do		.9		XS	Hevesy and Jantzen (1925).
109. Do		.7		D	Prandtl, Mayer, and Büttner (1937).
110. Madagascar, Diego Suarez		.8		XS	Hevesy (1925b); Hevesy and Jantzen (1925).
111. Madagascar, Mesatanana		2.0		D	Prandtl, Mayer, and Büttner (1937).
112. Nigeria		2.3		D	Do.
113. Unknown		6		XS	Hevesy and Jantzen (1923).

[1] Fresh.
[2] Analysis for ZrO_2 made on materials from the same locality similar to but not identical with the sample analyzed for Hf.
[3] Metamict.
[4] Ratio, $\frac{HfO_2}{ZrO_2+HfO_2}$.
[5] Placer.
[6] Acid rocks.
[7] Basic rocks.
[8] Zircon ores.
[9] Beccarite.

NOTE.—In addition to above references *see* Morgan and Auer (1941).

TABLE 5.—*The Hafnium and zirconium content and the Hf/Zr ratio in varieties of zircon*

[Varieties of zircon: (A), alvite; (C), cyrtolite; (H), hagatalite; (M), malacon; (N), naegite; (O), oyamalite; and (Y), yamagutilite. Methods of analysis: D, By density of oxides; XS, X-ray spectroscopic]

No. and locality	Varieties of zircon	Percent by weight		Ratio Hf/Zr	Method of analysis	References
		ZrO_2	HfO_2			
1. United States	(C)	40	9	0.26	XS	Hevesy and Jantzen (1923).
2. United States, Rockport, Mass.	(C)	--------	>10	[1] .22	XS	Hevesy and Würstlin (1928).
3. Do	(C)	44	17	.44	XS	Hevesy (1925b).
4. United States, Bedford, N. Y.	(C)	--------	ca. 5	[1].09-.11	XS	Hevesy and Würstlin (1928).
5. Ontario, Parry Sound	(C)	--------	2.36	--------	XS	Hevesy (1931).
6. Norway, Kragerö	(A)	34	16	.54	XS	Hevesy and Jantzen (1923).
7. Do	(A)	--------	3	--------	XS	Do.
8. Do	(A)	--------	8	--------	XS	Do.
9. Do	(A)	--------	15	--------	XS	Do.
10. Do	(A)	41.98	4.6	.13	XS	Hevesy (1925b).
11. (?)	(A)	41.92	4.66	.13	XS	Bedr-Chan (1925).
12. (?)	(A)	--------	5.9	--------	XS	Borovsky and Blochin (1937b).
13. Norway, Gjersted	(A)	--------	9	--------	XS	Hevesy and Jantzen (1923).
14. Norway, Hitterö	(M)	62.8	5	.088	XS	Hevesy and Jantzen (1924).
15. Do	(M)	65.18	2.6	.046	XS	Hevesy (1925b).
16. Norway, Risör	(A)	--------	10	--------	XS	Hevesy and Jantzen (1923).
17. Norway, southern	(A)	47.9	[2] 5.5	.13	D	Prandtl and others (1937).
18. Do	(A)	48.4	[2] 6.0	.14	D	Do.
19. U. S. S. R., Ilmen Gory	(M)	--------	.8	--------	--------	Kostyleva (1940).
20. U. S. S. R., Blumovskaya	(M-C)	--------	1.8	--------	--------	Do.
21. U. S. S. R., Karelia	(C)	--------	2.3	--------	XS	Hevesy (1931).
22. Do	(C)	--------	1.8	--------	--------	Kostyleva (1940).
23. U. S. S. R., Rozhkov Klucz	(M)	--------	2.6	--------	--------	Do.
24. U. S. S. R., Zap. oleniya varakh.	(C)	47.82	1.70	.041	--------	Kostyleva (1946).
25. Japan, Hagata	(H)	39.7	2.3	.066	--------	Harada (1936).
26. Japan, Mino	(N)	48.30	7	.17	XS	Hevesy and Jantzen (1923).
27. Japan, Naegi	(N)	49.8	3.5	.08	XS	Hevesy (1925b).
28. Japan, Oyama	(O)	38.7	2.2	.065	--------	Harada (1936).
29. Japan, Yamaguti	(Y)	ca. 40.2	ca. 3.4	.097	--------	Do.
30. Madagascar	(M)	--------	7	--------	XS	Hevesy and Jantzen (1924).
31. Do	(M)	53.2	4	.086	XS	Hevesy (1925b).
32. Madagascar, Ahi-Kambana	(M)	--------	2.0	--------	D	Prandtl and others (1937).

[1] Ratio, $\frac{HfO_2}{ZrO_2+HfO_2}$.

[2] It is stated in this reference that the oxides recovered from a large amount of these samples contained 2.2 percent HfO_2.

NOTE.—In addition to the above references *see* Morgan and Auer (1941).

TABLE 6.—*The hafnium and zirconium content and the Hf/Zr ratio in zirconium oxide minerals and ores*

[Methods of analysis: C, Chemical fractionation of phosphates; D, By density of mixed oxides; S, Spectrographic; XS, X-ray spectroscopic]

No.	Name of mineral and locality	Percent by weight		Ratio Hf/Zr	Method of analysis	References
		ZrO_2	HfO_2			
1	Baddeleyite, Brazil	97.1	1.8	0.021	XS	Hevesy and Jantzen (1923).
2	do	97.7	1.2	.014	XS	Hevesy (1925b).
3	Baddeleyite, Brazil, fava	92.42	.7	.009	XS	Do.
4	do	91.12	2	.025	XS	Hevesy and Jantzen (1923).
5	do	59	.5	.010	XS	Hevesy (1925b).
6	do	74	.5	.008	XS	Do.
7	Baddeleyite, Brazil, fava, shell	59	1	.019	XS	Hevesy and Jantzen (1923).
8	Baddeleyite, Brazil, fava, core	74	1	.015	XS	Do.
9	Baddeleyite, Brazil, Poços de Caldas.			.013	S	Cooley and others (1953).
10	do		2.1		D	Prandtl and others (1937).
11	do	73.2	1.1	.017	C	Loewenstein (1952).
12	do	92.1	1.4	.017	C	Do.
13	Fava, Brazil, Poços de Caldas			[1] .002	C	Do.
14	do			[1] .024	C	Do.
15	Caldasite, Brazil, Poços de Caldas.			[1] .022	C	Do.
16	do			[1] .034	C	Do.
17	do			[1] .041	C	Do.
18	Zirkite ore, Brazil			.012	S	Cooley and others (1953).
19	Baddeleyite, Colorado (sic) [2]			.068	S	Do.
20	ZrO_2 reagent			.010	S	Do.
21	Polymignite, Norway, Frederiksvärn.	28.71	.9	.036	XS	Hevesy and Jantzen (1923; 1924).
22	do	29.11	.6	.024	XS	Hevesy (1925b).
23	Zirkelite, Brazil	51.7	1.2	.026	XS	Hevesy and Jantzen (1924).
24	Zirkelite, Ceylon	51.89	1	.022	XS	Hevesy (1925b).

[1] Ratio, $\frac{HfO_2}{ZrO_2+HfO_2}$.

[2] Baddeleyite is not known from Colorado, U. S. A.

TABLE 7.—*The hafnium and zirconium content and the Hf/Zr ratio in zirconium silicates, analyzed by X-ray spectroscopic methods*

No.	Name of mineral and locality	Percent by weight		Ratio Hf/Zr	References
		ZrO_2	HfO_2		
1	Catapleite, Greenland	30.65	0.2	0.007	Hevesy and Jantzen (1923).
2	Do	31.53	.3	.011	Hevesy (1925b).
3	Catapleite, Norway	31.52	.3	.011	Do.
4	Catapleite, U. S. S. R., upper Tulia River.	30.5	.6	.023	Borovsky and Blochin (1937a).
5	Catapleite, U. S. S. R	----------	.35	----------	Borovsky and Blochin (1937b)
6	Do	----------	.1	----------	Do.
7	Catapleite, U. S. S. R., Pereval Lopar.[1]	----------	ca .3	----------	Kostyleva (1940).
8	Eudialyte, Greenland	14.30	.19	.015	Hevesy and Jantzen (1923).
9	Eudialyte, Greenland, Narsarsuk	12–16	.2	.014–.019	Hevesy and Jantzen (1924).
10	Do	12–16	.6	.042–.057	Do.
11	Do	12–20	.2	.019	Hevesy (1925b).
12	Eudialyte, Greenland, Kangerdluarsuk.	14.32	.17	.014	Do.
13	Eudialyte, Norway	14.47	.7	.055	Hevesy and Jantzen (1923).
14	Eudialyte, Norway, Barkevik	12.21	.2	.019	Hevesy (1925b).
15	Eudialyte, U. S. S. R., Kola Peninsula.	13	.2	.017	Borovsky and Blochin (1937a).
16	Do	19	.3	.018	Do.
17	Do	13	.3	.026	Do.
18	Do	----------	----------	[2] .021	Hevesy and Würstlin (1928).
19	Do	----------	.1	----------	Hevesy (1925b).
20	Eudialyte, altered, U. S. S. R., Poachvumchorr.[1]	30	.4	.015	Kostyleva (1940).
21	Eudialyte, U. S. S. R	13.5	.12	.010	Borovsky and Blochin (1937b).
22	Do	2.0	.12	.069	Do.
23	Do	2.7	.12	.051	Do.
24	Do	----------	.2	----------	Do.
25	Do	----------	.1	----------	Do.
26	Do	----------	.06	----------	Do.
27	Do	----------	.35	----------	Do.
28	Do	----------	.12	----------	Do.
29	Do	----------	.06	----------	Do.
30	Do	----------	.06	----------	Do.
31	Do	----------	.06	----------	Do.
32	Elpidite, Greenland, Narsarsuk	20.1	.4	.023	Hevesy and Jantzen (1924).
33	Elpidite, Greenland, Narsarsuk	20.28	.2	.011	Hevesy (1925b).
34	Rosenbuschite, Norway, Langesund.	19.80	.3	.017	Do.
35	Wöhlerite, Norway, Langesund	17.55	.7	.046	Hevesy and Jantzen (1923).
36	Do	----------	----------	[2] .031	Hevesy and Würstlin (1928).
37	Wöhlerite, Norway, Barkevik	15.61	.5	.037	Hevesy (1925b).

[1] Method of analysis not given.

[2] Ratio, $\frac{HfO_2}{Z_2O_2+HfO_2}$.

TABLE 8.—*The hafnium and zirconium content and the Hf/Zr ratio in other miscellaneous minerals, all analyzed by X-ray spectroscopic methods*

No.	Name of mineral and locality	Percent by weight		Ratio Hf/Zr	References
		ZrO_2	HfO_2		
1	Thortveitite, Norway, Iveland	1.2	2.0	1.9	Hevesy and Jantzen (1924).
2	Do			[1].20	Hevesy and Würstlin (1928).
3	Do	2	.5	.29	Hevesy (1925b).
4	Thortveitite, Norway, Unneland	.8	1.1	1.6	Hevesy and Jantzen (1924).
5	Thortveitite, Madagascar, Befanamo.	2.2	1.8	.94	Do.
6	Do	2.0	3.2	1.8	Do.
7	Do	1.3	1.0	.88	Hevesy (1925b).
8	Thalenite, Sweden, Österby		.13	.26	Hevesy and Würstlin (1928).
9	Pyrochlore, Sweden, Alnö	2.8	ca .1	ca. 04	Hevesy and Jantzen (1924).
10	Do	2.90	Tr.		Hevesy (1925b).
11	Pitchblende			[1].019	Hevesy and Würstlin (1928).
12	Fergusonite and euxenite			[1].05-.06	Do.

[1] Ratio, $\frac{HfO_2}{ZrO_2+HfO_2}$.

TABLE 9.—*Averages of Hf/Zr ratios of minerals according to source*

[Data from Hevesy (1925a) and Hevesy and Jantzen (1925)]

Mineral	Table no.[1]	Ratio Hf/Zr
Nepheline syenite minerals		
Baddeleyite	6	0.014
Baddeleyite, favas	6	.008
Catapleite	7	.011
Elpidite	7	.011
Eudialyte	7	.011
Polymignite	6	.023
Rosenbuschite	7	.017
Wöhlerite	7	.034
Zircon	4	.017
Granitic minerals		
Alvite	5	.13
Cyrtolite	5	.46
Malacon	5	.08
Naegite	5	.46
Thortveitite	8	.57
Zircon	4	.049

[1] The table numbers refer to this report.

ANNOTATED BIBLIOGRAPHY

Bedr-Chem, Safder, 1925, Analyse des Alvits: Zeitschr. anorg. allg. Chemie, v. 144, p. 304–306.

An X-ray spectroscopic analysis by Jantzen is given for a sample of alvite, locality not stated.

Borovsky, I. B., and Blochin, M. A., 1937a, Definition of hafnium in zirconium minerals of the U. S. S. R.: Acad. sci. U. R. S. S. Bull., Sér. géol., p. 185–193. [Russian with English summary.]

X-ray spectroscopic analyses are given of 14 samples. The accuracy of the analyses was not known as no pure zirconium was available, but analyses of similar mixtures of tantalum and tungsten were accurate within about 11 percent.

——— 1937b, The analysis of minerals by the X-ray spectroscopic method: Acad. sci. U. R. S. S. Bull., Sér. géol., p. 929. [Russian with English summary.]

Analyses are given of 31 samples. The accuracy is estimated to be within about 10 percent.

Cooley, R. A., Martin, A. V., Feldman, C., and Gillespie, J., 1953, The hafnium to zirconium abundance ratio and specific radioactivity of some ores: Acta geochim. et cosmochim., v. 3, p. 30–33.

Hafnium and zirconium were separated chemically from ores and their ratio was determined spectrographically for 14 samples by the porous cup method. The abundance ratios are believed to be accurate to ±5 percent.

Fleischer, Michael, 1953, Recent estimates of the abundances of the elements in the earth's crust: U. S. Geol. Survey Circ. 285, 7 p.

A compilation.

Harada, Zyunpei, 1936, Chemische analysenresultate japanischen Mineralien [Chemical analyses of Japanese minerals]: Hokkaido Imp. Univ. Fac. Sci. Jour., Ser. 4 Geol. and Mineral, v. 3, p. 221–362.

Six analyses of the hafnium content of minerals are quoted. See especially pages 296–299.

Hevesy, Georg v., 1925a, Chemical and physical properties of hafnium. Discovery and properties of hafnium: Chem. Rev., v. 2, p. 1–41.

A review. Averages are given for the HfO_2/ZrO_2 ratio of minerals.

——— 1925b, Recherches sur les propriétés du hafnium [Research on the properties of hafnium]: K. danske vidensk. Selsk., Math. fys. Medd. 6, no. 7, 149 p.

A detailed review, which gives many determinations of the ZrO_2 and HfO_2 content of minerals.

——— 1931, Chemistry and geochemistry of the titanium group: Chem. Soc. London Jour., p. 1–16.

A review.

Hevesy, Georg v., and Jantzen, V. T., 1923, The hafnium content of zirconium ores: Chem. Soc. London Jour., v. 123, p. 3218–3223; the same paper was published in Zeitschr. anorg. allg. Chemie, v. 133, p. 113–118, 1924.

X-ray spectroscopic analyses, with tantalum as internal indicator, are given for 31 samples.

Hevesy, Georg v., and Jantzen, V. T., 1924, Hafnium content of zirconium ores: Chem. News, v. 128, p. 341–342.

X-ray spectroscopic analyses are given for 13 samples.

——— 1925, The hafnium content of zirconium ores: Chem. News, v. 130, p. 179–180.

X-ray spectroscopic analyses are given for 20 zircon samples for which radioactivity, helium content, and specific gravity had previously been determined. There was no direct relationship between the radioactivity and the hafnium content.

Hevesy, Georg v., and Würstlin, K., 1928, Ueber das Hausfigskeitverhältnis Zirkonium/Hafnium und Niob/Tantal [The abundance ratios zirconium/hafnium and niobium/tantalum]: Zeitschr. physikal. Chemie, v. 139A, p. 605–614.

Previous work is summarized and some new determinations are given.

Kimura, Kenjiro, and Tanaka, Kazuo, 1936, The chemical analysis of zircon from Chinpyong-ni and Pokchin-san, Korea, with a supplement on the hafnium content in Japanese zirconium minerals: Chem. Soc. Japan Jour., v. 57, p. 1205–1207.

Analyses by the X-ray spectroscopic method are given for zircon associated with graphite, sphene, scapolite, and phlogopite at Chinpyong-ni, Korea, and from nepheline syenite at Pokchin-san, Korea. The ratio HfO_2/ZrO_2 is given for one other zircon sample and for five unusual zircon samples (naegite type).

Kostyleva, E. E., 1940, The geochemistry of hafnium in the U. S. S. R.: Trudy Inst. Geol. Nauk no. 39; Mineral.-Geokhim. Ser. 8, p. 41–47 [Russian with English summary]; Chem. Abs., v. 37, p. 6607 (1943).

Previous work is summarized and some new determinations of HfO_2 are given.

——— 1946, The metamict state of minerals of the zircon group [in Russian]: Fersman Memorial Vol., Acad. sci. U. R. S. S., p. 27–35.

An analysis of cyrtolite from Zap. Oleniya varakh, Karelia, is given.

Landergren, Sture, 1935, Bidrag till kännedomen om vara sulfidmalmers geokemi [Contribution to the knowledge of our sulfide ores]: Geol. fören. Förh., v. 57, p. 626–636.

Spectrographic analysis of zinc sulfide ore from Saxberg containing about 11 percent Zn, 30 percent SiO_2, gave Zr 140 g/ton, Hf 1 g/ton.

Larsen, E. S., Jr., Waring, C. L., and Berman, Joseph, 1953, Zoned zircon from Oklahoma: Am. Mineralogist, v. 38, p. 1118–1125.

Spectrographic analyses were made on fresh and metamict zircon from pegmatite in granite. The fresh zircon contained 0.9 percent Hf; 2 samples consisting chiefly of metamict zircon contained 0.7 and 0.5 percent Hf. Chemical analysis of similar fresh zircon gave 67.6 percent ZrO_2 a + HfO_2, of similar metamict material gave 60.3 percent ZrO_2+HfO_2.

Lee, O. I., 1928, Mineralogy of hafnium: Chem. Rev., v. 5, p. 17–37.

A review, in which Hevesy's determinations are quoted.

Spectrographic analyses are given, in terms of the relative intensities, of a pair of Hf–Zr lines. The results are as follows:

No.	Mineral	Locality	Ratio intensity Hf/Zr
1	Zircon [1]	Minnesota	0.52
2	do [1]	Andover, N. J	.41
3	do [1]	Mellen, Wis	.53
4	do	Wausau, Wis	(2)
5	do [1]	Oxford, Manitoba	.45
6	do [1]	do	.30
7	do [1]	do	.25
8	do [1]	do	.53
9	Malacon	Cheyenne Canyon, Colo	.26
10	Cyrtolite	Bedford, N. Y	.51
11	Malacon	Hybla, Ontario	.42
12	Alvite	Helle, Norway	.70

[1] In granite.
[2] Trace of hafnium.

Loewenstein, Walter, 1952, Estudos sôbre as propriedades quimicas dos minerais de zirconio da região de Poços da Caldas, Minas Gerais [Chemical properties of zirconium from Poços da Caldas, Minas Gerais]: Univ. São Paulo, Fac. fil., cienç. e letras Bol. 147, Mineral. no. 9, p. 41–74.

Chemical analyses of 12 samples of zircon and baddeleyite were made by fractional precipitation as phosphate.

Morgan, J. H., and Auer, M. L., 1941, Optical, spectrographic, and radioactivity studies of zircon: Am. Jour. Sci., v. 239, p. 305–311.

As no determinations of the absolute content of zirconium and hafnium were made, these can be related to the determinations given in tables 4 and 5 only if no. 10 above is assumed to contain about 5 percent HfO_2 (table 5). If so, the zircon samples listed above have remarkably high hafnium content.

Prandtl, Wilhelm, Mayer, Georg, and Büttner, Leonhard, 1937, Über die Trennung von Hafnium und Zirkonium. II. Die Rolle der Phosphorsäure in der Chemie des Zirkoniums [The separation of hafnium and zirconium. II. The role of phosphoric acid in the chemistry of zirconium]: Zeitschr. anorg. allg. Chemie, v. 230, p. 419–426.

Analyses by the determination of the density of the mixed oxides, $(Zr,Hf)O_2$, are given for 14 samples.

Sahama, T. G., 1945, On the chemistry of the east Fennoscandian rapakivi granites: Comm. géol. Finlande Bull. 136, p. 15–67.

Spectrographic analysis of a standard mixture of 54 rapakivi granites gave 0.12 percent ZrO_2, 0.0028 percent HfO_2.

Tröger, E., 1935, Der Gehalt an selteneren Elementen bei Eruptivgesteinen [The content of rare elements in eruptive rocks]: Chemie der Erde, v. 9, p. 286–310.

Eruptive rocks are estimated to contain on the average 0.039 percent ZrO_2, 0.001 percent HfO_2.

O