SPECTROCHEMICAL STUDIES ON SOME BRAZILIAN ZIRCONS

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RESUMO

O presente trabalho estuda a variação da relação Hf/Zr e a variação da concentração de HfO_2, Y_2O_3 e ThO_2 em várias amostras de zircão, a maioria delas provenientes de pegmatitos.

Na primeira parte descreve-se o método espectroquímico usado para tôdas as determinações e na segunda parte são apresentados os resultados obtidos para 27 amostras de pegmatito e 4 de aluvião. Foram estudadas também 7 amostras de zircão e de outros silicatos de zircônio provenientes de rochas alcalinas.

O pegmatito de Rio Piracicaba e os da região de São João del Rei, Minas Gerais, revelaram possuir relações Hf/Zr anômalas, variando de 0,130 a 0,290, com o conteúdo de HfO_2 alcançando um máximo de 11,0%. Os resultados analíticos obtidos em partes mais frescas e em partes mais alteradas de dois agregados cristalinos e também em amostras individuais de um mesmo pegmatito sugerem haver uma perda de háfnio em relação ao zircônio devido a alteração do mineral.

INTRODUCTION

In view of the need for information on the hafnium/zirconium ratio in minerals, considering its geochemical features and significance as a source of primary materials for nuclear reactors, the Instituto de Pesquisas Radioativas resolved to undertake a research program in this particular field.

This paper discusses the spectrochemical method followed along with the results obtained so far in the study of specimens from the State of Minas Gerais and elsewhere in Brazil.

Zirconium and hafnium possess similar chemical properties and invariably occur together. Methods for the recovery of hafnium-free zirconium have only recently been developed. Zirconium is of great significance in nuclear technology due to high resistance to corrosion and low thermal neutron cross-section, (0,178 barns). Contrariwise, hafnium has an extremely high cross section, (120 barns), that makes it unfit for zirconium alloys required in nuclear reactors. This very feature, however, added to high mechanical resistance and resistance to corrosion at high temperatures, renders hafnium an efficient control element in nuclear reactors, when high thermal neutron cross-section is required.

The Hf/Zr ratio plays a decisive part when nuclearly pure zirconium is needed. Hence there is a necessity to know more about it, with work starting preferably from minerals which have the lowest hafnium percentage compared with zirconium. Inversely, minerals of high Hf/Zr ratio are preferred for the production of hafnium.

From the geochemical standpoint, the study of the Hf/Zr ratio and absolute HfO_2 content in some zirconium bearing minerals is of great interest. Rankama and Sahama, (1950, page 567), assert that there is no independent hafnium-bearing mineral, zircon beeing the chief source of the element. Zirconium and hafnium constitute the most perfect "geochemically coherent pair" of the whole periodic table.

Thanks are due to Clécio Campi Murta for X-ray determinations of some minerals species and to Milton Campos for the preparation of a synthetic sample that was used to check the accuracy of the method described in this paper. Thanks are also due to C. Bruno Conti for this English translation and to Norman Herz, U. S. Geological Survey, for his critical reading of the manuscript.

Some of the work was carried out in the Laboratory of Spectrochemistry of the Instituto de Tecnologia Industrial de Minas Gerais, using equipment of the Conselho Nacional de Pesquisas.

METHOD OF ANALYSIS

The inadequacy of chemical procedure por Hf/Zr determination has led to the use of X-ray fluorescence, and emission spectroscopy. All data available on hafnium geochemistry has resulted from these two techniques. In ordinary chemical determination of rocks and minerals, what is reported as "ZrO_2" is, in effect, the sum of two oxides: $ZrO_2 + HfO_2$.

The main papers on hafnium and zirconium spectrochemistry were reviewed by Ahrens (1950) and recently by Waring and Worthing (1956).

The spectrochemical method for determination of the Hf/Zr ratio in minerals, described in this paper is aimed chiefly at the following points:

1. The great variation of this ratio in the minerals under study, (0.005 to 0.30);

2. The variety of minerals to be analysed. (Matrix composition in rare earths, thorium, iron, silicon, zirconium and sodium can vary considerably, as in cyrtolite, baddeleyite, eudyalite, etc.);

3. The possibility of obtaining a maximum of information from each spectrogram (as the absolute percentage of HfO_2, ZrO_2, ThO_2 and Rare Earths).

EXCITATION CONDITIONS AND SAMPLE PREPARATION

High sensitivity was attained in a D. C. arc of 17 amperes. Zirconium and hafnium being highly refractory, volatilization in the D. C. arc is erratic and there is a tendency to form Zr and Hf hard-burning carbides. The main consequence of this is low reproductibility.

To obviate this drawback, several tests were made with mixtures of sample and pegmatite-graphite base. This diluent has been employed in this Laboratory for several years as a spectrographic buffer. Pegmatite base as spectrographic diluent was first used by K. J. Murata of the U. S. Geological Survey and subsequently described in several publications. (Gordon and Murata 1952, Dutra and Murata 1954, Bastron and others 1960)

The mixture of 1 part sample plus 7 parts pegmatite base and 8 parts graphite powder, burns smoothly in 17 Amperes DC arc current giving neither refractory beads nor flashes characteristic of zirconium burning completely in 80 to 90 seconds. Observations made by menas of cases, due to its good reproductibility of exposures.

Using 20 mgs of this mixture in the crater of an undercut electrode only 1,25 mgs of zirconium mineral is introduced in the arc column, burning completely in 80 to 90 seconds. Observations made by means of moving plate technique showed that an exposure made over 90 seconds emits no Zr and Hf line whatsoever.

The pegmatite diluent proved efficient in eliminating the influence of matrix on the IHf/IZr ratio. This matter was studied taking into account the Y, U, Th, Fe added in certain quantities to a zircon from Guarapari (State of Espírito Santo) of known Hf/Zr ratio, diluting the mixture in 1:7 pegmatite base, plus 8 parts graphite. The small discrepancy reported in Table No. 1 cannot be considered derived from matrix influence, since the values recorded lie within the limits of experimental error. The influence ascribed a larger or smaller amount of SiO_2, Al_2O_3, Na_2O in zirconium-bearing minerals was neglected here, for, as major components of the pegmatite base, they cannot be attributed any variation of matrix.

TABLE N.° 1

Zircon Sample	Dilutions	IHf 3012902 / IZr 3013321		Hf/Zr
Guaraparí	1+7pb+8g(*)	0,480	Average of 5 determinations	0,0278
Guaraparí + 2% Fe_2O_3 5% Y_2O_3 3% ThO_2 1% U_3O_8	1+7pb+8g	0,468	Average of 5 determinations	0,0271

(*) pb — Pegmatite base
g — Graphite powder

Deviation in percent: — 2,5%

STANDARDS

To synthetize all standards, zirconium and hafnium oxides were obtained from Chemical Commerce, Newark, N. J., believed to be the purest available. Zirconium oxide was certified to contain 44 ppm Hf, and hafnium oxide, 0.15% Zr only. A spectrogram revealed no hafnium line in zirconium oxide, while spectrochemical quantitative analysis of the Zr content in hafnium oxide, using zirconium standards in pegmatite base containing Th as internal standard verified 0.15% Zr as correct.

From these two oxides, two primary standards were synthetized, one of which contained known quantities of Y_2O_3 and ThO_2.

Standard N.º 1: 60% ZrO_2 + 40% SiO_2 (clear quartz crystal)
Standard N.º 2: 60% HfO_2 + 15% Y_2O_3 + 8% ThO_2 + 17% SiO_2

Synthetic standards no. 1 and 2 were mixed in different proportions in order to obtain 9 intermediate standars with Hf/Zr ratios and elements content varying in the following range:

Hf/Zr ratio	0,68	to	0,0044	%
Y_2O_3	7,5	to	0,058	%
ThO_2	4,0	to	0,031	%
HfO_2	30,0	to	0,23	%

In computing the Hf/Zr ratio of each standard, the correction of residual Hf and Zr from original oxides was duly taken into account. The sum of the two, HfO_2 + ZrO_2, is constant and equals 60% in all standards which is the average concentration found in all minerals studied.

Each and all of the 9 resulting standards was then mixed with the diluent, always in the given proportion of 1 part standard, 7 parts pegmatite base, 8 parts graphite powder.

LINES USED AND PHOTOMETRY

Lines selected were among those least subject to interference and most likely to meet, as far as possible, the requirements already established for a good internal standard: nearness of wave-length and similar excitation conditions. To cover the whole Hf/Zr ratio range, two pairs of lines were used, all of them belonging to singly ionized atoms.

Absolute HfO_2, Y_2O_3, ThO_2 concentrations were determined without internal standard, plotting the intensity of each line against concentration. Analytical lines are shown in Table N.º 2, which gives the concentration interval for which they were used and analytical curves are shown in Figures 1 and 2.

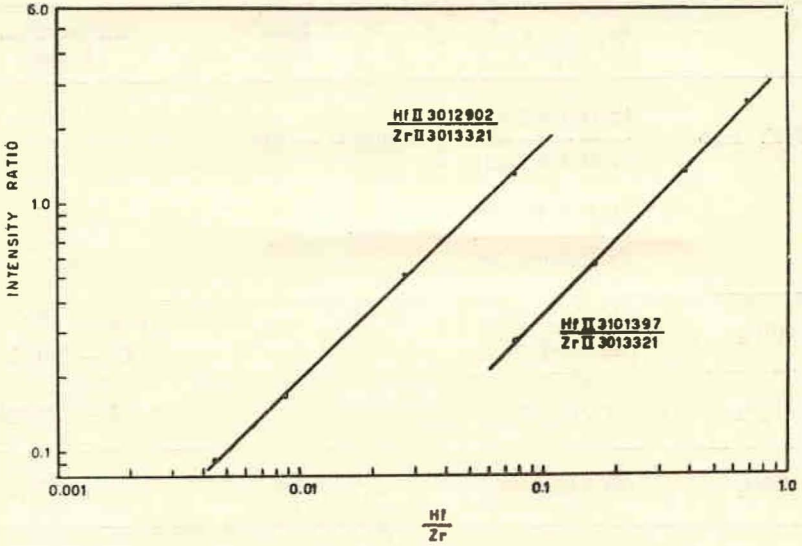

Figure 1. — Working curves for the determination of Hf/Zr ratio

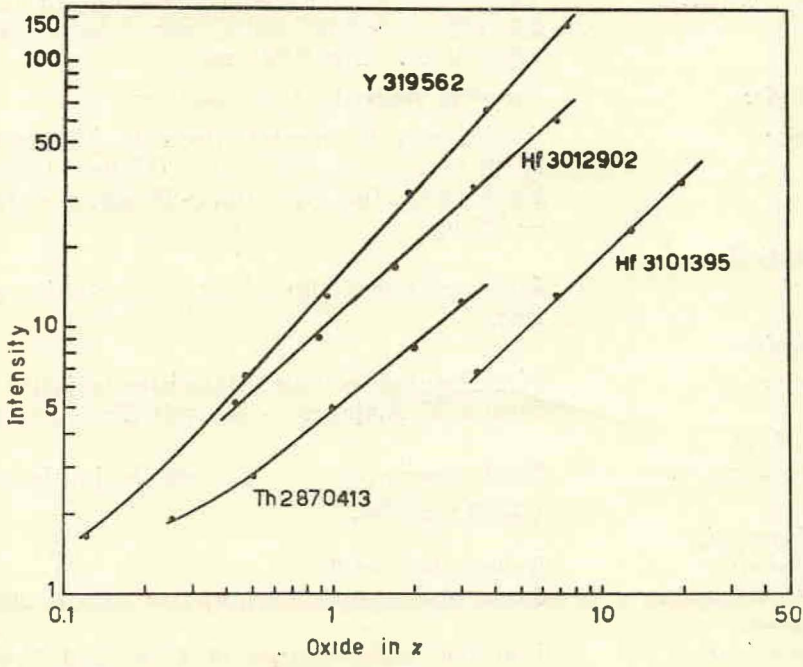

Figure 2. — Working curves for the determination of Y_2O_3, HfO_2 and ThO_2

TABLE N.º 2 — LINES USED

	Wavelength (A)	Ratio Range	Concentration Range
Hf/Zr ratio	Hf II 3 012 902 / Zr II 3 013 321	0,0044 — 0,08	
	Hf II 3 101 397 / Zr II 3 013 321	0,08 — 0,68	
% HfO_2	Hf 3 012 902		0,23 — 7.0%
	Hf 3 101 397		4,0 — 20,0%
% Y_2O_3	Y 319 562		7,5 — 0,058%
% ThO_2	Th 2 870 413		4,0 — 0,25%

OPERATING CONDITIONS

Spectrograph: Three meter grating spectrograph, Eagle mount, 2.5 A/mm, second order, wave-length range 2720-3400A. Slit 0.025 mm.

Cathode: Graphite electrode, 1/8" diameter.

Anode: Preformed 1/4" Graphite electrode, with crater 3/12 inch deep, undercut. (United Carbon Products Co. Inc. type 101-L) Weight of charge — 20 mg.

Analytical Gap: 4mm maintained throughout the excitation period.

Excitation Source: Manufactured by Baird Associates, adjusted to furnish 17 Amperes — 250 volt direct-current.

Length of Exposure: Total consumption of the sample in the arc (± 80 seconds).

Photographic Emulsion: Kodak plate SA-1

Microphotometer: Jarrell-Ash comparator-projector (Model 200)

Emulsion Calibration: Iron line group method of Dieke and Crosswhite, (1943)

ACCURACY

Accuracy of the procedure was ascertained by samples analysed by another method, and by an unknown synthetic sample.

Dr. Isidore Adler, U.S. Geological Survey, kindly supplied two zircon specimens analysed by X-Ray fluorescence, while Dr. Milton Campos, Instituto de Pesquisas Radioativas, Belo Horizonte, gave invaluable assistance by synthetizing a sample from pure oxides.

Results are given in Table No. 3.

TABLE N.º 3 — DATA ON ACCURACY

Samples	Hf/Zr ratio		
	X-Ray Fluorescence (Adler, USGS)	Expected value	This spectrochemical method
Zircon * z-5510	0,026	—	0,027 — 0,028
Zircon * z-554	0,012	—	0,012 — 0,013
Synthetic Sample	—	0,119	0,113 — 0,110

* Standard samples supplyed by the USGS.

Maximum probable error of each determination has been ascertained to be of the order of 8%. The validity of the working curves was proved in scores of plates, with but a slight eventual modification in slope; a careful calibration of photographic emulsion brings such modification down to the minimum possible, so that the same curve can be used a considerable number of times, pending a mere occasional check by standards.

Photographing the spectrum in the second order, the separation between Hf II 3012902 and Zr II 3013321 Å lines becomes greater, while line/background ratio and sensitivity increase.

ANALYTICAL RESULTS

Results presented in this paper were obtained from 38 zircon analyses of samples mostly from the State of Minas Gerais. Hafnium/zirconium ratios, as well as contents in HfO_2, Y_2O_3, ThO_2, are recorded.

ZrO_2 percentage was calculated considering both HfO_2 content and Hf/Zr ratio. Some water determinations were also made to assess the degree of weathering of minerals.

Pegmatite zircons are described in Table N.º 4; other varieties are given in Table N.º 5; alluvial zircons are shown in Table N.º 6.

Zirconium minerals from alkalic rocks are shown in Table N.º 7.

All samples were pure, mostly hand-picked under a binocular lens from concentrates of heavy minerals. In certain cases, zircons were carefully separated in groups of different color; in others, according to apparent degree of alteration.

Michael Fleischer compiled in 1955 a list of all works on the distribution of hafnium in rocks and minerals, published up to that date, computing the Hf/Zr ratio found in 113 zircons, in 32 varieties of zircon, in 37 other silicates and in 24 samples of oxides. The maximum, minimum, and average, Hf/Zr ratios, in zircons, given in this work, are 0.100, 0.0024, 0.027, respectively. Maximum and minimum HfO_2 content in zircons is given as 6.0% and 0.2%, while the average in 91 specimens is 1.44%.

In a recent paper, John B. Mertie Jr. (1958), besides reporting Hf/Zr ratio found in 33 zircons from granites and alluvium in the United States, makes reference to four Russian publications on this subject.

In zircons from North-American granites and alluvium, and also in 6 other specimens from other countries, Mertie found none possessing either a very high or a very low ratio, and stated the average as 0.0242 in all granites studied. The four Russian publications mentioned above gave the results of 94 zircons from various rocks, giving the maximum and minimum Hf/Zr ratios as 0.082 and 0.005, respectively. The general average is 0.0242 for all 94 specimens.

Most zircons described in the present paper are from pegmatites some of them revealing anomalous Hf/Zr ratio. The pegmatite from Rio Piracicaba, and those from São João del Rei, provided the most samples, the reason for such preference being that the first samples sent to the Laboratory revealed an exceptionally high Hf/Zr ratio and HfO_2 content so that further study of additional material from the same source seemed desirable. The first 8 samples of Rio Piracicaba pegmatite gave 0.22, 0.14, 0.172 as maximum, minimum, and average Hf/Zr ratio, and 10.5, 4.2, 7.6 maximum minimum and average HfO_2 percentage.

The highest Hf/Zr values were found in material that was either fresh or slightly altered. Small fresh crystals from a large (9 cm) crystalline aggregate, (Sample no. 5), contained the least amount of H_2O, ThO_2 and Y_2O_3 along with the highest Hf/Zr ratio, (0.22). The more hydrated portions of the same aggregate, which contained higher Y_2O_3, ThO_2 contents, possessed lower ratios: 0.165 and 0.180. Hafnium

loss due to mineral alteration was also noted in another crystalline Aggregate (minerals N.º 7 and N.º 8, Table N.º 4). The lowest Hf/Zr value obtained for this pegmatite, (0.138), was from a thoroughly altered zircon (malacon), Sample no. 6, containing 9.47% H_2O, 2.1% ThO_2, and 0.56% Y_2O_3. X-Ray observation of this zircon showed no diffraction line, further evidence of complete structural disorder.

The São João del Rei area pegmatites furnished 11 samples, 3 of which were from saprolite. These pegmatites are mined for cassiterite, tantalite, and djalmaite, but also yield a remarkable amount of spodumene. Guimarães and Belezkij (1956) made a detailed geologic survey of the region.

The maximum, minimum and average Hf/Zr figures found in 8 samples collected directly from these pegmatites were 0 290, 0.190, 0.242, the hafnium content being 11.0%, 3.5%, 8.4%. Analytical results from the 3 saprolites were not entered in these calculations, because these sources generally yield granite zircons, known to possess a lower Hf/Zr ratio.

Since the zircons from the São João del Rei area were found to vary in hue, though homogeneous in size and crystalline form, a preliminary classification was attempted, (Sample N.º 10), according to color. Five different types were hand-selected and analysed. Each fraction revealed unlike Hf/Zr ratios, ranging 0.26 to 0.225, while ThO_2 attained 10.0 to 0.2%, and Y_2O_3 ranged 0.30 to 1.03%.

The Hf/Zr ratio in these São João del Rei samples diminishes together with a decrease of $HfO_2 + ZrO_2$ totals, which drop from 59.7 to 38.0%. Loss of hafnium in relation to zirconium, due to mineral alteration, is thus suggested once more.

Most samples from the São João del Rei area were obtained through the courtesy of the D.N.P.M. plant for the recovery of cassiterite. Thus, it was impossible to correlate the sample with its parent pegmatite which would have provided useful data in checking the possible fractionation of hafnium compared with zirconium during cooling of the pegmatitic liquor. An investigation of this kind, however, is under way for the Rio Piracicaba pegmatite.

As pointed out, zircons from the Piracicaba River and São João del Rei pegmatites reveal, as a whole, an unusual hafnium content. Noteworthy is the fact that only one zircon has been reported up to date with a HfO_2 content over 11.0% or a Hf/Zr ratio above 0.29, as described in this paper. This is the case of the zircon recently studied by Levinson and Borup (1960), stated to contain 24% HfO_2 and a Hf/Zr ratio equalling 0.65. This zircon was found included in a sample of the extremely rare mineral thortveitite from Iveland, Norway.

Table 5 refers to two varieties of zircons. The cyrtolite from Córrego Tatu displayed zones of distinct colors suggesting varying alteration

TABLE 5 VARIETIES OF ZIRCON

Sample Nr.	DESCRIPTION	Hf/Zr	HfO_2%	ZrO_2% (calculated)	Y_2O_3%	ThO_2%	H_2O%	Other Rare Elements
26	Yttrian-Zircon (Ribeirite), Macarani pegmatite, Bahia, as described by Florencio (1952); sample supplied by W. Florencio	0,0735	3,1	48,5	2,28	2,05	8,40	Total Rare(*) Earth: 7,30%
27	Altered-Zircon (Cyrtolite), Córrego do Tatu pegmatite, Serro, M.G., sample collected by Luciano Jacques de Moraes.	0,078	3,4	50,0	1,05	4,30	7,05	Total Rare(*) Earth: 12,25%
28	Altered-Zircon (Cyrtolite), from the same locality	0,079	3,6	52,7	1,05	4,00	7,00	Yb, Gd, Ce La, Er, P
29	Altered-Zircon (Cyrtolite); red oxidation outer part of sample Nr. 28	0,080	3,5	50,3	1,30	4,00		do
30	Altered-Zircon (Cyrtolite); non oxidized light-gray core of sample Nr. 28	0,080	3,5	50,3	1,05	3,40		do
31	Altered-Zircon (Cyrtolite); intergrown yellow spots extracted from sample Nr. 30	0,080	3,5	50,3	0,82	3,90		do

(*)Chemical determination by Fernando Peixoto.

TABLE 4 — ZIRCON FROM PEGMATITE

Sample Nr.	DESCRIPTION	Hf/Zr	HfO_2%	ZrO_2% (calculated)	Y_2O_3%	ThO_2%	H_2O%	Other rare Elements
1	Pale brown crystal, 1 cm. long, collected in a tantalite bearing pegmatite, Morro Agudo, Rio Piracicaba district, M.G.	0,148	7,2	55,5	0,34	1,40		Yb, Bi
2	Crystalline aggregate, cauliflower in shape, consisting mostly of fresh material, Morro Agudo, Rio Piracicaba district, M.G.	0,210	10,5	57,4	0,30	1,45	1,55	Yb
3	Central part of a large brownish gray crystalline aggregate, cauliflower like in shape, (radiating prisms), Rio Piracicaba district, M.G.	0,180	9,0	57,2	0,22	2,10	0,80	Yb
4	Tapered altered portion from sample Nr. 3	0,165	6,6	46,0	0,27	1,40		
5	Small clear crystals, almost transparent, from sample Nr. 3, (diagonally opposit the sample Nr. 4)	0,220	10,3	54,0	0,16	0,40	0,50	
6	Amorphous pale brown material (malacon) giving no X-ray pattern, Morro Agudo, Rio Piracicaba district, M.G.	0,138	6,0	49,8	0,56	2,10	9,47	Yb, Gd, P.
7	Brownish gray least altered portion of a large crystalline aggregate giving good X-ray pattern· Morro Agudo, Rio Piracicaba district, M.G.	0,173	7,0	46,5	0,26	1,30		Yb
8	Light brownish gray, most altered portion of sample Nr. 7	0,140	4,2	33,4	0,28	2,00		Yb
9	Small euhedral crystals white to purple in color, from a tantalite and cassiterite bearing pegmatite, Nazareno district, M.G.	0,290	10,5	41,7	0,46	0,46		Sn, Nb, Ta, Yb, Bi.
10	Small euhedral crystals of unlike colors from DNPM cassiterite concentration plant of Nazareno, M.G. (Original ore from Volta Grande pegmatite, S. João Del Rei, M. G.	0,250	9,8	45,0	0,61	1,32		Sn, Nb, Ta, Bi, Yb
11	Euhedral crystals, moderate orange pink only, picked from sample Nr. 10, (Volta Grande, S. João Del Rei, M.G.)	0,260	11,0	48,7	0,56	0,21		Ta, Nb, Bi, Yb
12	Ditto pale red purple only. (This fraction more abundant)	0,250	10,8	49,7	0,60	0,39		Ta, Yb,
13	Ditto yellowish gray only	0,240	9,4	45,0	1,03	6,80		Yb, Bi
14	Ditto grayish black only	0,230	6,4	32,0	0,57	0,23		Ta, Nb, Yb, Bi
15	Ditto pale red only	0,225	6,0	30,7	0,76	10,00		
16	Small euhedral crystals of different colors, separated from quartz tailing of DNPM electrostatic concentration plant, Nazareno, M.G.	0,190	3,5	21,4	0,30	1,15		Yb, Ta
17	Pink and transparent crystals separated from a pegmatite saprolite, Fazenda Coqueiros, S. João Del Rei, M. G. (Beleskije and Guimarães, 1956).	0,021	1,21	65,0	0,13	0,20		Yb, Ta
18	Concentrated of zircons, heterogeneous in size, shape and color, from a pegmatite saprolite, Fazenda Coqueiros, São João Del Rei, M. G.	0,029	1,62	64,2	0,31	ne*		Yb, Ta
19	Heterogeneous zircon concentrate from a pegmatite saprolite, Paiol Mine, Santa Rita, M.G.	0,045	1,35	34,5	1,05	2,00		Yb, Sn
20	Homogeneous crystals collected in a beryl-cassiterite bearing pegmatite, Fazenda das Porteiras, Salinas, M.G.	0,076	3,5	53,0	0,75	0,61		Yb, Sn
21	From the same locality	0,075	3,8	58,0	0,40	0,27		Yb, Sn
22	Small homogeneous light gray, euhedral crystals, collected from a monazite-tantalite bearing pegmatite, Fazenda Julio Drumond, Ferros, M.G.	0,082	3,5	49,0	5,50	0,62		Yb, Gd, La Ce
23	Crystals associated with bismutite, "Alto Onça", Paraiba, as described by Rolff (1946)	0,080	4,0	57,5				Bi, Cu, Yb
24	Crystals associated with bismutite, "Alto Feio", Paraiba, as described by Rolff (1946)	0,065	3,5	62,0	0,16	nd.		Bi, Cu, Yb
25	Large zircon crystal from Barbacena, M.G., kindness of the Mineral Display, Secretaria da Agricultura, M.G.	0,032	18	65,0	0,41	nd.		Yb

stages, but revealed no additional significant feature. The Hf/Zr ratios in these two specimens are somewhat lower than usually found in cyrtolite and other varieties of zircons.

Table 6 refers to alluvial zircon, with one specimen from Guaraparí Beach (State of Espírito Santo) added as reference. The Guaraparí deposit is being mined and has been studied by others.

The Hf/Zr ratio was found to average 0.028 in 12 determinations of a 5 gram, thoroughly homogenized sample which agrees with Mertie's (1958) 0.027 value for a sample from the same source.

Table 7 records several mineral species from alkaline rocks, with four zircons also added. Two of them are related to the pre-Cambrian? alkaline Matola (São João del Rei area) massif of syenitic gneiss, described by Ebert (1956).

The Hf/Zr ratio of 0 018 — 0.017 for these samples agrees with the general tendency for the hafnium content of minerals associated with alkaline rocks (as are those of Poços de Caldas) to be a little lower than those from calc-alkaline rocks and appreciably lower than those from granitic rocks. (Rankama and Sahama, 1950).

The results shown here for the Hf/Zr ratio by the samples from the Poços de Caldas plateau and by the samples from the beach of the State of Espírito Santo are slightly higher than those recently found by Bergstron Lourenço (1960) who gave 0.0076 as an average for 20 samples from Poços de Caldas and 0.0221 and 0.0234 for two samples from the beach of Espírito Santo.

TABLE Nr. 6 — ALUVIAL ZIRCON

Sample Nr.	DESCRIPTION	Hf/Zr	HfO_2%	ZrO_2% (calculated)	Y_2O_3%	ThO_2%
32	Guaraparí Beach, Espirito Santo; obtained in the Orquima concentration plant; Average of 12 determinations	0,028	1,55	63,8		nd.
33	Marataise Beach, Southern Espirito Santo	0,027	1,50	64,0	0,13	nd.
34	Crucilândia, Minas Gerais	0,036	1,95	62,5	0,55	0,21
35	Zircon from Rio das Mortes, S. João Del Rei, M.G.	0,024	1,40	66,0	0,12	nd.

TABLE Nr. 7 — ZIRCONIUM MINERALS FROM ALKALIC ROCKS

Sample Nr.	DESCRIPTION	Hf/Zr	HfO_2%	ZrO_2% (calculated)	Y_2O_3%	ThO_2%
36	Large baddeleyite radial-fibrous crystal, from Poços de Caldas, M.G.	0,009	0,77	99,0		
37	Caldasite — (Zirconium ore) Poços de Caldas, M.G.	0,011				
38	Eudialyte — Extracted from Foyaite, Pedra Balão, Poços de Caldas, M.G. Sample supplied by Norman Herz, U.S.G.S.	0,010				
39	Zircon — Perfect bipyramidal crystal, Taquarí, Poços de Caldas, M.G.	0,013	0,77	66,0		0,12
40	Zircon — Perfect bipyramidal crystal, Caldas, (Parreiras,), M.G.	0,0165	0,95	65,5	0,24	0,21
41	Zircon — Prismatic bipyramidal crystal, Matola, South of S. João Del Rei (Alkaline pre-Cambrian, massif, Ebert 1956); Sample supplied by C. M. Mendes	0,018	1,0	63,6	0,17	nd.
42	Zircon — Prismatic bipyramidal crystal, from the same locality	0,017	0,97	65,3	0,15	nd.

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