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HIGH HAFNIUM ZIRCON FROM NORWAY

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Abstract

High hafnium zircons from Iveland, Norway are described which have been found to contain 22–24% HfO_2. The ratio Hf/Zr is about 0.6. The zircons occurred protruding from a crystal of thortveitite (scandium silicate). The presence of hafnium and zirconium within the structure of thortveitite is confirmed.

Introduction

The study of the hafnium content and the Hf/Zr ratio in minerals and rocks has received considerable attention in recent years. Fleischer compiled all published data on the subject until 1955. Since then at least half a dozen papers have been published in the U. S. S. R. on the Hf/Zr ratio of various rock types and minerals mainly from that country. Mertie (1958) has also published on the hafnium content of zircons from the Southeastern Atlantic States.

Fleischer (1955) and others previously have pointed out that minerals from granite pegmatites have the highest Hf/Zr ratios especially some of the varieties of zircon (alvite, cyrtolite, etc.) and thortveitite, the rare scandium mineral reported only from Norway and Madagascar. However, Fleischer (1955, p. 3) notes that the Hf/Zr ratios in zircons (as distinct from the varieties alvite, cyrtolite, etc.) are surprisingly low.

This paper describes true zircons from Norway with a high Hf/Zr ratio and verifies the presence of hafnium and zirconium within the structure of thortveitite.

Description of Thortveitite Specimens

Three specimens labelled thortveitite from Iveland, Norway were purchased from Minerals Unlimited, Berkeley, California with the original intent to verify the high Hf/Zr ratio reported in this mineral. The samples were identified by qualitative *x*-ray fluorescence analysis in which scandium was found to be a major constituent, measurement of indices of refraction, and powder *x*-ray diffraction patterns. Two specimens are $\frac{1}{8}$–$\frac{1}{4}$ inch in length and dark grayish-green in color. The third is a larger incomplete prismatic crystal $\frac{3}{4}$ inch in length and dark reddish-brown in color; the reddish color is due to iron oxide staining. This crystal had one small cluster of brown crystals 4–5 mm. across protruding from the front of the crystal and a similar cluster protruding from the side. It was these protrusions which were isolated and found to be high hafnium zircons.

Properties and Analysis of the High Hafnium Zircon Crystals

Both of the zircon clusters consisted of about five distorted zircon crystals each about 1 mm. in width and 3 mm. in length. Each cluster weighed about 50 mg. The individual crystals radiated from a point giving the cluster a "cauliflower" structure. At the widest part of the cluster protruding from the thortveitite crystal distorted tetragonal pyramid faces were evident. The clusters were easily separated from the thortveitite host owing to the good cleavage of the latter. The streak of the zircon crystals was definitely brownish because of the presence of iron oxides related to alteration.

Optical examination of the powdered zircon from the cluster on the side of the thortveitite host showed the material to have ω close to 1.92 (measured in white light). Birefringence was high but ϵ was not measured. A good uniaxial positive interference figure was obtained. No optical examination was made of the other cluster.

X-ray diffraction patterns were obtained on powdered material from both clusters. The patterns are identical to zircon with all lines clearly visible. However, it was definitely evident that the high hafnium zircon crystals were slightly altered because the diffraction lines were not as sharp as the pattern of an unaltered zircon standard.

Specific gravity determinations were made of both clusters. The side cluster had G = 5.1 and the front cluster had G = 4.8; the latter gave the slightly more diffuse *x*-ray diffraction pattern. The specific gravity of normal (low hafnium) unaltered zircon is 4.6–4.7. The specific gravities of the specimens under study, although higher than those usually reported, are still lower than would be expected from a high hafnium zircon. This can be explained in part by the fact that some thortveitite was still attached to the zircons as scandium was found in small amounts during analysis and also by the fact that the material was probably hydrated to a minor extent as a result of the alteration evidenced by the slightly diffuse *x*-ray diffraction patterns and the presence of an iron oxide mineral.

The isolated high hafnium zircons were analyzed by *x*-ray fluorescence spectroscopy quantitatively for hafnium, zirconium and iron. In addition to these elements only yttrium and scandium in small amounts were noted by this technique in which our instrumentation is able to detect elements from potassium through uranium. Significantly, no thorium or uranium were detected and if present were in amounts less than 100 ppm. The few per cent of scandium is believed to be from some thortveitite

which was not completely separated from the zircon. Yttrium, estimated at not more than 4%, was probably in part from the thortveitite in which it substitutes for scandium and, also, in part contained within the zircon crystals.

In the x-ray fluorescence analysis the first order lines $HfL_{\beta 1-6}$ doublet, ZrK_{β} and FeK_{α} were used. The results are presented in Table 1. Our experience with analysis by x-ray fluorescence indicates that these data reported are accurate to within 10% of the amount present.

A semi-quantitative emission spectrographic analysis showed the presence of beryllium in trace amounts in the order of 100 ppm.

TABLE 1. ANALYSIS OF HIGH HAFNIUM ZIRCON

	HfO_2	ZrO_2	Fe_2O_3	Y_2O_3	Hf/Zr
Side Cluster	22	47	4	1–3	.54
Front Cluster	24	42	4	2–4	.65

Notes:

1. X-ray fluorescence analysis in weight per cent.
2. All values are quantitative (±10 per cent of the amount present) except yttrium, which is estimated.
3. All Hf/Zr ratios in this paper are weight ratios unless otherwise indicated.
4. The highest previously reported HfO_2 for zircon is 6 per cent. The highest HfO_2 reported for cyrtolite, alvite, etc., is 17 per cent. (From Fleischer, 1955)
5. Analyst: R. A. Borup.

DISCUSSION

The designation of the clusters as zircon and not alvite, cyrtolite, pseudo-zircon, or any other of the imperfectly known varieties is considered correct because the specimens are crystalline, they have a high specific gravity, no uranium or thorium were detected, and only traces of beryllium and small amounts of yttrium were found. The significance of these zircon crystals is that they are believed to be the first true zircons reported with high hafnium and a correspondingly high Hf/Zr ratio. Unfortunately, no material remained after the above analyses for further studies such as determination of the water content, etc.

In view of the finding of high hafnium zircons protruding from thortveitite, investigation was undertaken to determine whether the hafnium and zirconium reported in the literature as being within the structure of thortveitite possibly resulted from inclusion of small amounts of zircon. In this connection, both of these elements were found qualitatively to be present in all three samples of thortveitite obtained for this study. Ac-

cordingly, x-ray diffraction patterns were obtained on thortveitite using exposures six times longer than usual. The patterns did not record the strongest (3.30 Å) line of zircon and it is presumed that the hafnium and zirconium are present within the thortveitite structure. As a further check on the largest (reddish-brown) thortveitite, portions of the crystal were ground and digested in HCl and H_2SO_4 for several hours. The hafnium and zirconium still remained within the unreacted thortveitite except for traces which were found in the dried acid residues along with significantly larger amounts of scandium and yttrium. This indicates slight decomposition of thortveitite with acid digestion. Although the contents of the hafnium and zirconium were not determined quantitatively, the qualitative results correspond with those reported in the literature; that is, hafnium appears very abundant in comparison with zirconium and may well exceed it.

The possibility of finding the first mineral in which hafnium is more abundant than zirconium seems particularly favorable in the Norwegian and Madagascan pegmatites in which thortveitite is found. The highest Hf/Zr weight ratio reported in a mineral is 1.9 (Fleischer 1955, Table 8) from Norwegian thortveitite. This, on an atomic ratio basis, is a little less than one. If a zircon-type crystal with an atomic ratio Hf/Zr greater than one can be found, it will be a new mineral.

Finally, it is worthwhile emphasizing again, in agreement with Fleischer (1955) and others, that there is not necessarily a correlation between radioactivity and hafnium content in zircon.

References

Fleischer, M. (1955), Hafnium content and hafnium-zirconium ratio in minerals and rocks: U. S. Geol. Surv. Bull. 1021-A, 1–13.

Mertie, J. B. (1958), Zirconium and hafnium in the Southeastern Atlantic States: U. S. Geol. Surv. Bull. 1082-A, 1–28.

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